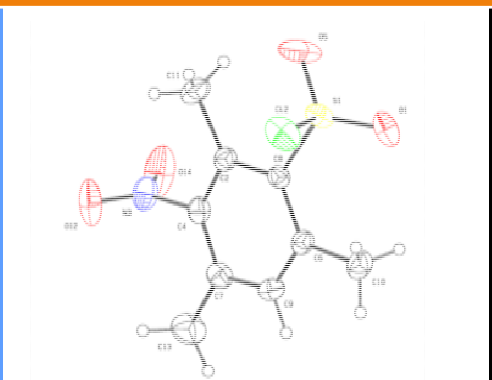
DONETSK NATIONAL TECHNICAL UNIVERSITY

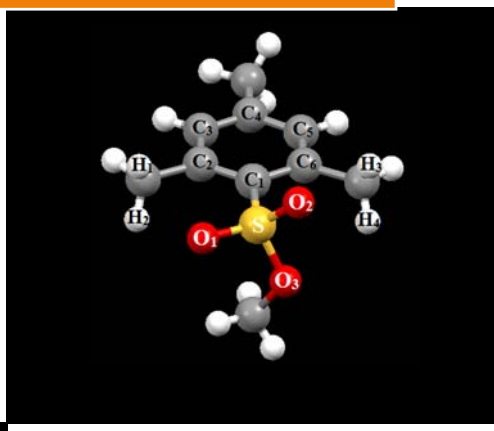
Dept. of General Chemistry

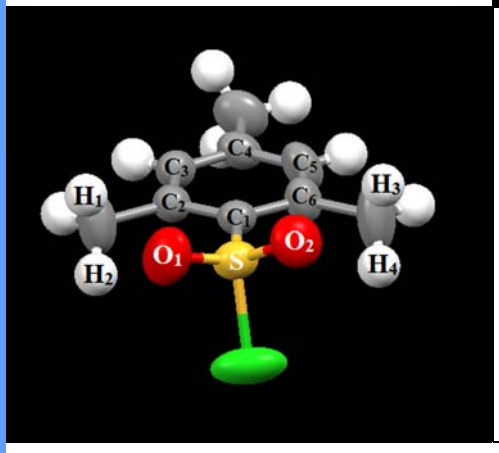
UNIVERSITY OF A CORUÑA

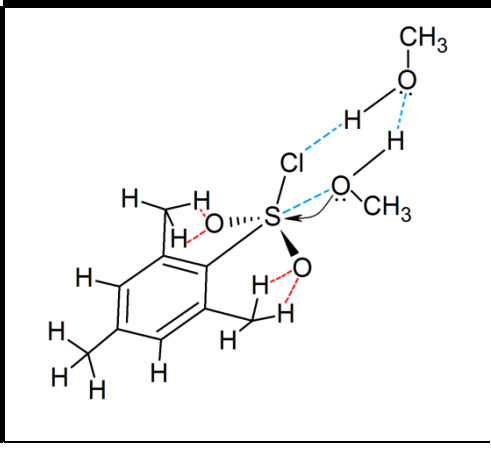
Dpt. of Physical Chemistry & Chemical Engineering

MECHANISTIC STUDY OF STRUCTURAL EFFECTS ON NUCLEOPHILIC SUBSTITUTION REACTIONS AT SULFONYL CENTERS









A Coruña

January, 2016

Ph.D Thesis

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UNIVERSIDADE DA CORUÑA

Programa oficial de doutoramento en

Ciencia e Tecnoloxía Ambiental

Mechanistic study of structural effects on nucleophilic substitution reactions at sulfonyl centers

Dissertation presented by:

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in fulfilment of the requirements for the degree of Doctor

JANUARY 2016

UNIVERSIDADE DA CORUÑA

Programa oficial de doutoramento en

Ciencia e Tecnoloxía Ambiental

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Estudio mecanístico de los efectos estructurales en reacciones de sustitución nucleofílica en centros sufonilo

Estudo mecanístico dos efectos estructurais en reaccións de sustitución nucleofílica en centros sufonilo

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para opta-lo Grao de Doutor

XANEIRO 2016

Programa oficial de doutoramento en
Ciencia e Tecnoloxía Ambiental

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Don J. Arturo Santaballa López, coordinador da Comisión Académica do programa oficial de doutoramento en Ciencia e Tecnoloxía Ambiental,

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Asdo. J. Arturo Santaballa López

Facultade de Ciencias
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UNIVERSIDADE DA CORUÑA

Os doutores Dona Lyudmyla Rublova, Don Moisés Canle López, e Don J. Arturo Santaballa López

CERTIFICAN

Que o traballo de investigación orixinal titulado: "*Mechanistic study of structural effects on nucleophilic substitution reactions at sulfonyl centers*" ("*Estudo mecanístico dos efectos estructurais en reaccións de sustitución nucleofílica en centros sufonilo*") foi realizado neste departamento por Don Mykyta Iazykov, e que como directores do mesmo autorizamo-la súa presentación como memoria de Tese de Doutoramento co gallo de que sexa xulgada polo tribunal correspondente.

E para que así conste, expedimos e asinamo-la na cidade da Coruña o dezasete de setembro de dous mil quince.

Asdo. Lyudmyla Rublova Asdo. Moisés Canle López Asdo. J. Arturo Santaballa López

Acknowledgements

Over the past years I would not have been able to complete my Ph.D. without the aid and support of countless people.

I must first express my gratitude towards my advisor, Professor Ludmila Rublova. Her leadership, support, attention to details, and hard work have set an example I hope to match some day. I would like to especially thank Professors Moisés Canle López and Juan Arturo Santaballa López, for many discussions and much encouragement. Their insights and comments were invaluable over the years.

I gratefully acknowledge the funding sources that made my Ph.D. work possible. During 2013/14 I received a EU financial support of my mobility of to the UDC within the trans-European mobility Erasmus Mundus action TEMPO (372283-1-2012-1-PT-ERA MUNDUS-EMA21).

I thank my labmates and friends in DonNTU and UDC for the stimulating discussions, and for all the fun we have had in the last years. In particular I am grateful to Elena Poberezhnyak, Elena Belyaeva and Victor Levandovsky. I would also like to acknowledge to Dr. Yenya V.I. and to Pr. Mysyk D.D. for their support and good advices.

Finally, I thank my parents who raised me with a love of science and supported me in all my pursuits. I really appreciate their concern and encouragement over these years.

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SUMMARY

Nucleophilic substitution processes at the sulphur atom of arenesulfonyl compounds have been the subject of numerous discussions among experts for many years. This is due to the ambiguity of the solvolysis mechanism, which is often treated as a bimolecular with different symmetry at the transition state, catalytic assistance of the solvent, a possible rearrangement during the nucleophilic attack, etc.

In the last years, the problem has become more complicated by the study of these reactions involving sterically overloaded sulfonyl systems in which the attack on the sulphur atom presumably is inhibited by the presence of *ortho*-alkyl groups.

However, researchers have paid little attention to the solvolysis of sterically hindered aromatic sulfo derivatives, particularly to arenesulfonyl acid derivatives. Hindered substrates based on derivatives of benzenesulfonyl chlorides show a significant increase in reactivity, and disagree with the classical criteria on the electronic effect of the substituents on the reaction rate of the S_N2 process.

Nevertheless, it is clear that sterically hindered derivatives of aromatic sulfonic acids have a number of kinetic features that allow having doubts on the existing classical point of view on the mechanism of nucleophilic substitution at sulfonyl atom, and assume the existence of the so called "Positive steric effect" putting these compounds in the category of abnormally reactive. Such “positive *ortho*-effect” has been widely omitted in the literature with the exception of the neutral hydrolysis of hindered arenesulfonyl chlorides in dioxane-water mixtures.

This research is dedicated to the chemical kinetic study of the origin of the positive *ortho*-effect in the hindered arenesulfonyl chlorides solvolysis. To answer the question on the role of the substrate structure on the reactivity the following central issues should be unravelled:

1. The influence of solvent composition, the nature and the position of the substituents in hindered and unhindered substrates and the nature of the nucleophile on the reaction rate and the substitution kinetic mechanism.

2. The values of the thermodynamic transition state parameters in different alcohols (methanol, ethanol, propanol and *iso*-propanol).
3. The leaving group effect, the secondary kinetic isotope effect (SKIE) and the solvent isotope effect (SIE) on the alcoholysis conditions.

Structure and purity of the obtained sulfonyl compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy and monocrystal X-ray diffraction.

Kinetic studies were carried out spectrophotometrically under pseudo-first order with respect to the nucleophile on a Cary 1E UV-Vis spectrophotometer, in a thermostated quartz cuvette l=1 cm, temperature range 303-323K.

The alcoholysis of arenesulfonyl chlorides X-$ArSO_2Cl$ at 323 K (X=H-, 4-Me-, 4-*t*-Bu-, 4-Cl-, 4-Br-, 3-NO_2-, 2,4,6-Me_3-, 2,4,6-Et_3-, 2,4,6-*i*-Pr_3-, 2-Me-, 2,4-Me_2-, 2,5-Me_2-, 2-Me-5-*t*-Bu-, 2,6-Me_2-4-*t*-Bu-, 2,3,5,6-Me_4-, 2-Me-5-NO_2-, 2,4-Me_2-5-NO_2-, 2,4,6-Me_3-3-NO_2- and 2,4,6-$(OMe)_3$) in methanol, ethanol, propanol and *iso*-propanol was studied. The obtained kinetic data were analyzed, by the linear regression, using the following models: Hammett equation, Arrhenius equation, Grunwald–Winstein equation, Brønsted equation and Kirkwood function.

The electronic nature of the *X* substituent has ambiguous effect. The process in unbranched alcohols is quite similar: an increase of electron withdrawing properties of the *X* substituents in unhindered compounds leads to lower reactivity. The solvolysis by *iso*-propyl alcohol shows the opposite tendency. On the other hand, sterically-hindered compounds show anomalous acceleration for all alcohols.

All studied compounds demonstrate similar thermodynamic activation parameters (large negative activation entropy values, and low, and similar, activation enthalpy values) and it is also common the existence of good $logk_{T1}$ *vs.* $logk_{T2}$ correlations, *i.e.* isokinetic dependences.

Studied substrates are characterized by low values of the leaving group effect (k_{Br}/k_{Cl} = 4 – 6). The observed SIE is *ca.* 1.35 for ethanolysis, comparable to literature data. No SKIE was observed when hydrogens of the *ortho*-alkyl groups are replaced by deuteriums.

The reaction order of the nucleophile varies between 2 and 3 in all alcohols. Electron withdrawing substituents tend to decrease both the sensitivity to the ionizing power of solvent and the Brønsted exponent, whereas electron-donor ones increase them.

All previous indirect evidences on the mechanism of solvolysis of arenesulfonyl chlorides (kinetic rate laws, kinetic isotope effect, change of the nucleophile, solvent, etc.), as well as the X-ray structures, the presence of isokinetic dependency and the similar thermodynamic activation parameters for all the investigated series of substrates point to a single bimolecular mechanism of substitution similar to S_N2 involving the of at least a second molecule of the solvent by the general base catalysis type, and likely the formation of a cyclic transition state.

In conclusion, it follows that the positive steric effect is a complex phenomenon that implies the formation of a cyclic TS structure, likely generated by a frontal attack of the nucleophile, the alcohol, and stabilized by additional non-bonded interactions between the *o*-methyl hydrogens and the oxygen atoms of the sulfonyl group.

RESUMEN

Durante muchos años los procesos de sustitución nucleófila en el átomo de azufre de arenosulfonilos han sido objeto de numerosas discusiones entre expertos. Ello es debido a las ambigüedades halladas en el mecanismo de su solvólisis, el cual a menudo es tratado como bimolecular con diferente simetría en el estado de transición, asistencia catalítica del disolvente y el posible reordenamiento durante el ataque nucleofílico, etc.

En los últimos años el tema se ha complicado con el estudio de estas reacciones involucrando sistemas sulfonilo estéricamente congestionados en los que el ataque sobre el átomo de azufre presumiblemente es inhibido por la presencia de grupos alquilo en *orto*.

Sin embargo los investigadores han prestado escasa atención a la solvólisis de compuestos aromáticos de sulfonilo, estéricamente congestionados, particularmente a los derivados de ácidos arenosulfonilos. Los sustratos con impedimento estérico derivados de los cloruros de arenosulfonilo muestran un notable aumento de reactividad, apartándose del criterio clásico sobre el efecto electrónico de los sustituyentes sobre la velocidad de reacción de los procesos S_N2.

Sin embargo, es evidente que los derivados, con impedimento estérico, de ácidos sulfónicos aromáticos presentan una serie de características cinéticas que hacen dudar de la visión clásica sobre los mecanismos de sustitución nucleófila en el átomo de azufre del grupo sulfonilo, y permiten hablar del así llamado “efecto estérico positivo”, con lo que sitúan dichos compuestos en la categoría de anormalmente reactivos. Tal “efecto estérico positivo” ha sido generalmente omitido en la bibliografía con la excepción de la hidrólisis de cloruros de arenosulfonilos, estéricamente congestionados, en mezclas dioxano-agua.

Esta investigación se ha centrado en el estudio cinetoquímico del origen del efecto *orto* positivo en la solvólisis de cloruros de arenosulfonilo, estéricamente congestionados. Para responder la cuestión del papel de la estructura de estos

sustratos sobre la reactividad los siguientes aspectos fundamentales han de ser aclarados:

1. La influencia de la composición del disolvente, la naturaleza y la posición de los sustituyentes en el sustrato y la naturaleza del nucleófilo en la velocidad de reacción y en el mecanismo cinético de la misma.
2. Los valores de los parámetros termodinámicos de activación en diferentes alcoholes (metanol, etanol, propanol e *iso*-propanol).
3. El efecto del grupo saliente, el efecto isotópico secundario (SKIE) y el efecto isotópico del disolvente (SIE) sobre las condiciones de la alcoholisis.

La estructura y pureza de los compuestos sulfonilo obtenidos fue confirmada por espectroscopia RMN ^{1}H y ^{13}C, y por difracción de rayos X de monocristal.

Los estudios cinéticos se llevaron a cabo espectrofotométricamente en condiciones de pseudo-orden uno con respecto al nucleófilo en un espectrofotómetro UV-Vis Cary 1E con cubetas de cuarzo termostatizable, l=1 cm, intervalo de temperatura 303-323K.

Se estudió la alcoholisis de los siguientes cloruros de arenosulfonilo: X-$ArSO_2Cl$ at 323 K (X=H-, 4-Me-, 4-*t*-Bu-, 4-Cl-, 4-Br-, 3-NO_2-, 2,4,6-Me_3-, 2,4,6-Et_3-, 2,4,6-*i*-Pr_3-, 2-Me-, 2,4-Me_2-, 2,5-Me_2-, 2-Me-5-*t*-Bu-, 2,6-Me_2-4-*t*-Bu-, 2,3,5,6-Me_4-, 2-Me-5-NO_2-, 2,4-Me_2-5-NO_2-, 2,4,6-Me_3-3-NO_2- and 2,4,6-$(OMe)_3$) en metanol, etanol, propanol e *iso*-propanol. Los datos cinéticos obtenidos se analizaron, mediante regresión lineal, con los siguientes modelos: ecuación de Hammett, ecuación de Arrhenius, ecuación de Grunwald–Winstein, ecuación de Brønsted y función de Kirkwood.

Los sustituyentes X presentan un efecto ambiguo. El proceso en alcoholes lineales es muy similar: según aumenta la capacidad de retirar carga del sustituyente, en compuestos sin impedimento estérico, la reactividad disminuye. La solvólisis en *iso*-propanol muestra la tendencia contraria. Por otra parte, los compuestos estéricamente congestionados muestran una aceleración anómala en todos los alcoholes.

Todos los compuestos estudiados muestran similares parámetros termodinámicos de activación (grandes valores negativos de entropía, y bajos valores de entalpía), siendo también común la existencia de buenas correlaciones $logk_{T1}$ *vs.* $logk_{T2}$, es decir, dependencias isocinéticas.

Los sustratos estudiados presentan pequeños valores del efecto del grupo saliente (k_{Br}/k_{Cl} = 4 – 6). El valor del SIE está en el entorno de 1.35 para la etanolisis, similar a lo que figura en la bibliografía. No se observa SKIE cuando los hidrógenos de los grupos alquilo en *orto* se reemplazan por deuterios.

El orden de reacción del nucleófilo varia entre 2 y 3 en todos los alcoholes. Los sustituyentes que retiran carga tienden a reducir tanto el efecto de disolventes que generan iones como el exponente de Brønsted, mientras que los que ceden carga producen el efecto contrario.

Todas las evidencias previas, indirectas, sobre el mecanismo de solvólisis de cloruros de arenosulfonilo (ecuaciones cinéticas de velocidad, efectos isotópicos cinéticos, cambio de nucleófilo, de disolvente, etc.) así como las estructuras de difracción de rayos X, la existencia de dependencias isocinéticas y los similares valores de los parámetros termodinámicos de activación para todos los sustratos estudiados apuntan a un único mecanismo de sustitución bimolecular similar a S_N2 involucrando la asistencia nucleófila de al menos una segunda molécula de disolvente mediante catálisis general básica, y probablemente la formación de un estado de transición cíclico.

En conclusión se puede decir que el efecto estérico positive es un fenómeno complejo que consiste en la formación de un estado de transición cíclico, generado por un ataque frontal del nucleófilo, el alcohol, que es estabilizado por interacción no covalente entre los hidrógenos del, o de los, grupo metilo en *orto* y los átomos de oxígeno del grupo sulfonilo.

RESUMO

Durante moitos anos os procesos de substitución nucleófila no átomo de sofre de arenosulfonilos teñen sido obxecto de numerosas discusións entre expertos. Elo é debido ás ambigüidades atopadas no mecanismo da súa solvólise, a que a miúdo é tratada como bimolecular con diferente simetría no estado de transición, asistencia catalítica do disolvente e o posible reordenamento durante o ataque nucleofílico, etc.

Nos últimos anos o tema tense complicado co estudio destas reaccións involucrando sistemas sulfonilo estéricamente conxestionados nos que o ataque sobre o átomo de sofre presumiblemente é inhibido pola presenza de grupos alquilo en *orto*.

Nembargante os investigadores teñen prestado escasa atención á solvólise de compostos aromáticos de sulfonilo, estéricamente conxestionados, particularmente os derivados de ácidos arenosulfonilos. Os substratos con impedimento estérico derivados dos cloruros de arenosulfonilo amosan un notable aumento de reactividade, apartándose do criterio clásico sobre o efecto electrónico dos substituinte sobre a velocidade de reacción dos procesos S_N2.

É evidente que os derivados, con impedimento estérico, de ácidos sulfónicos aromáticos presentan unha serie de características cinéticas que fan dubidar da visión clásica sobre os mecanismos de substitución nucleófila no átomo de sofre do grupo sulfonilo, e permiten falar do así chamado "efecto estérico positivo", co o que sitúan ditos compostos na categoría de anormalmente reactivos. Tal "efecto estérico positivo" ten sido xeralmente omitido na bibliografía coa excepción da hidrólise de cloruros de arenosulfonilos, estéricamente conxestionados, en mesturas dioxan-auga.

Esta investigación céntrase no estudio cinetoquímico da orixe do efecto *orto* positivo na solvólise de cloruros de arenosulfonilo, estéricamente conxestionados.

Para respostar á cuestión do papel da estrutura destes substratos sobre a reactividade os seguintes aspectos fundamentais teñen que ser clarexados:

1. A influencia da composición do disolvente, a naturaliza e a posición dos substituinte no substrato e a natureza do nucleófilo na velocidade da reacción e no mecanismo cinético da mesma.
2. Os valores dos parámetros termodinámicos de activación en diferentes alcohois (metanol, etanol, propanol e *iso*-propanol).
3. O efecto do grupo saínte, o efecto isotópico secundario (SKIE) e o efecto isotópico do disolvente (SIE) sobre as condicións da alcoholise.

La estrutura e pureza dos compostos sulfonilo obtidos foi confirmada por espectroscopia RMN ^{1}H e ^{13}C, e por difracción de raios X de monocristal.

Os estudios cinéticos leváronse a cabo espectrofotométricamente en condicións de pseudo-orden un con respecto o nucleófilo nun espectrofotómetro UV-Vis Cary 1E con cubetas de cuarzo termostatizable, l=1 cm, intervalo de temperatura 303-323K.

Estudouse a alcoholise dos seguintes cloruros de arenosulfonilo: X-$ArSO_2Cl$ at 323 K (X=H-, 4-Me-, 4-*t*-Bu-, 4-Cl-, 4-Br-, 3-NO_2-, 2,4,6-Me_3-, 2,4,6-Et_3-, 2,4,6-*i*-Pr_3-, 2-Me-, 2,4-Me_2-, 2,5-Me_2-, 2-Me-5-*t*-Bu-, 2,6-Me_2-4-*t*-Bu-, 2,3,5,6-Me_4-, 2-Me-5-NO_2-, 2,4-Me_2-5-NO_2-, 2,4,6-Me_3-3-NO_2- and 2,4,6-$(OMe)_3$) en metanol, etanol, propanol e *iso*-propanol. Os datos cinéticos obtidos analizáronse, mediante regresión linear, cos seguintes modelos: ecuación de Hammett, ecuación de Arrhenius, ecuación de Grunwald–Winstein, ecuación de Brønsted e función de Kirkwood.

Os substituintes X presentan un efecto ambiguo. O proceso en alcohois lineais é moi similar: o aumenta-la capacidade de retirar carga do substituinte, en compostos sen impedimento estérico, a reactividade diminúe. A solvólise en *iso*-propanol amosa a tendencia contraria. Por outra banda, os compostos estéricamente conxestionados amosan unha aceleración anómala en tódolos alcohois.

Tódolos compostos estudados amosan similares parámetros termodinámicos de activación (grandes valores negativos de entropía, e baixos valores de entalpía), sendo tamén común a existencia de boas correlacións $logk_{T1}$ *vs.* $logk_{T2}$, é dicir, dependencias isocinéticas.

Os substratos estudados presentan pequenos valores do efecto do grupo saínte ($k_{Br}/k_{Cl} = 4 – 6$). O valor do SIE está no entorno de 1.35 para a etanolise, similar o que figura na bibliografía. Non se observa SKIE cando os hidróxenos dos grupos alquilo en *orto* reemprázanse por deuterios.

O orden de reacción do nucleófilo varia entre 2 e 3 en tódolos alcohois. Os substituintes que retiran carga tenden a reducir tanto o efecto de disolventes que xeran ións como o expoñente de Brønsted, namentres que os que ceden carga producen o efecto contrario.

Todas as evidencias previas, indirectas, sobre o mecanismo de solvólise de cloruros de arenosulfonilo (ecuacións cinéticas de velocidade, efectos isotópicos cinéticos, cambio de nucleófilo, de disolvente, etc.) así como as estruturas de difracción de raios X, a existencia de dependencias isocinéticas e os similares valores dos parámetros termodinámicos de activación para tódolos substratos estudados apuntan a un único mecanismo de substitución bimolecular similar a S_N2 involucrando a asistencia nucleófila de alúmenos unha segunda molécula de disolvente mediante catálise xeral básica, e probablemente a formación dun estado de transición cíclico.

En conclusión pódese dicir que o efecto estérico positivo é un fenómeno complexo que consiste na formación dun estado de transición cíclico, xerado polo ataque frontal do nucleófilo, o alcol, que é estabilizado pola interacción non covalente entre os hidróxenos do, ou dos, grupo metilo en *orto* e os átomos de osíxeno do grupo sulfonilo.

1 INTRODUCTION

Nucleophilic substitution processes at tetracoordinated sulfur atoms have been the subject of detailed research for many years. Due to the nature of the electronic structure of the sulfur atom (heterovalent nature, participation of 3d-orbitals in the formation of chemical bonds, tetrahedricity of sulfonyl group caused by sp^3-d^2 hybridization of its atomic orbitals), sulfo derivatives have a variety of interesting reactivity features.

However, researchers have paid little attention to solvolysis of sterically hindered aromatic sulfo derivatives, particularly to arenesulfonyl acid derivatives. Perhaps, this has been caused by the lack of a unified approach to the behaviour of compounds with *ortho*-alkyl substituents at the reaction center, due to the high specificity of the structure of such substrates [1]. Surprisingly, hindered derivatives of arensulfonyl acids exhibit enhanced reactivity in solvolytic reactions. Such "positive *ortho*-effect" has been widely omitted in the literature with the exception of the neutral hydrolysis of hindered arensulfonyl chlorides in dioxane-water mixtures[2-4].

Therefore, it is relevant to study these compounds in order to model their reactions, such as the alcoholysis of sterically hindered aromatic sulfonyl halides. It is generally known that the nature of the solvent affects the solvolysis process greatly [5]. In the case of highly structured solvents such as water or alcohols additional solvation effects arise that may play a crucial role in formation of the transition state structure[5].

Derivatives of aromatic sulfonic acids have a great diversity of properties and are widely used in industry[6], medicine (group of sulfa drugs)[7], agriculture[8], as high polymers[9], extractants[10], dyes (Leukanol)[11], detergents[12], or as heat-sensitive recording materials [13].

High reactivity makes such structures very promising agents of organic synthesis. Biological activity of hindered arenesulfonyl chlorides allow to anticipate them as potential new broad-spectrum antibacterial drugs. There have been also

attempts to use them as agents for reduction of the phenol content from sewage of by-product coke plants[14, 15].

Identification of solvation effects patterns of substitution in hindered sulfonyl reaction center allows predicting the effects of the media in the processes occurring in other reaction centers of bioactive compounds, based on such substrates.

The goal of the research is to unravel the origin of the positive *ortho*-effect in the solvolytic reactions of nucleophilic substitution of hindered arenesulfonyl chlorides. To find the answer to the question about the role of influence of the substrate structure on the reactivity we need to highlight some central issues:

1. To study the influence of the solvent composition, nature and position of the substituents in the substrate, and the nature of the nucleophile.
2. To determinate the thermodynamic transition state parameters for the model reaction in different alcohols (methanol, ethanol, propanol and *iso*-propanol).
3. To evaluate the nature of the leaving group effect, secondary kinetic isotope effect and solvent isotope effect.

The scientific novelty of this research consists in the in-depth study of the mechanism of nucleophilic substitution at hindered tetra-coordinated sulfur atoms that provide an appropriate approach to the understanding of positive *ortho*-effects.

The practical importance of the work is the production of new data for structural parameters of aromatic sulfonic acids derivatives (sulfonyl chlorides; arenesulfonates of some alcohols), rate constants of solvolysis of arenesulfonyl derivatives in various alcohols, and kinetic correlations to describe the reactivity of substituted arenesulfonyl derivatives in these systems. New concepts of the substitution mechanism at the sterically shielded sulfonyl center develop the theory of nucleophilic substitution processes in coordination-unsaturated centers. The information obtained for the reactivity of arenesulfonyl halides in media of highly structured solvents will improve the knowledge on the reactivity of arenesulfonyl compounds.

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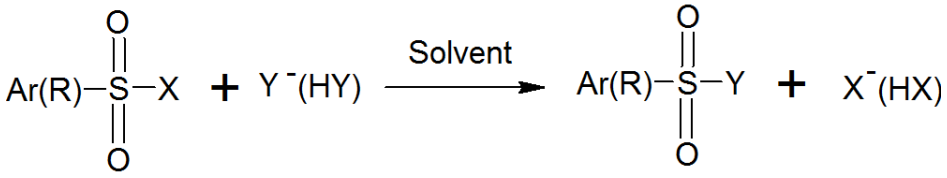
2 STATE OF ART

2.1 NUCLEOPHILIC SUBSTITUTION AT TETRACOORDINATE SULFUR ATOMS

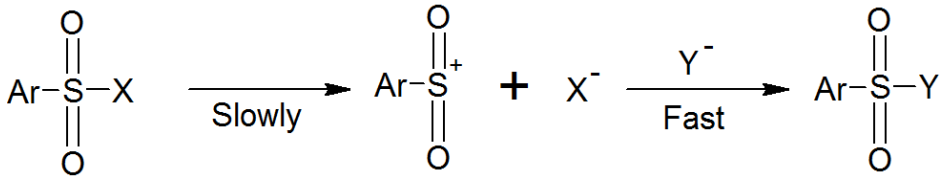
2.1.1 Interaction of arenesulfonic acids derivatives with nucleophilic reagents in water-organic mixtures

This review focuses on the substitution at the four coordinated sulfur atom as shown in scheme 2.1, where X^- and Y^- are the nucleofuge and the nucleophile, respectively.



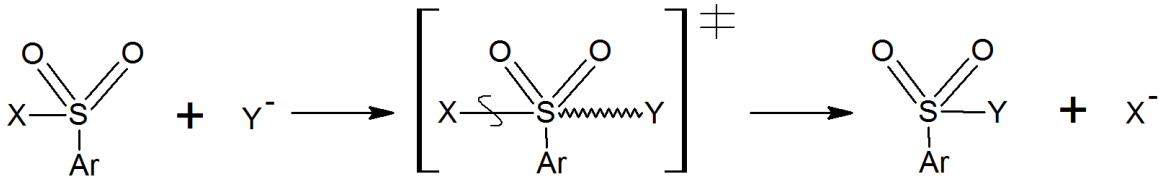
Scheme 2.1 Nucleophilic substitution in sulfonyl compounds

The reaction mechanism has been described by several authors [1-3]; three reaction routes have been proposed depending on the rate law: unimolecular (S_N1) and bimolecular (S_N2 & S_AN). The unimolecular S_N1-mechanism (Scheme 2.2) involves the slow heterolysis of the $ArSO_2X$ compounds forming an unstable cation $ArSO_2^+$, which is stabilized by the presence either of strong electron substituents in the sulfonyl compound or of strong Lewis acids[4].In the second step the sulfonyl cation quickly reacts with the nucleophile.



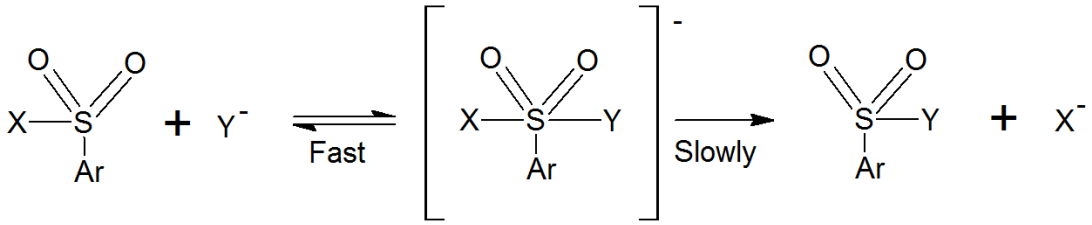
Scheme 2.2 Unimolecular nucleophilic substitution (S_N1) in sulfonyl compounds

Bimolecular substitution reactions at the sulfonyl center might be described as one-step (S_N2) or as two-step (S_AN) mechanism, the second step being the slow one. The S_N2 pathway (Scheme 2.3) involves simultaneous, not necessarily synchronous, S-X bond breaking and S-Y bond forming at the transition state (TS):



Scheme 2.3 One-step bimolecular substitution (S_N2)

In the S_AN-mechanism, also known as nucleophilic addition/elimination, (Scheme 2.4) the fast addition of the nucleophile (Y^-) is followed by a rate limiting elimination process where the nucleofuge (X^-) leaves the metastable trigonal-bipyramidal intermediate formed in the addition step.



Scheme 2.4 Bimolecular addition/elimination mechanism (S_AN)

The feasibility of this mechanism might come from the role played by the X-group solvation.

Both stepwise mechanisms,S_N1 and S_AN can be considered as limiting cases of the one-step S_N2 mechanism as shown in the More O'Ferrall-Jencks diagram (Figure 2.1).[5-9] Parallel and perpendicular displacements on the potential energy surface leading to various transition state (TS) can also be discussed in terms of the O'Ferrall-Jencks diagram.[8,9]

Concerted and synchronous TS occurs when the relative progress of nucleophile bond formation and leaving group bond breaking is the same, *i.e.* those bond orders are equal ($\Delta\rho_{Y\text{-}S} = \Delta\rho_{S\text{-}X}$), and concerted and asynchronous TS where those bond orders sum is equal to 1 ($\Delta\rho_{Y\text{-}S} + \Delta\rho_{S\text{-}X} = 1$). Concerted transition states are also classified as "loose" ($\Sigma\Delta\rho_i<1$) and "tight" ($\Sigma\Delta\rho_i> 1$).

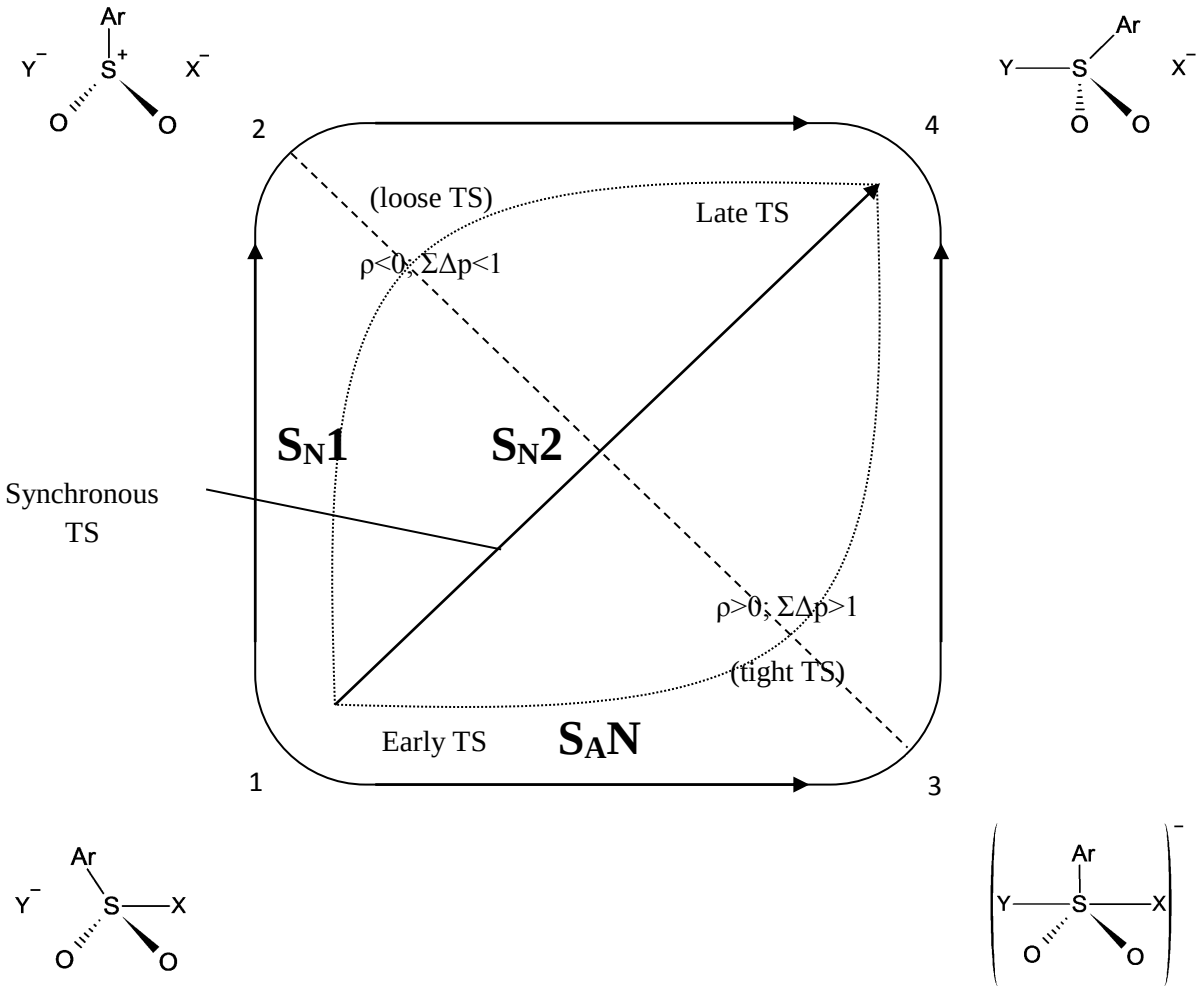
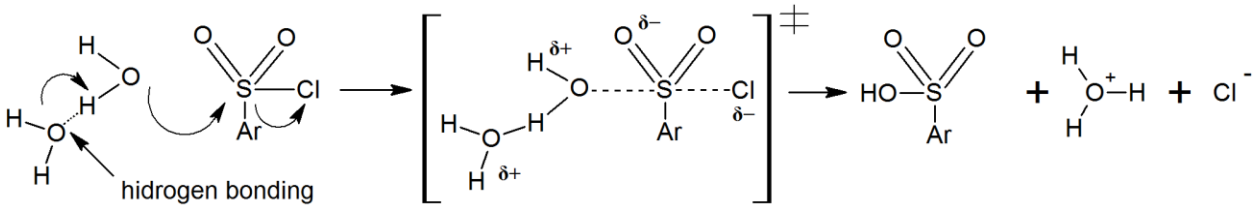


Figure 2.1 More O'Ferrall-Jencks diagram for S_N1, S_N2, S_AN mechanisms for sulfonyl substitution reactions like those in scheme 2.1

Concerted TS can be “early”, resembling the reactants, or “late”, similar to products, depending on to which corner (1 or 4, Fig. 2.1) the TS is closer.

References to the S_N3-mechanism in the solvolysis of sulfonyl compounds have been recently published [10-13]. Such mechanism (Scheme 2.5) accounts for the participation of a second solvent molecule in the TS, which facilitates the formation of S···O bond, like in general base catalysis in water:



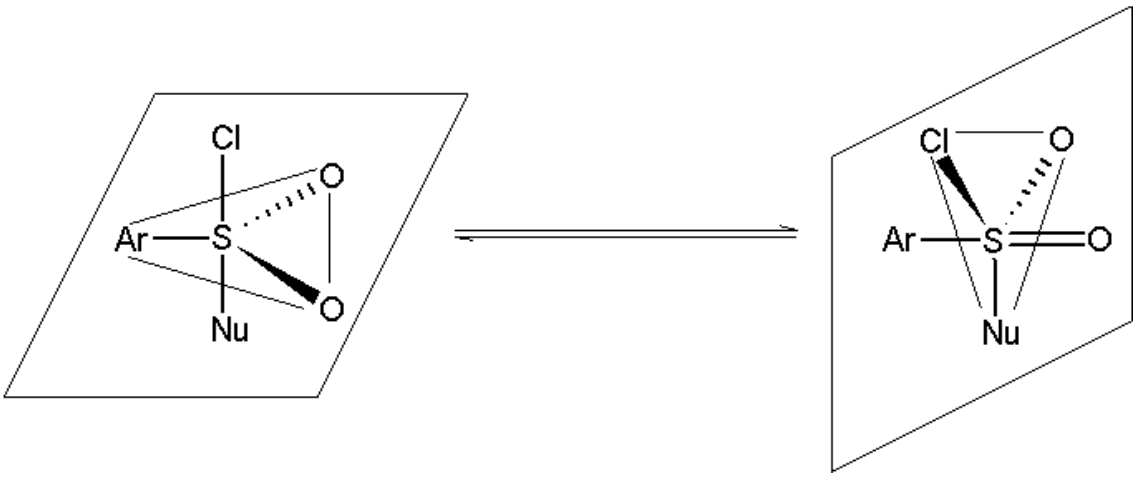
Scheme 2.5 Trimolecular mechanism (S_N3) in the hydrolysis of sulfonyl chlorides

The S_N3-mechanism is consistent with:

—a sufficiently high kinetic isotope effect (KIE)> 2;

—a great influence of solvent nucleophilicity into the reactivity.

According to the literature this mechanism works with substrates like 4-NO_2-$C_6H_4SO_2Cl$ and 4-OMe-$C_6H_4SO_2Cl$. The process of the scheme 2.5 can be considered as bimolecular with the additional participation of solvent molecules. Some authors [14] assume the existence of a TS S_N2-type followed by pseudo rotation mechanism similar to that proposed by Berry for other compounds:[15]



Scheme 2.6 Pseudorotation process for trigonal-bypyramydal compound.

The fact that substitution at a sulfonyl center in organic solvents has often attracted the attention of researchers [16], shows that its reaction mechanism remains insufficiently covered and requires further study.

2.1.1.1 Neutral hydrolysis of arenesulfonyl halides in binary aqueous-organic solvent mixtures

Absence of acid catalysis in hydrolysis of arenesulfonyl chlorides has been found, as there is no acidity dependence of the pseudo-first order rate constants in the pH range 1 to 9.[17, 18, 19] On the contrary, the presence HO^- ions in alkaline medium leads to a significant hydrolysis acceleration; *e.g.* for benzenesulfonyl chloride k_{HO}-/k_{H2O} is $3.0 \cdot 10^5$.[19]

It is generally accepted [16-35] that most of sulfonyl chlorides undergo solvolysis by bimolecular mechanism. However, there are known S_N1-type reaction for several substrates. Thus, Hall and Robertson [18, 36] have made the assumption about unimolecularity in the hydrolysis of N,N-dimetylsulfonyl chloride. Author's conclusions are based on the small solvent KIE (k_{H2O}/k_{D2O}= 1.33) and low sensitivity of substrate to nucleophile changes in aqueous 1,4-dioxane solutions (86.1/13.9%V/V) (piperidine, 0.0231M – k =4.6 s^{-1}; NaOH, 0.0138M – k=4.9 s^{-1}; $NaClO_4$, 0.0068M – k = 5.09 s^{-1}).

Also, it has been proposed that the solvolysis of arenesulfonyl halides implies the formation of a pentacoordinate intermediate (Scheme 2.4). [37] The addition-elimination mechanism (S_AN) has also been proposed in the case of the interaction of thiophene-2-sulfo halides with anionic and neutral nucleophiles [38-40], and in the alkaline hydrolysis of arenesulfonyl fluorides [41, 42], and 2,4,6-trimethylbenzenesulfonyl chloride [43], but the presence of the corresponding intermediates has not yet been proved.

At the same time, there are convincing evidences on the nature of S_N2 solvolysis for most of compounds: absence of salt effect and "common ion" effect, [20] growth of reactivity in the presence of a strong nucleophile, sensitivity to ionizing power of the solvent, and no detection of sulfonium intermediate ions.[34,44,45] By the way, the assertion that the solvolytic reactions of alkanesulfonyl chlorides occurs at least partially through a S_N1-mechanism in polar solvents [46] is not supported.[16, 21] Also, it was assumed that the solvolysis of

2,4,6-trimethylbenzenesulfonyl chloride corresponds to S_N1 mechanism [47] , but after the weakness of this hypothesis was shown [16, 21, 31]. Maskill based on data on solvolysis in 2,2,2-trifluoroethanol, suppossed that the solvolysis of 4-N,N-(dimethylamino)benzenesulfonyl chloride runs under a S_N2 mechanism where bond-breaking significantly prevails over bond-formation in the transition state.[28] Later results on the solvolysis of this compound in 80% aqueous acetic acid and hydrolysis at different pH confirmed this conclusion.[29, 30]

Currently, there is no convincing evidence of the S_N1-reaction mechanism for solvolysis of arenesulfonyl chlorides. However, the detailed aspects of the bimolecular mechanism remain under debate, mainly focused on the relevance of the S_N2 and S_AN pathways,[35, 48, 12] many issues related to the TS involving two solvent molecules (S_N3) [10-12]. Nowadays S_AN mechanism is considered only for the gas phase [16].

In the solvolysis of 2,4,6-trimethylbenzenesulphonyl chloride parallel reaction pathways have been proposed: S_N2 and S_AN, with or without catalyst [31].

The influence of the electronic nature of substituents on the substituted benzenesulfonyl chlorides hydrolysis reaction rate was investigated in several studies [19, 37, 49-51]. Hammett dependences (Eq. 2.1) for the hydrolysis of *meta*- and *para*- substituted benzenesulfonyl chlorides in water [37] and in aqueous 1,4-dioxane [52] are U-shaped (Table 2.1, Figure 2.2).

$$log\frac{k_X}{k_0} = \rho \cdot \Sigma\sigma_X \qquad \text{(Eq. 2.1)}$$

where σ_X is electronic effect of substituent *X*.

The dependence of ln k_{eff} *vs*. $\Sigma\sigma$ can be considered linear only for 13 of the 25 studied benzenesulfonyl chlorides (Table 2.1), in this case the ρ-value at 298K is -0.42±0.04; r = 0.913 [37]. Positive deviation from Hammett plot are most pronounced in the case of 4-OCH_3-, 4-NO_2-, 4-CN-substituted sulfonyl chlorides and the negative for 4-F-derivative. Behavior of sterically hindered substrates will

be discussed later. According to hypothesis [52], the reaction mechanism for the growth of Σσ magnitude is not changed and corresponds to S_N2-mechanism, but changes the relation between the bond-formation of S-OH_2 and bond-cleavage of S-Cl in TS.

Table 2.1 Activation parameters and rate constants for hydrolysis of arenesulfonyl chloride in 1%V/V 1,4-dioxane-water solution at 298 K

Sulfonyl chloride	$k_{obs}\cdot10^3$/ s^{-1}	E_A/ kJ·mol^{-1}	log A/ s^{-1}	$\Delta H^{\neq}$/ kJ·mol^{-1}
Sterically unhindered substrates				
$C_6H_5SO_2Cl$	2.97	56.2	7.31	53.6
4-OMe-$C_6H_4SO_2Cl$	6.57	72.3	10.48	69.8
4-Me-$C_6H_4SO_2Cl$	3.25	69.5	9.68	67.0
4-Br-$C_6H_4SO_2Cl$	2.12	80.0	11.33	77.5
4-Cl-$C_6H_4SO_2Cl$	2.03	70.9	9.72	68.3
4-F-$C_6H_4SO_2Cl$	1.70	82.1	11.62	79.6
4-I-$C_6H_4SO_2Cl$	2.25	72.3	10.02	69.8
4-CN-$C_6H_4SO_2Cl$	2.10	74.5	10.37	71.9
4-NO_2-$C_6H_4SO_2Cl$	2.41	71.8	9.95	69.2
3-Br-$C_6H_4SO_2Cl$	1.91	86.9	12.51	84.4
3-Cl-$C_6H_4SO_2Cl$	1.67	68.7	9.26	66.2
3-I-$C_6H_4SO_2Cl$	1.70	69.3	9.37	66.9
3-NO_2-$C_6H_4SO_2Cl$	1.27	94.4	13.65	91.9
3-OH-$C_6H_4SO_2Cl$	2.50	84.1	12.13	81.6
3,4-Cl_2-$C_6H_3SO_2Cl$	1.49	73.4	10.01	70.9
4-Cl-3-NO_2-$C_6H_3SO_2Cl$	1.28	61.4	7.42	58.9
Sterically hindered substrates				
2-Me-$C_6H_4SO_2Cl$	4.73	69.87	9.92	67.4
4-Cl-2-Me-$C_6H_3SO_2Cl$	2.45	54.67	6.97	52.2
2-Me-5-NO_2-$C_6H_3SO_2Cl$	2.22	70.43	9.69	67.9
2,4,6-Me_3-$C_6H_2SO_2Cl$	3.51	62.50	8.50	60.0
2,3,4-Cl_3-$C_6H_2SO_2Cl$	0.663	65.05	8.21	62.5
2,4,5-Cl_3-$C_6H_2SO_2Cl$	0.708	73.54	9.73	71.0
2-Cl-5-NO_2-$C_6H_3SO_2Cl$	0.932	77.80	10.57	75.3
2-NO_2-$C_6H_4SO_2Cl$	0.645	72.18	9.45	69.7
4-Cl-2-NO_2-$C_6H_3SO_2Cl$	0.462	61.37	7.42	58.9

The authors of the review [53] also, believe that the observed bend in to the correlation graphs of the dependence of the reactivity of electronic nature of the substituent can be explained in a single bimolecular mechanism. Electron-donating substituents will promote breaking of S-Cl bond to a greater extent than the bonding of S-Nu, and would lead to reaction rate increasing, (ρ <0). Electron withdrawing substituents will contribute to a greater extent bond formation S-Nu than bond-breaking of S-Cl, and will also lead to speed increasing, however (ρ> 0).

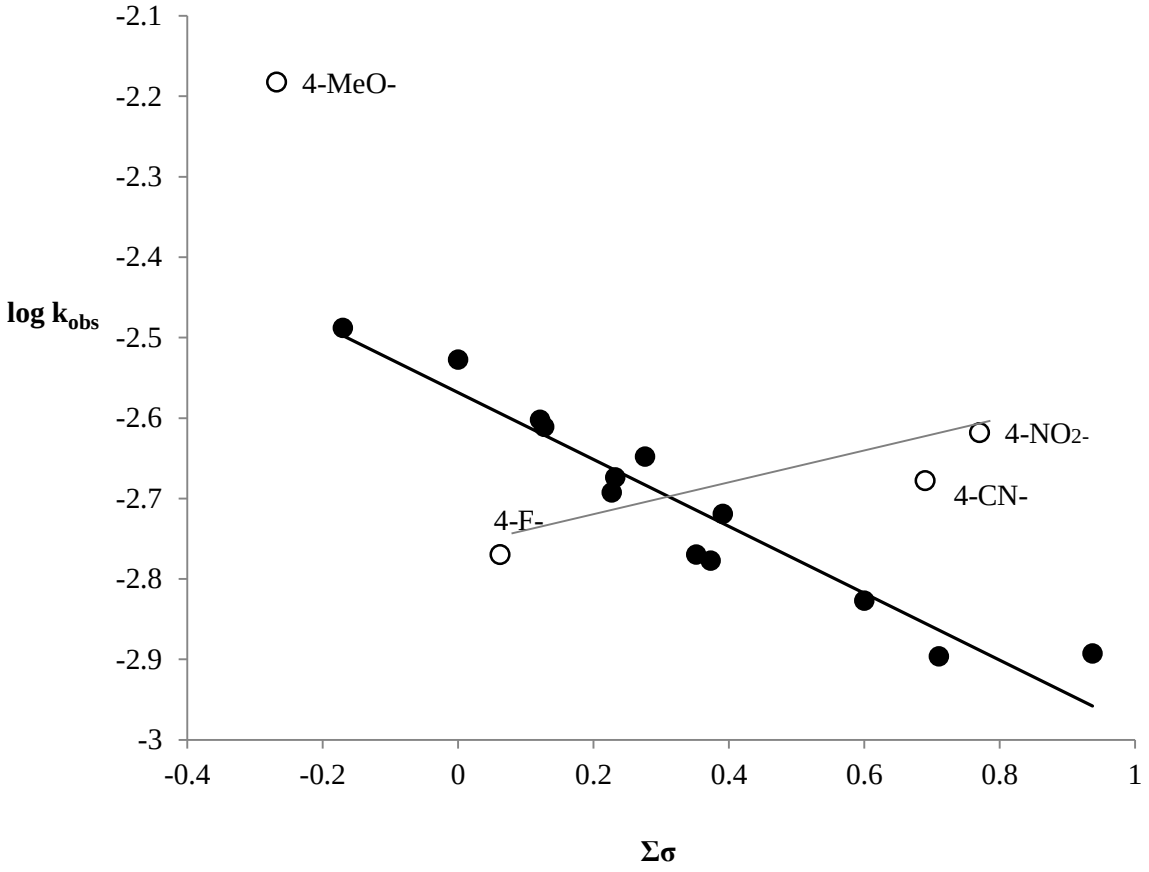


Figure 2.2 Hammett plot for hydrolysis of arenesulfonyl chloride in 1%V/V 1,4-dioxane-water solution at 298 K; $R^2 = 0.913$

● – Basic series substrates; ○ – Deviating substrates.

Balistreri *et al.* [40] compared the behavior of aliphatic and aromatic sulfonyl halides (Fig. 2.3) using the Taft-Pavelich equation:

$$\log \frac{k}{k_0} = \rho^* \sigma^* + \delta E_S, \qquad \text{(Eq. 2.2)}$$

where σ^* and E_S are Taft parameters that characterize the polar and steric effects of the substituents, respectively.

They conclude that the TS is stabilized by electron-withdrawing groups that facilitate the leaving of chloride ion. The transition state is located, in the More O'Ferrall-Jencks diagram, between S_AN and S_N2 mechanisms, with bond formation ahead of bond breaking.

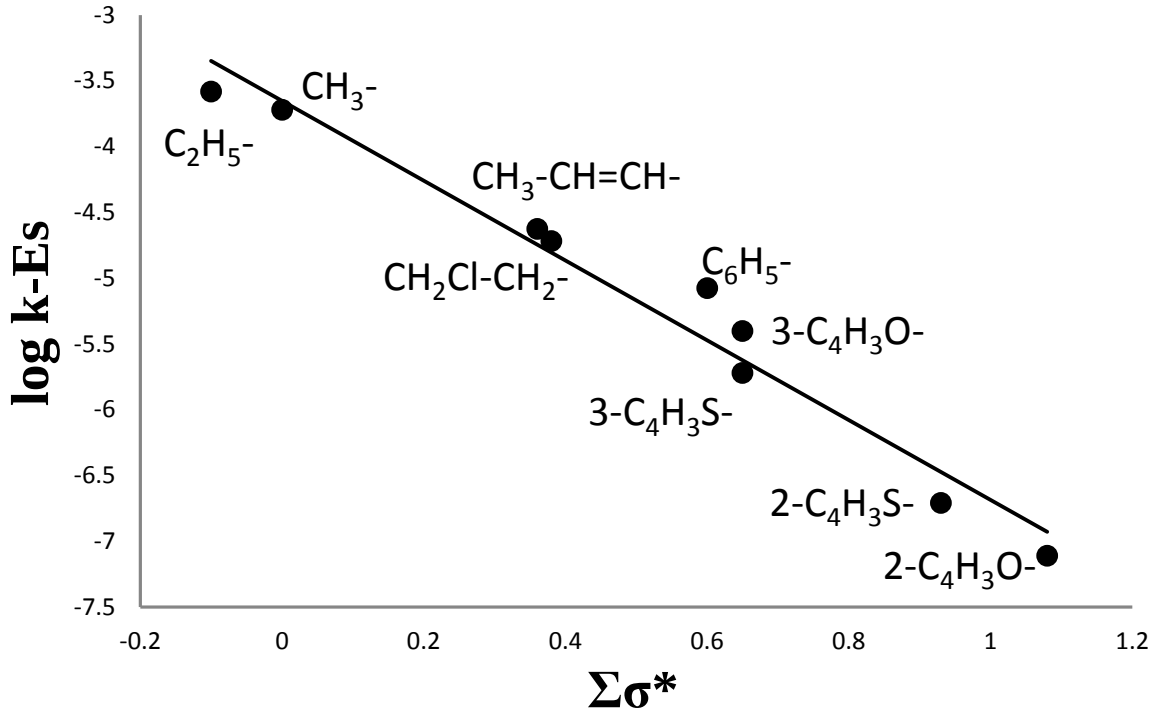


Figure 2.3 Taft-Pavelich plot for the hydrolysis of aliphatic and aromatic sulfonyl chlorides X-SO_2Cl in water at 25 °C; $R^2 = 0.967$

Tonnet and Hembly significantly contributed to unravel the neutral hydrolysis mechanism of the arenesulfonyl chlorides. [47] They found the solvent polarity has a key role on the transition state structure (Table. 2.2).The formation of S···O bond is more relevant in solvents with low dielectric constant than the stretching and polarization of S-Cl bond in more polar media. These authors suggest that all substrates react by the S_N2 mechanism, except 2,4,6-trimethylbenzenesulfonyl chloride. Analysis of the activation parameters[47] supports the S_N2 mechanism for all substrates (Figure 2.4).

Table 2.2 Rate constants and activation parameters for the hydrolysis of arenesulfonyl chlorides in1,4-dioxane-water mixtures at 298 K

Sulfonyl chloride	Mole fraction of water	$k_{eff} \cdot 10^{-4}$/ s^{-1}	$\Delta G^{\neq}$/ kJ / mol	$\Delta H^{\neq}$/ kJ / mol	$-\Delta S^{\neq}$/ J / (mol·K)
$C_6H_5SO_2Cl$	1	30.78	87.4	69.1	61.5
	0.978	24.27	88.0	67.8	67.8
	0.956	14.23	88.7	62.8	87.0
	0.903	9.48	90.3	63.1	91.2
4-$MeC_6H_4SO_2Cl$	1	37.27	86.9	72.7	47.7
	0.978	29.3	87.5	71.0	55.6
	0.956	22.04	88.2	68.0	67.8
	0.903	7.17	91.0	60.6	102.0
4-$OMeC_6H_4SO_2Cl$	1	68.6	85.4	73.6	39.7
	0.978	41.31	86.7	67.7	63.6
	0.956	26.34	87.7	66.2	72.4
	0.903	8.72	90.5	63.5	90.8
4-$BrC_6H_4SO_2Cl$	1	20.44	88.4	76.6	39.3
	0.978	18.75	88.6	71.0	59.0
	0.956	16.6	88.9	70.9	60.2
	0.903	9.14	90.4	68.1	74.9
4-$NO_2C_6H_4SO_2Cl$	1	26.62	87.7	77.4	34.3
	0.978	30.02	87.4	73.6	46.4
	0.956	32.82	87.2	69.5	59.4
	0.903	30.72	87.4	59.2	94.6
3-$NO_2C_6H_4SO_2Cl$	1	13.51	89.4	79.1	34.3
	0.978	14.97	89.2	75.6	45.6
	0.956	14.97	89.2	68.9	67.8
	0.903	15.52	89.1	64.8	81.6
2,4,6-$Me_3C_6H_2SO_2Cl$	0.903	49.7	86.2	52.6	113
	0.823	12.48	89.6	56.1	112

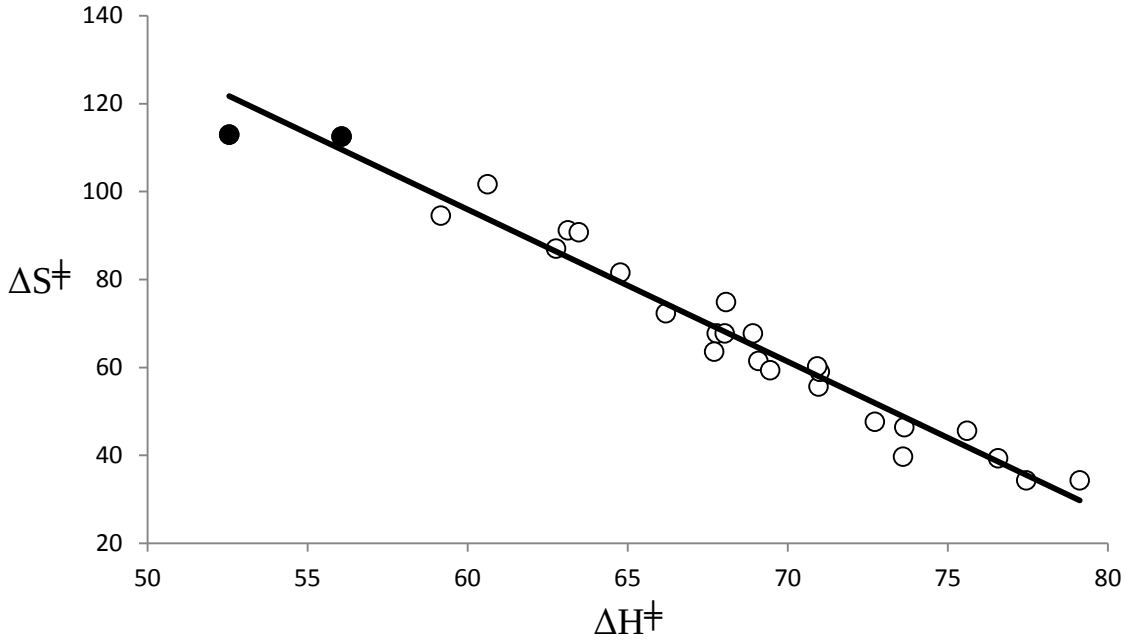


Figure 2.4 Isokinetic dependence for the hydrolysis of arenesulfonyl chlorides in aqueous 1,4-dioxane of various polarity, 25 °C according to [47], (R^2 = 0,96)

● – 2,4,6-trimethylbenzenesulfonyl chloride; ○ – other sulfonyl chlorides.

Thus hydrolysis of arenesulfonyl halides in water-organic solvents is characterized by several features such as the sensitivity to the polarity of the medium, catalysis in alkaline media, and the dependence of electronic structure of the transition state from the nature of the substituent in the benzene ring; however, despite the popularity of the aforementioned topic, a common view on the reaction mechanism has not been formed yet.

2.1.1.2 Arenesulfonyl halides alcoholysis

There are a myriad of papers devoted to nucleophilic substitution in arenesulfonyl halides with the participation of alcohols,[10-13,48,54-62] most of them in alcohol-water mixtures, which implies the presence of two competing solvolysis pathways: alcoholysis and hydrolysis. In addition to the main process some side reaction might occur[54]:

$$R\text{-}SO_2Cl + R'OH \rightarrow RSO_2OH + R'Cl$$
$$R\text{-}SO_3R' + R'OH \rightarrow RSO_2OH + R'OR'$$
$$R\text{-}SO_3R' + HOH \rightarrow RSO_2OH + R'OH$$

In pure alcohols just alcoholysis of sulfonyl chlorides takes place, side reactions are very slow and do not affect the main process.[54]

Theoretical studies in gas phase on hydrolysis or methanolysis of methylsulfonyl chlorides are in favour of the S_N2 process including a four-membered cyclic TS [55-57]. Investigation on the kinetics [57-59], of the solvolysis of *p*-substituted benzenesulfonyl chlorides in aqueous binary mixtures of acetone, methanol, ethanol, acetonitrile and 1,4-dioxane have shown that the reaction was of third order, with a first order observed rate constant, which is determined mainly by proton molar concentration of the solvent, so that the reaction rate probably depends on the stoichiometry of the solvent. A change in the mechanism of the reaction depending on the water content and solvent polarity has been proposed.[48]

In agreement with previous studies,[60] the cited two concurrent reaction channels play a role, S_N1 being more relevant in aqueous media. The chemical kinetic mechanism of methanolysis of *p*-substituted benzenesulfonyl chlorides under the different solvents concentration, mechanism consists of a mixture of S_N1 and S_N2 reaction paths, but in methanol-ethylene glycol the S_N2-mechanism dominates.[61]

Table 2.3 collects alcoholysis constants of some benzenesulfonyl chlorides in absolute alcohols. Methanolysis is several times faster than ethanolysis which is in agreement with the general idea – the increasing of the media polarity causes acceleration of those reactions in which the TS more polar comparatively with the reagents.

Table 2.3 First order kinetic rate constants for the alcoholysis of some benzensulfonyl chlorides in methanol and ethanol

Substrate	T. °C	$k \cdot 10^4 / s^{-1}$		Reference
		Methanol	Ethanol	
4-NO_2-$C_6H_4SO_2Cl$	25	1.71	0.54	[48]
	35	2.18	1.07	[13]
	40	6.42	1.87	[62]*
	52	12.73	4.17	
$C_6H_5SO_2Cl$	25	0.815	1.83	[62]*
	35	1.51	0.36	[13]
	40	2.82	0.608	[62]*
	52	7.98	1.63	
C_6H_5-CH=CH-SO_2Cl	25	1.14	0.272	[13]
	35	2.67	0.832	
	45	6.33	2.18	
	55	12.2	5.64	
4-Me-$C_6H_4SO_2Cl$	25	1.1	0.198	[63]
	40	2.98	0.633	[62]*
	52	8.05	1.66	
4-Br-$C_6H_4SO_2Cl$	25	0.823	0.202	[62]*
	40	2.97	0.773	
	52	8.17	1.92	
4-Cl-$C_6H_4SO_2Cl$	25	0.83	0.22	[10]
4-OMe-$C_6H_4SO_2Cl$	25	1.28	0.22	[63]
3,4-$(OMe)_2$-$C_6H_3SO_2Cl$	25	1.44	0.299	[12]
2,4-$(OMe)_2$-$C_6H_3SO_2Cl$	25	0.813	0.197	[11]
2,6-Me_2-4-OMe-$C_6H_2SO_2Cl$	25	19.6	2.48	[63]
2,4,6-Me_3-$C_6H_2SO_2Cl$	25	10.4	1.54	[31]

* Kinetics in acetone-alcohol mixtures, the mole fraction of ethanol is 0.93, 0.95 for methanol

Kinetic mechanism of benzenesulfonyl chlorides in alcoholic solutions has been scarcely investigated in a systematic way, studies under different conditions and with the addition of other substances complicates the detailed knowledge of the reaction mechanism.

2.1.1.3 Influence of the solvent on the arenesulfonyl chloride solvolysis: *o*-alkyl substrates

The original Grunwald-Winstein equation (Eq. 2.3) was developed in 1948 [64] to describe the influence of solvents in chemical reactions where a bond is heterolytically broken or formed:

$$\log\left(\frac{k}{k_0}\right) = mY, \qquad \text{(Eq. 2.3)}$$

where k and k_0 is a rate constant in the tested solvent and in the standard solvent (80% ethanol), m reflects the sensitivity to changes in solvent ionizing power Y.

Rubleva *et al.*[49] investigated the influence of media polarity, their results for the neutral hydrolysis arenesulfonyl chlorides1,4-dioxane-water mixtures at 313 K are collected in table 2.4. These substrates demonstrate one peculiarity: as the system reactivity increases the m parameter decreases, whereas it augments for alkyl-*ortho* sterically hindered substrates (№ 1 – 5, see table 2.4); thus, this behavior apparently contradicts "reactivity-selectivity" Hammond postulate, which is likely due to the strong specific solvation of alkyl-*ortho* substituted compounds, which is typical of the S_N2-type reaction.

Table 2.4 First order rate constants for the hydrolysis of X-ArSO_2Cl in 40-70%V/V 1,4-dioxane-water solutions at 313K and their correlation with constant parameters Y to equation (2.3)

№	X	$k_{eff}\cdot10^{-4}$/ s^{-1} %V/V 1,4-dioxane-water				*m*	*r*
		70%	60%	50%	40%		
1	2,6-Me_2-4-*i*-Pr-	3.84	12.0	32.4	70.8	0.60±0.03	0.999
2	2,4,6-*i*-Pr_3-	0.351	1.15	2.98	5.63	0.57±0.04	0.992
3	2,6-Me_2-4-*t*-Bu-	3.65	11.7	29.5	74.1	0.62±0.01	0.999
4	2,4,6-Et_3-	0.794	1.99	4.47	9.55	0.51±0.01	0.999
5	2,4,6-Me_3	4.47	13.2	34.2	87.0	0.61±0.01	0.999
6	2-Me-	2.25	5.01	10.7	22.9	0.45±0.01	0.999
7	H-	1.71	4.60	9.57	19.5	0.50±0.02	0.999
8	4-Br-	3.74	6.87	15.0	25.2	0.40±0.02	0.999
9	4-NO_2-	24.0	35.1	46.3	60.1	0.19±0.01	0.997
10	4-*t*-Bu-	0.888	2.74	6.24	9.57	0.49±0.05	0.991

For bimolecular reactions where solvent also acts as a nucleophile (or base) the original Grunwald-Winstein equation (Eq. 2.3) can be modified to take into account of the sensitivity (*l*) to changes in solvent nucleophility (*N*):

$$\log\left(\frac{k}{k_0}\right) = lN + mY \qquad \text{(Eq. 2.4)}$$

In these solvolytic reactions, the leaving group is a neutral molecule, thus avoiding the significant interaction solvent - leaving group, which is not the case if the leaving group is anionic. The development of nucleophilic reactivity scales of solvents has been reviewed.[21, 65] It was shown that different leaving groups require different *Y* values.[66] There are many references for similar substrates where the solvolysis reaction of adamantyl chloride [13, 21, 33, 34, 65, 67-72] or adamantyl bromide [73] being used as reference instead of the classical *t*-butyl chloride. Therefore, in what follows correlations will be made relative to this compound. The results of correlation analysis of reaction of some sulfonyl chloride according to the equation (Eq. 2.4) are presented in Table 2.5. In calculations data from solvolysis of various aqueous mixtures of ethanol, methanol, acetone, 2,2,2-trifluoroethanol, 1,4-dioxane, 1,1,1,3,3,3-hexafluoro-2-propanol, heavy water, and solutions of 2,2,2-trifluoroethanol and ethanol or water were used.

Sensitivity parameter (*l*) measures the sensitivity to changes in the nucleophilicity of the solvent varying from the smallest value of l_3 = 1.07 of unhindered derivatives arenesulfonyl chlorides to l_2 = 1.44 (the index corresponds to the number of the substance in Table 2.5).

Usually for this series mean values like for l_1 = 1.26 are typical. The ratio l / m is also very close for the whole series of sterically unhindered substrates $(l_2/m_2)_{\min}$ = 1.78; $(l_1/m_1)_{max}$= 2.53. However, sterically hindered compounds show lower sensitivity (l_6=0.96; l_7=0.97), with a relatively *m* constant for all substrates. This variation of *l/m* is usually explained by a single S_N2 mechanism for all series, ranging from a "loose" transition state for electron-donor groups (*p*-OMe), to a

more "tight" TS with (*p*-NO_2) group,[13,33-34, 74] Such low statistical indicators (R^2 = 0.917) likely suggest a tendency than a clear dependence (Figure 2.5).

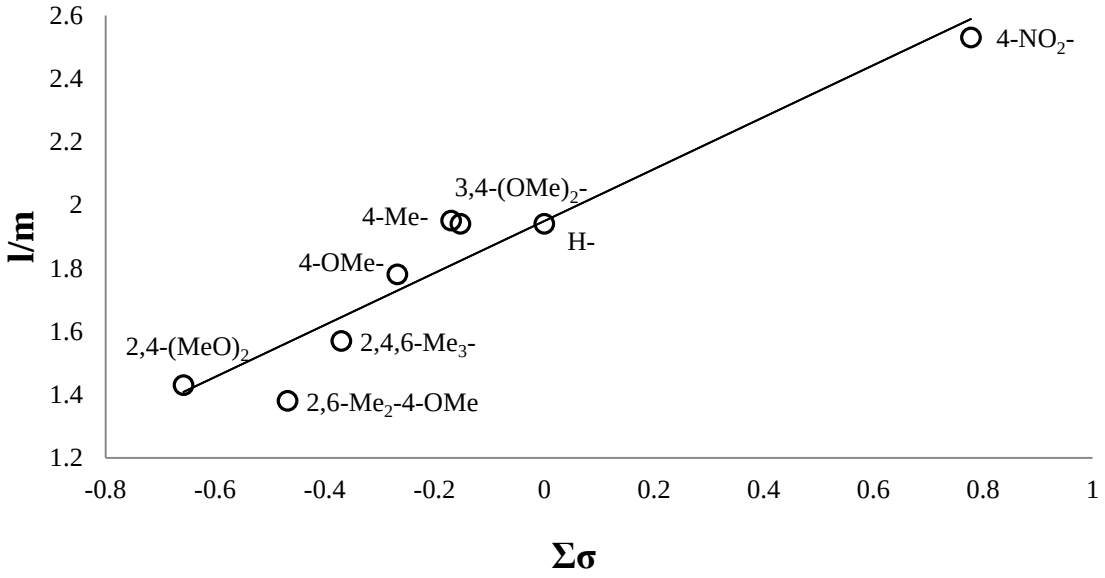


Figure 2.5 Dependence* *l/m=f(Σσ)* for arenesulfonyl chlorides from Table 2.5 (R^2 = 0,917)

The presented material is sufficient evidence for the S_N2-mechanism in the solvolysis all these arenesulfonyl chlorides in various solvents with different water content.

Table 2.5 Correlation of the specific rates of solvolytic nucleophilic displacement at the sulfur of sulfonyl chlorides using the extended Grunwald-Winstein equation (Eq. 2.4)

№	Substrate	T, °C	n	*l*	*m*	*c*	R	*l/m*	Reference
1	$C_6H_5SO_2Cl$	35.0	29	1.26±0.03	0.65±0.03	0.13±0.05	0.979	1.94	[13]
2	4-NO_2-$C_6H_4SO_2Cl$	35.0	23	1.4±0.1	0.57±0.06	0.2±0.1	0.945	2.53	[13]
3	4-OMe-$C_6H_4SO_2Cl$	25.0	38	1.07±0.08	0.60±0.03	0.22±0.06	0.967	1.78	[13]
4	4-Me-$C_6H_4SO_2Cl$	35.0	13	1.3± 0.2	0.66±0.06	0.2±0.1	0.975	2.00	[13]
		25.0	34	1.19±0.07	0.61±0.02	0.20±0.05	0.975	1.95	
5	3,4-$(OMe)_2$-$C_6H_3SO_2Cl$	25.0	40	1.24±0.07	0.64±0.03	0.14±0.06	0.967	1.94	[13]
6	2,4-$(OMe)_2$-$C_6H_3SO_2Cl$	25.0	30	0.9±0.1	0.65±0.06	0.30±0.10	0.918	1.43	[11]
6	2,4,6-Me_3-$C_6H_2SO_2Cl$	25.0	37	1.0±0.1	0.61±0.04	0.24±0.01	0.936	1.57	[33]
7	2,6-Me_2-4-OMe-$C_6H_2SO_2Cl$	25.0	36	1.0±0.1	0.70±0.05	0.13±0.01	0.94	1.38	[33]
8	C_6H_5-CH_2-SO_2Cl	45.0	25	0.80±0.06	0.39±0.04	0.21±0.06	0.947	2.05	[33]
9	C_6H_5-CH=CH-SO_2Cl	45.0	43	1.24 ± 0.04	0.58±0.02	0.07±0.04	0.982	2.14	[13]
10	Me-SO_2Cl	45.0	39	1.17±0.04	0.49±0.02	0.23±0.05	0.981	2.39	[13]
11	*i*-Pr-SO_2Cl	45.0	19	1.28±0.05	0.64±0.03	0.80±0.06	0.988	2.00	[13]
12	Me_2N-SO_2Cl	25.0	25	1.20±0.04	0.72±0.03	0.11±0.04	0.985	1.67	[13]
13	2-thiophene -SO_2Cl	25.0	34	1.35±0.05	0.70±0.02	0.28±0.05	0.983	1.93	[13]

where n - sample size;
R –correlation coefficient of multiparameter regression;
T - temperature.

2.1.1.4 Kinetic solvent isotope effect (KSIE)

Kinetic isotope effect (KIE) accounts for the effect of reactivity change after isotopic replacement in the bond being broken/formed in the rate limiting step. Also in case of solvolytic KIE the reactivity change is caused by unequal solvation of reactants and transition state in protonated and deuterated solvents (solvent KIE). For hydrolysis of arenesulfonyl chlorides KSIE lies between 1.35 and 1.86 (Table 2.6).

Table 2.6 KSIE for solvolysis of X-ArSO_2Cl at 25 ° C

X	k_{H_2O}/k_{D_2O}	k_{MeOH}/k_{MeOD}
H	1.58 [75]	1.79[13]
4-OMe-	1.41 [75]	1.58[13]
4-Me-	1.50 [75]	1.72[13]
4-Br-	1.63 [75]	-
4-Cl	1.65 [75]	1.89[13]
4-NO_2-	1.82 [75]	2.31[13]
2,4,6-Me_3-	-	1.68[13]
3,4-$(OMe)_2$-	1.35[12]	1.45[12]
2,4-$(OMe)_2$-	1.86[11]	1.74[11]

KSIE value increases during the transition from electron-donor to the electron-withdrawing substituent, which is consistent with an increase in the contribution of bond O···H, *i.e.* a more "tight" TS. The kinetic isotope effect for methanolysis ($KSIE_M$) is slightly higher than for hydrolysis ($KSIE_W$) - $KSIE_M$ / $KSIE_W \approx 1.13$, which may suggest the same nucleophilic substitution mechanism, and also about more "tight" TS for methanolysis.

Bentley [10] assumes that a high KIE (> 2) is a criterion for trimolecularity, *i.e.* S_N3 mechanism (Scheme 2.5). According to Table 2.6 alcoholysis of all substrate by methanol fulfill this criterion, but the 4-NO_2-derivative. It should be noted that nitro substituted compounds show anomalous reactivity within Hammett equation, and also in other solvolytic processes [37, 52]. Perhaps this is due to the

large acceptor properties of the *p*-nitro group which enters into conjugation with the reaction center.

KSIE in 70% and 40%V/V 1,4-dioxane-D_2O for sterically hindered and unhindered arenesulfonyl chlorides (Table 2.7) shows that the mechanism of hydrolysis corresponds to a synchronous S_N2, and likely the attack of a H_2O or D_2O molecule is not accompanied by proton transfer to the leaving group Cl^- [76].

Table 2.7 Kinetic solvent isotope effects (k_{H2O}/k_{D2O}) for hydrolysis of X-$ArSO_2Cl$ 70%V/V and 40%V/V 1,4-dioxane-D_2O at 313K

X	k_{H2O}/k_{D2O}	
	70% 1,4-dioxane-D_2O	40% 1,4-dioxane-D_2O
2,4,6-*i*-Pr_3-	1.20	1.15
2,6-Me_2-4-*t*-Bu-	1.18	1.12
2,4,6-Me_3-	1.16	1.10
2,6-Me_2-4-*i*-Pr -	1.18	-
4-*t*-Bu-	1.24	1.22
2-Me-	1.48	1.36
H-	1.44	1.39
4-Br-	1.46	1.37
4-NO_2-	1.88	1.77

Thus the values of the solvolytic kinetic isotope effects of arenesulfonyl chlorides indicate the bimolecularity of solvolytic processes. This view is supported by several authors [11-13, 75, 76], which is not inconsistent with fundamental concepts about reactivity of organic compounds.

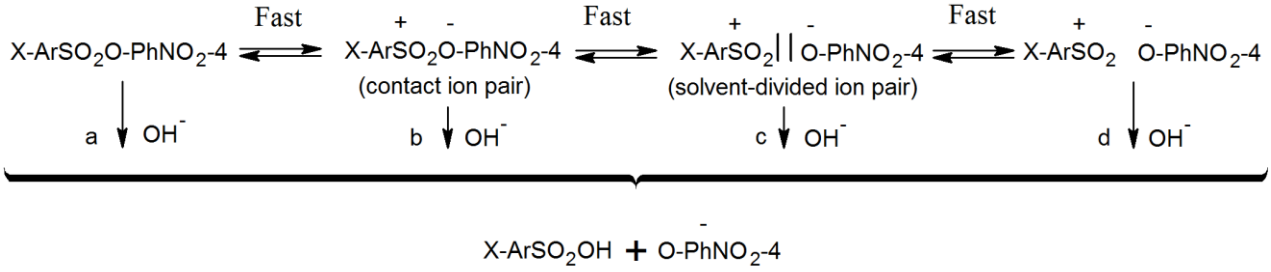
2.2 STERIC EFFECTS OF THE SUBSTRATE'S STRUCTURE IN NUCLEOPHILIC SUBSTITUTION AT A SULFONYL CENTER

We are talking about the accelerating effect of *o*-alkyl groups on the nucleophilic substitution at the sulfur atom of the sulfo group. It should be noted that for the last 50 years a lot of evidences of this phenomenon have been gathered [31, 37, 40, 77-94]. This section will summarize and analyze everything related thereto.

2.2.1 Nucleophilic substitution in sterically hindered arenesulfonates

Steric effects of spatially hindered leaving group in crowded arenesulfonates were studied as in the reaction of trifluoracidolysis of *iso*-propyl, di-*tert*-butyl-carbinol, 2-adamantyl esters of 2,4,6-trimethylbenzensulfo, 2,4,6-tri-*iso*-propilbenzensulfo, 4-methylbenzensulfo acids [77]. The authors found that at an increase of steric tensions in the molecule augments the sulfonate solvolysis rate constant. A possible reason in the author's opinion is the interaction between the oxygens of the sulfo groups and *o*-alkyl groups.

Influence of structural features of the substrate on the kinetic peculiarities of nucleophilic substitution near the sulfonyl center was investigated. For example, the reaction of alkaline hydrolysis of arenesulfonates in the media of 70%V/V aqueous 1,4-dioxane [78-79]. A general scheme of the process can be represented as follows:



Scheme 2.7 Mechanism of alkaline hydrolysis of arenesulfonates in 70%V/V aqueous 1,4-dioxane

The classical S_N2-mechanism is the *a* reaction. It is clear that nucleophile attack can also take place in paths *b*, *c*, *d* in varying degrees of bond breaking S···O. But all the variations of the mechanism in rate limiting step are relevant to bond formation S····Nu, which should be manifested in the kinetic regularities of solvolysis reactions.

Table 2.8 shows that the reactivity of all studied compounds increases with increasing temperature and electron-withdrawing properties of the substituent. However, in some cases of the accumulation of electron-donor alkyl groups in the acid part of molecule leads to an increase in the reaction rate of substitution (I-IV, Table 2.8). Some authors do not assume the existence of concurrent hydrolysis mechanisms in the studied compounds. [78-79]

Table 2.8 Rate constants k_{II}, and activation parameters of alkaline hydrolysis XAr-SO_2-O-Ph-NO_2-4 in 70%V/V aqueous 1,4-dioxane

№	X	$k_{II}\cdot10^2$, $dm^3\cdot mol^{-1}\cdot s^{-1}$			$\Delta H^{\neq}$/	$-\Delta S^{\neq}$/
		303 K	313 K	323 K	$kJ\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$
I	2,4,6-*i*-Pr_3-	0.633	2.17	6.27	83±2	-13±8
II	2,6-Me_2-4-*t*-Bu-	0.427	1.47	3.16	79±10	29±7
III	2,4,6-Me_3-	3.33	10.4	22.4	75±8	25±24
IV	2,6-Me_2-4-*i*-Pr-	0.850	2.78	6.26	79±7	24±23
V	4-OEt-	0.895	2.23	4.94	66.9±0.6	63±1
VI	3,4-Me_2-	0.739	1.56	3.45	60±2	88±7
VII	4-*t*-Bu-	0.600	2.10	4.73	81±8	19±27
VIII	2,5-Me_2-	0.591	1.36	4.09	75±8	37±25
IX	4-Me-	1.59	3.21	7.33	60±4	83±13
X	4-Et-	1.20	2.81	8.32	76±7	31±22
XI	4-Cl-	6.54	15.0	27.2	55±4	85±14
XII	4-Br-	11.7	29.5	50.0	56±8	75±27
XIII	2,4,6-Me_3-3-NO_2-	24.7	41.5	83.0	46±5	103±16
XIV	4-NO_2-	303	461	648	40±6	102±20

Features of the reaction mechanism can be roughly grouped into two groups (Figure 2.6). The first (*A*) includes compounds containing *m*- and *p*- substituents of small volume irrespective of its electronic donor-acceptor properties (V, VI, IX, XI-XIV in Table 2.8). They are characterized by changes in enthalpy and entropy

of activation within 40-65 kJ·mol^{-1} and - (60-100) J·mol^{-1}·K^{-1}, respectively (Figure 2.6). The enthalpy of activation varies in the range of 75-82 kJ·mol^{-1}; the entropy of activation taking into account the calculated error is close to zero (Figure 2.6). Thus, for substrates *A* there is a profit in enthalpy of activation, but the transition state is characterized by large steric requirements. For compounds *B* (Figure 2.6), the increase of the activation enthalpy should lead to a decrease in the hydrolysis reaction rate. But at the same time a sharp increase in the activation entropy points to an increase in the number of degrees of freedom of TS in comparison with the initial state. Thus, the increase of reactivity within the studied set of substrates can be explained by two different factors: the low value of enthalpy of activation $\Delta H^{\ddagger}$ (*m*- and *p*- substituted derivatives) and close to the initial entropy of the transition state ($\Delta S^{\ddagger} \approx 0$, *o*-alkyl derivatives). This fact is quite unexpected, in terms of steric requirements of nucleophilic attack of sulfur atom for the second group of compounds (*B*).

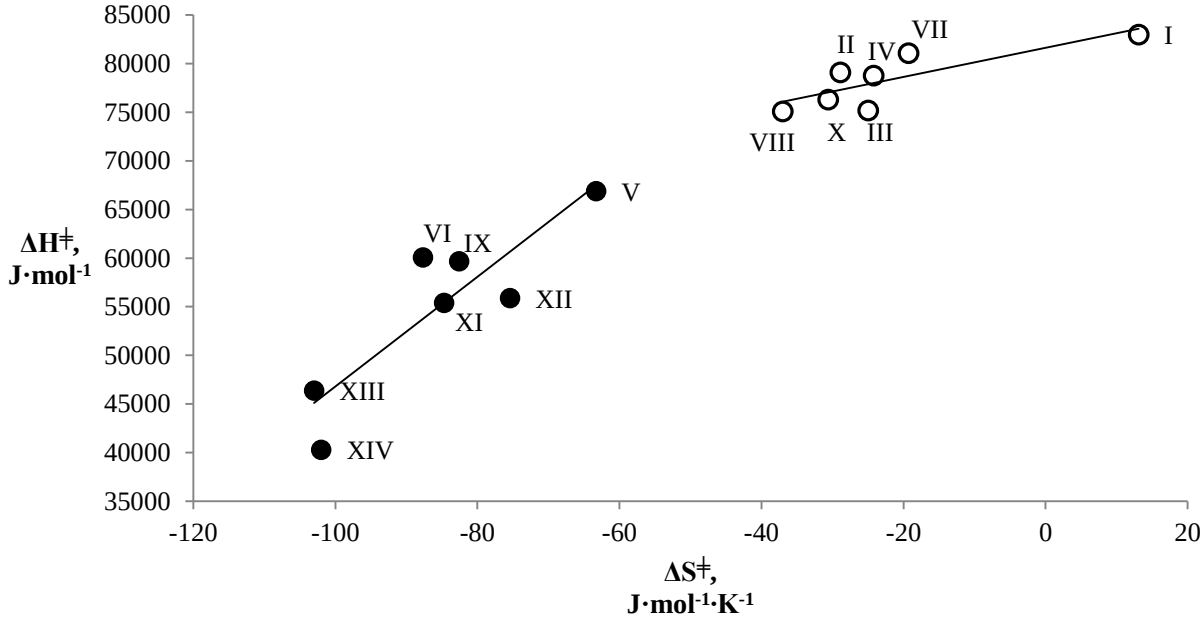


Figure 2.6 $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ for alkaline hydrolysis of arenesulfonates X-ArSO_2OPh-NO_2-4 in 70% aqueous 1,4-dioxane.

● – A group; ○ – B group.

Some authors [79-80] make assumptions about the conformational rigidity of sterically hindered sulfonyl systems and about the significant change in stereoelectronic nature of the transition state by varying the structure of the substrates acyl moiety. Also, it was concluded that the increase in reactivity in the series can be attributed to steric interactions that facilitate a transition state of trigonal-bipyramidal structure due to the high conformational flexibility of substrates.

2.2.2 Steric effects in the nucleophilic substitution of arenesulfonyl halides

Many authors showed a positive of *o*-effect at sulfur atom in their studies, [14, 31, 37, 40, 80-94] but the contradictory views about the nature of this phenomenon suggest the issue is still insufficiently and incompletely addressed.

Studies on chlorine isotopic exchange between sulfonyl chlorides and tetraethylamine chloride (acetonitrile, -28-0 ° C) show that the presence of *o*-alkyl substituents near the sulfur atom accelerates the nucleophilic substitution at the sulfonyl center (Table 2.9). [14, 81] Reactivity order of X-SO_2Cl:

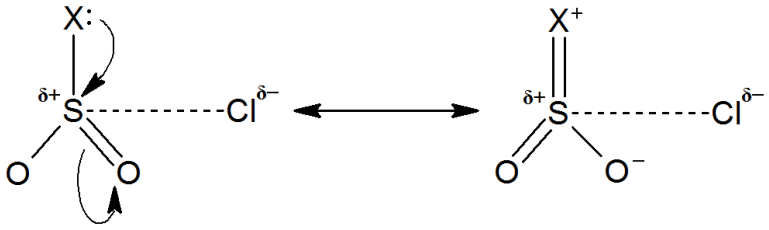
2,4,6-Me_3>2,4,6-*i*-Pr_3≈2,4,6-Et_3>2-Et>2,5-Me_2>2-Me>H>2-*i*-Pr>
>2,4-Me_2≈2,3,4,5,6-Me_5>4-Me≈3,4-Me_2.

Table 2.9 First order rate constants and activation parameters for isotopic exchange of chlorine between arenesulfonyl chloride and Et_4NCl[36]

Sulfonyl chloride	$k_{eff}\cdot 10$/ $L\cdot mol^{-1}\cdot s^{-1}$	E/ $kJ\cdot mol^{-1}$	$\Delta S^{\neq}$/ $J\cdot mol^{-1}\cdot K^{-1}$
$C_6H_5SO_2Cl$	1.33 ± 0.04	60 ± 3	49.4
4-Me-$C_6H_4SO_2Cl$	0.67 ± 0.05	61 ± 5	52.6
2,4,6-Me_3-$C_6H_2SO_2Cl$	6.1 ± 0.3	52 ± 7	67.4
2,4,6-*i*-Pr_3-$C_6H_2SO_2Cl$	3.7 ± 0.8	54 ± 3	65.3

According to the authors [81] this may be due to a decrease in steric interactions in the TS in going from the tetrahedral structure of sulfonyl chloride to the trigonalbipyramid.

Balistreri *et al.* [40] found an enhanced reactivity for 2,4,6-trimethylbenzenesulfonyl chloride versus benzenesulfonyl chloride in the hydrolysis reaction. Authors highlight the significant contribution of *o*-alkyl substituents in the reactivity, and associate it with the effect of hyperconjugation, and with steric effects acting in the only direction, both accelerating the reaction rate. Conjugation might accelerate the reaction by stabilizing the "loose" transition state:



Scheme 2.8 - Effects of conjugation at sulfur atom

Bentley also obtained similar results.[31] According to this author the nucleophilic attack of primary alcohols or amines is not strongly inhibited by 2,6-dialkyl groups, and 2,6-dimethyl and even 2,6-di-*iso*-propyl group due to the rotation of the -SO_2Cl, [82-84] and gives asceleration rate less than tenfold. This author assumes the existence of two-channel mechanism in the hydrolysis of 2,4,6-trimethylbenzenesulfonyl chloride: S_AN-type and general base catalysis.

Haughton and collaborators [37] studied the solvolysis of sterically hindered and unhindered substrates 1%V/V 1,4-dioxane-water mixtures. As shown in table 2.1 acceleration is only observed in the presence of *o*-methyl groups; on the contrary, the presence of other *o*-substituents leads to a noticeable deceleration.

Electron-withdrawing substituents stabilize the transition state more strongly in comparison with the initial state, and accelerate the reaction. If the influence of electron-withdrawing substituents on the reactivity can be explained by their steric effect, then in the case of *o*-alkyl substituents it is the opposite regarded to their

electronic effects and structural requirements of the TS. Those authors believe that all substrates react by the two-step reaction, rate-limiting step being the decomposition of the five-coordinated intermediate.

Another example of solvolysis of sterically hindered aromatic sulfonyl chlorides was reported by Gnedinyn and Ivanov [85]; in this case the solvolysis was carried out in 99.72% H_2SO_4. *o*-substituted substrates react a bit slower than *p*-substituted ones. However, the deceleration does not change the reactivity order coming from the inductive effect of alkyl groups:

o-*i*-Pr>*o*-Et>*o*-Me

This reagent has different steric requirements in comparison with water, and reaction mechanisms are likely different. In fact, they argue that the complex is formed between sulfonyl chloride and $H_3SO_4^+$. Later this was confirmed by other researchers [86, 87] who studied they hydrolysis of arenesulfonyl chloride in water and 50% sulfuric acid, where was registered the overestimated reactivity of *o*-toluene sulfonyl chloride, which is consistent with previous data.

Rubleva *et al.* [49, 76, 88-92] have investigated the kinetics of hydrolysis of sterically hindered arenesulfonyl chlorides in 1,4-dioxane-water mixtures (Table 2.10). They studied the influence of KIE [76], the structural features of the substrate [49, 88, 89], the polarity of the medium,[90] and the nature of leaving group [71]. All of *o*-methylated substrates demonstrate acceleration in comparison with *p*- and *m*-compounds in the framework of the Hammett equation (Fig. 2.7). They proposed an asymmetric TS as the result of an S_N2-type process, which depends on the properties of the benzene ring substituent(s). For *o*-methyl derivatives proposed "loose" TS, where part of the old bond breaking is dominated.

Ortho-effect is explained by the stabilization of TS due to the interaction of the hydrogens of the *ortho*-alkyl groups and the oxygens of the sulfonyl group, *i.e.* hyperconjugation during the transition from the initial tetrahedral structure to a trigonal-pyramidal [91, 92].

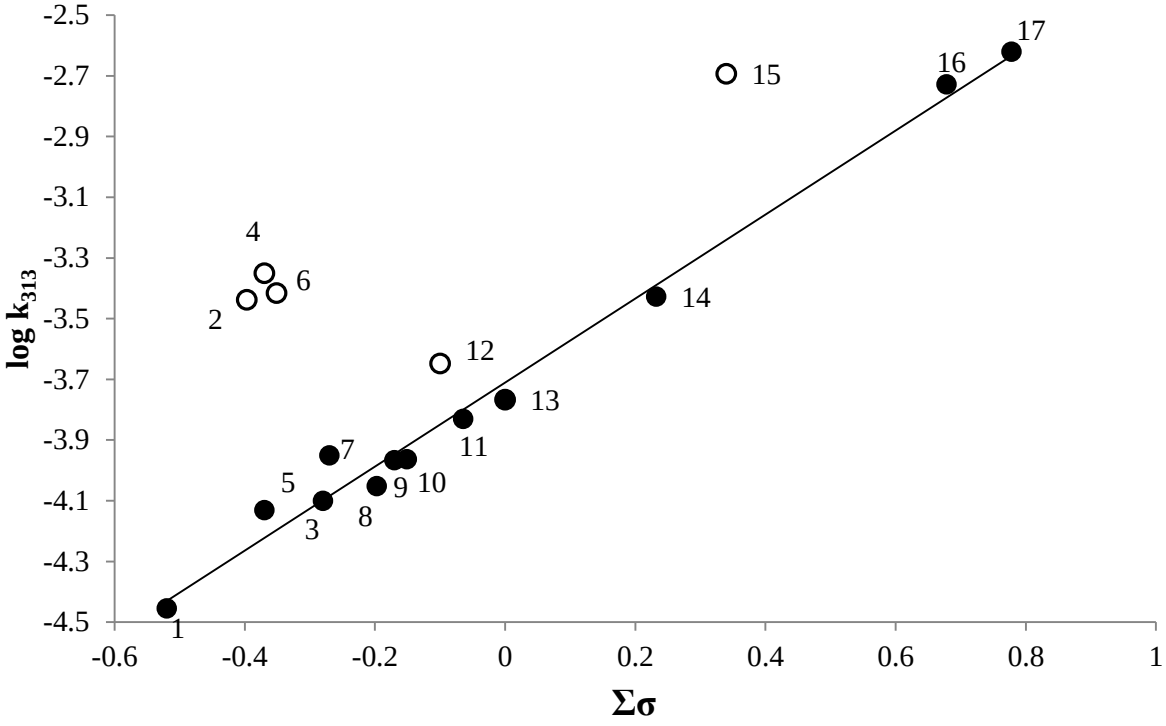


Figure 2.7 Hammett plot for hydrolysis X-$ArSO_2Cl$* in 70%V/V 1,4-dioxane-water solution at 313 K.

*Compounds numbering is that of Table 2.10.

Table 2.10 First order rate constants and activation parameters for the hydrolysis of X-$ArSO_2Cl$ in70%V/V 1,4-dioxane-water solution at 313 K

№	X	$k_{eff}\cdot10^4$/ s^{-1}	$\Delta H^{\ddagger}$/ $kJ\cdot mol^{-1}$	$-\Delta S^{\ddagger}$/ $J\cdot mol^{-1}\cdot K^{-1}$
1	2,4,6-*i*-Pr_3-	0.351±0.007	67±7	118±21
2	2,6-Me_2-4-*t*-Bu-	3.65±0.03	59±2	130±8
3	2,4,6-Et_3-	0.79±0.05	71±8	104±22
4	2,4,6-Me_3-	4.47±0.01	60.2±0.2	117±1
5	2,5-*t*-Bu-	0.74±0.01	59±1	142±4
6	2,6-Me_2-4-*i*-Pr-	3.84±0.05	54.3±0.1	137±4
7	2,4-Me_2-	1.12±0.03	64±1	123±4
8	4-*t*-Bu-	0.89±0.01	72±1	95±4
9	4-Me-	1.08±0.02	54±5	154±17
10	4-Et-	1.09±0.02	64.7±0.3	121±1
11	2-Et-	1.48±0.02	69.5±0.8	97±3
12	2-Me-	2.25±0.02	57.8±0.6	137±2
13	H-	1.71±0.03	53±1	148±4
14	4-Br-	3.74±0.02	49±4	154±11
15	2,4,6-Me_3-3-NO_2-	20.3±0.5	38±2	175±5
16	2-Me-4-NO_2-	18.7±0.1	39±6	172±6
17	4-NO_2-	24.0±0.2	41±4	164±12

Further, Rubleva and collaborators investigated the neutral hydrolysis of sulfonyl chlorides of anilides of sulfonic acids of general formula 5-[N($XArSO_2$)-NMe]-$YArSO_2Cl$, where *X* =4-Me, H, 4-Cl, 4-F, 3-NO_2, 4-NO_2; *Y*=2,4-Me_2; 2,6-Me_2; 2,4,6-Me_3in the 70%V/V aqueous 1,4-dioxane at 303-323K. [93, 94] These substrates also show a significant reaction rate acceleration in the presence of 2,6-dimethyl and 2,4,6-trimethyl derivatives. Authors conclude that the TS of the S_N2 mechanism is associated primarily with steric factors rather than with the electronic nature of the substituents *X* and *Y*.

A comparison of reactivity between benzoyl chloride and arenesulfonyl chloride in various solvents shows a sharp increase in rate constants that is shielded by *o*-methyl groups (Table 2.11). In the case of benzoyl chlorides, this fact is easily explained by the change from S_N2 mechanism for unhindered substrates to S_N1 for sterically hindered mesityl chlorides.[95]

Hudson and co-workers suggested that a complex mixture of steric and electronic effects in the solvolysis of sterically overloaded benzoyl chlorides causes their enhanced reactivity within the S_N1 mechanism. They consider that the steric hindrance of solvation, allocate polar effects, steric containment carbonium ion resonance and stabilization of the cation by intramolecular bonds -CH- as probable causes of the acceleration.[96] For all arenesulfonyl chlorides it has only been proved the S_N2-mechanism previously discussed. Therefore acceleration causes must be sought in steric effects of sulfo groups that are shielded by *o*-alkyl substituents.

Table 2.11 Rate constants for the solvolysis of aromatic carboxyl X-ArCOCl and sulfonyl chlorides X-ArSO_2Cl in various solvents at 25 °C

X	Solvent	X-ArCOCl		X-ArSO_2Cl	
		$k \cdot 10^3$	Reference	$k \cdot 10^3$	Reference
H	Et-OH	0.748	[97]	0.183	[62]
	H_2O	1540	[97]	3.07	[10]
	TFE(97%)*	3.63	[98]	0.0003	[96-97]
	Me-OH	4.3	[97]	0.815	[62]
4-NO_2	Et-OH	1.16	[100]	0.054	[101]
	H_2O	55.5	[100]	2.62	[101]
	TFE(97%)*	0.0099	[98]	0.00016	[98-99]
	Me-OH	40.8	[98]	0.171	[101]
4-OMe	Et-OH	0.986	[102]	0.022	[63]
	H_2O	-	-	6.5	[63]
	TFE(97%)*	566	[98]	0.0033	[98-99]
	Me-OH	10.7	[98]	0.128	[63]
2,4,6-Me_3	Et-OH	413	[102]	0.154	[31]
	H_2O	-	-	85.2	[31]
	TFE(97%)*	-	-	0.035	[98-99]
	Me-OH	8100	[102]	1.04	[31]
2,6-Me_2	Et-OH	41.8	[102]	-	-
	TFE(97%)*	80000	[100]	-	-
	Me-OH	840	[102]	-	-
4-Me	Et-OH	-	-	0.0198	[63]
	H_2O	-	-	3.64	[63]
	TFE(97%)*	34.9	[98]	0.0013	[98-99]
	Me-OH	3.6	[98]	0.11	[63]
4-Cl	Et-OH	-	-	0.022	[10]
	H_2O	-	-	2	[10]
	TFE(97%)*	0.446	[98]	0.00035	[10]
	Me-OH	6.05	[98]	0.083	[10]

* TFE (97%) - 97% is solution of 2,2,2-triftoretanol-water

There are a lot of evidences of a positive *o*-effect in the framework of the basic S_N2 mechanism. Most authors were not purposefully engaged with this issue as their research interests went in another direction. In addition this study is complicated by the joint influence of several factors affecting the reactivity of these systems, and because the diverse manifestations under different experimental conditions, which precludes the consensus about the nature of positive *o*-effect.

2.3 MOLECULAR MODELING OF THE SOLVOLYSIS MECHANISM

Understanding both the chemical kinetic mechanism of the solvolysis of arenesulfonyl halides and the structure of the corresponding TS implies to pay attention to the structure of the substrate.

Nowadays there are many ways to identify compounds structure. The most common are: X-ray analysis, gas-phase electron diffraction, electron paramagnetic resonance spectroscopy, nuclear magnetic resonance spectroscopy, microwave spectroscopy, Raman spectra, photoacoustic spectroscopy, infrared spectroscopy, and others.

According to the X-ray analysis results benzene ring in benzenesulfonyl chloride is similar to the actual geometry of benzene. On the other hand, configuration of sulfur atom is similar to that found in sulfonyl compounds. Sulfo group undergoes rotation around the C-S-bond.[103, 104] Geometric parameters of some arenesulfonyl chlorides are presented in Table 2.12.

Table 2.12 Geometric parameters of some X-ArSO_2Cl

X	Bond length / Å				Angle between atoms, degrees				Reference
	C-C	S-O	C-S	S-Cl	C-S-Cl	C-S-O	O-S-O	O-S-Cl	
H-	1.403	1.417	1.764	2.047	100.9	110.0	122.5	105.5	[103]
2-Me-	1.411	1.418	1.763	2.048	100.8	110.6	120.8	106.3	[105]
4-Me-	1.396	1.413	1.755	2.045	101.3	110.4	120.5	106.1	[106]
2-NO_2-	1.402	1.428	1.765	2.034	101.3	109.3	118.9	107.7	[107]
4-NO_3-	1.396	1.423	1.773	2.048	100.2	109.0	122.9	106.7	[108]
2-Cl-	1.405	1.425	1.783	2.048	102.1	109.9	122.3	107.3	[109]
2,4,6-*i*-Pr_3-	1.419	1.424	1.776	2.058	102.4	112.6	118.1	106.4	[110]

Gas-phase electron diffraction study of the structure *o*-methyl-benzenesulfonyl chloride showed the S-Cl bond orientated toward the methyl group (10-25° from the perpendicular position). Internal rotation barriers of SO_2Cl and CH_3 groups are higher than the corresponding ones for *p*-isomer by 2.9 and 35 times, respectively; consequently, the methyl group does not undergo free rotation.[105]

The main difference from the classical structure is found for 2,4,6-tri-*iso*-propyl benzenesulfonyl chloride.[110] Steric bulkiness in the molecule provokes the deviation from the plane of the benzene ring (plane r.m.s. ± 0.021Å).The ring conformation imagined as strongly flattened "bath." Intermolecular short contacts between a hydrogen atom of the isopropyl group and the oxygen atoms of the sulfo group have been found; sulfo and *o*-isopropyl groups are fixed in space and its rotation was not observed.

2-nitro-benzene-sulfonyl chloride shows very low of hydrolysis reactivity [37] in comparison with the *o*- and *p*-isomers; it also shows the highest rotational barriers of both functional groups, resulting in steric repulsion.[107]

o-substituted arenesulfonyl radicals ($ArSO_2$•) showed slow rotation of sulfo group relative to the steric unhindered ones, which is explained by the presence of the steric constraints.[111]

The X-ray study of dihydrate of 2,4,6-trimethylbenzenesulfonic acid [112] indicates the presence of hydrogen bonding between the water hydrogens and the oxygens of the sulfo group, indicating the important role of specific solvation in the TS during solvolysis sulfonic acid derivatives.

Recently, S. Yamabe has investigated theoretically hydrolysis of benzenesulfonyl chlorides with the density functional theory method, where the water molecules are explicitly considered [113]. The substituent effect was examined with clusters of different water content n=6 to 17. TS geometries and energies were calculated in water by B3LYP, B3PW91, M062X, and wB97XD functionals with 6–31G, 6–311G, 6–311G, 6–311(1)G, and 6–31111G basis sets, respectively. For the hydrolysis of benzenesulfonyl chlorides the S_N2-S_N3 spectrum of TS is considered (Figure 2.8). The S_N2 mechanism was found for the combination of large n values (n > 9) and electron-donating Z groups (EDG). However, the mechanism changes to an S_N3 when the n value is small and electron-withdrawing Z groups (EWG) are used.

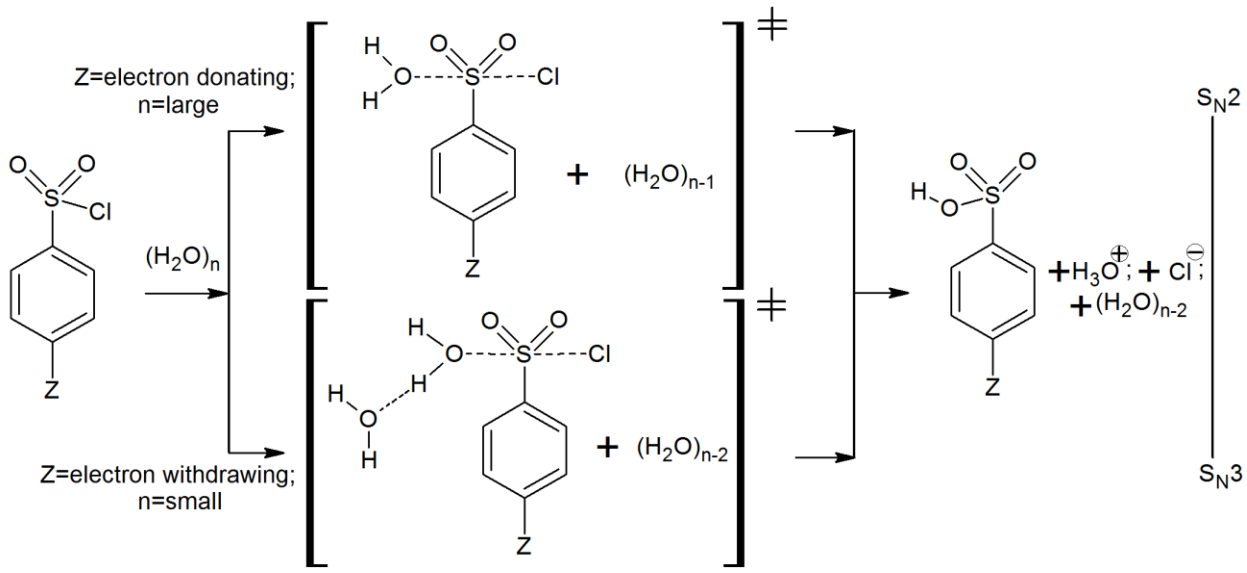


Figure 2.8 Calculated TSs for the hydrolysis of benzenesulfonyl chlorides

Those authors explain the mechanistic change from S_N2 to S_N3 is as follows: the EWG lowers the lowest unoccupied molecular orbital of the substrate, which induces the access of the first H_2O molecule, leading to the weakening of the O-H bond. Conversely, H_2O is of poor nucleophilicity in the case of small *n* values, and thus, the elongation of the O-H bond is required to enhance its nucleophilicity. These two factors lead to a significant elongation of the O-H bond in the attacking water molecule and the proton dissociates in the TS; to stabilize such proton, a second H_2O is necessary to take part in the reaction, which successfully converts the reaction process to a termolecular course.

Outstanding contribution to the modeling of solvolytic reactions involving arenesulfonyl chlorides was made by the Ivanovo State University scientific school. They investigated the hydrolysis of benzenesulfonyl chloride in the gas phase [114]. Calculations were carried out by the quantum-chemical semi empirical method PM3. The authors searched the most probable type of nucleophilic attack on the reaction center (Figure 2.9). According to calculations the backside attack, an example of the classical transition state of reactions with S_N2-mechanism (trigonal bipyramid), is not supported. More favorable is the front axial attack; the proximity of the chlorine atom and the water hydrogen allows the HCl splitting off. However, the PM3 study of gas-phase benzene sulfonylation of

glycine suggests the front equatorial attack as the most energetically favorable. [115]

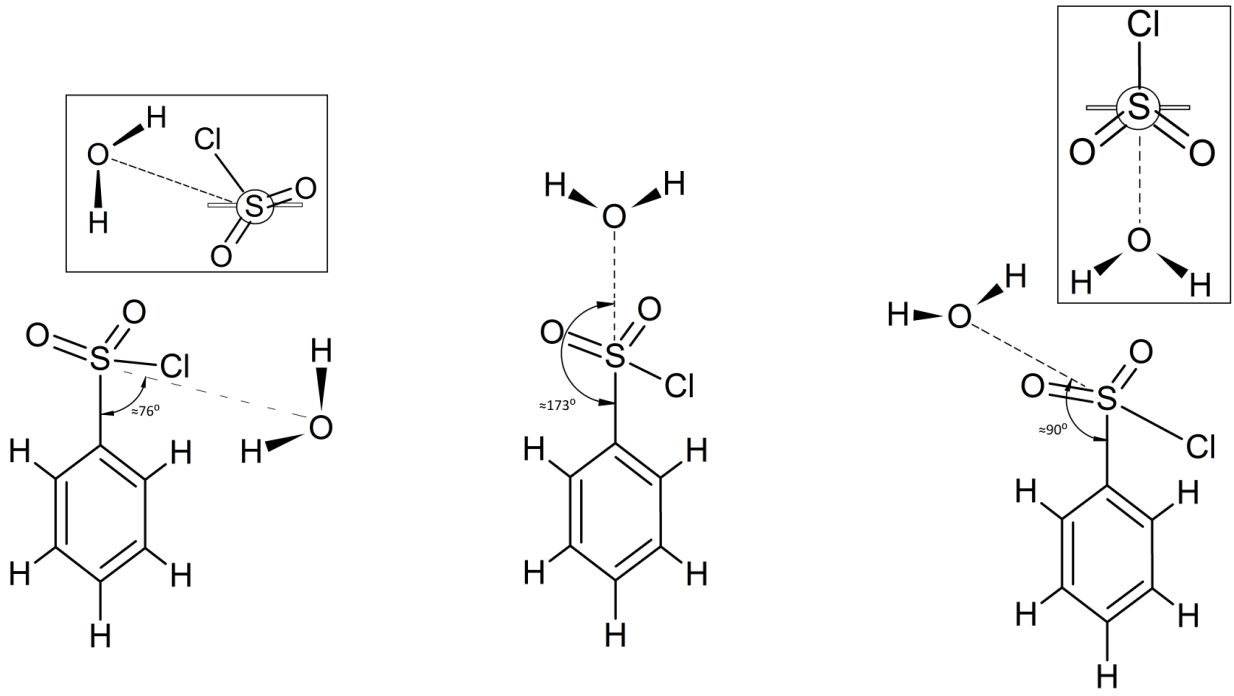


Figure 2.9 Different types of nucleophilic attack at the reaction center during benzenesulfonyl chloride hydrolysis

a - Frontal equatorial attack; b - Frontal axial attack; c - Backside attack.

In another study, Ivanov and co-workers propose a TS involving several molecules of the nucleophile (water), linked by hydrogen bonding forming a water cluster. They proposed cyclic TSs involving the $H^{\delta+}$–O–S–$Cl^{\delta+}$fragment an up to three water molecules (Figure 2.10).[116]

Liquid water molecules associates in an extensive network of hydrogen bonding, so, according to the authors, hydrogen bonding increase stabilization, thus reducing the entropy and the enthalpy of the reaction; strictly speaking this mechanism is very similar to the S_N3- mechanism discussed earlier.[10-13,113]

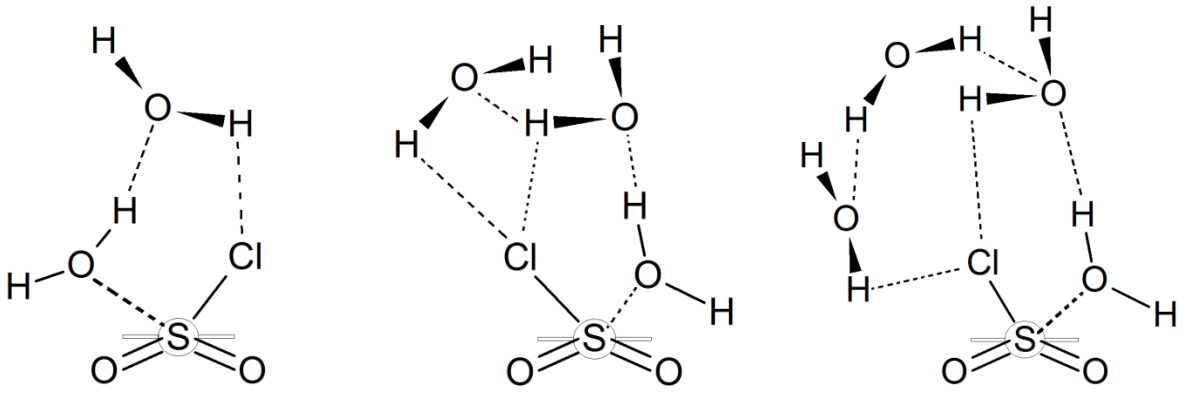


Figure 2.10 Optimized structure of TS with the inclusion of (a) one, (b) two, and (c) three additional water molecules

Activation parameters for the hydrolysis reaction of arenesulfonyl chlorides in 70%V/V 1,4-dioxane-water mixtures at 313K calculated by *ab initio* quantum chemical methods, model chemistry B3LYP/6-31G (d), suggest as most probable the "classic" backside attack of the nucleophile.[117]

Geometrical features of sterically hindered substrates may be a significant factor influencing the differences in the structure of TS, and/or the type of nucleophile attack

From the previous analysis of published data it follows that the study of structural effects in nucleophilic substitution at a sulfonyl center in alcoholysis is important from the theoretical and practical points of view. Although similar processes for structurally related compounds (benzoyl chlorides and sterically unhindered arenesulfonyl chlorides) have been described in sufficient detail, features of the alcoholysis of sterically hindered arenesulfonyl chlorides demand further investigation.

2.4 CONCLUSIONS

As a result we can suggest some interim conclusions:

- It is generally accepted that most of unhindered arenesulfonyl chlorides undergo solvolysis by bimolecular mechanism S_N2.

- There is no established opinion on the solvolysis of hindered arenesulfonyl chlorides. Nevertheless the evidences of S_N2 similar TS look convincingly.

- Few factors that affect nucleophilic substitution can be selected: steric hindrance of *ortho*-alkyl groups, electronic effect of substituents in the benzene ring and specific solvation of sulfonyl compounds.

- Structural studies show characteristics of hindered substrates structure such as spatial fixing sulfo group and distortions of the benzene ring plane, which may affect the structure of the TS.

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3 EXPERIMENTAL

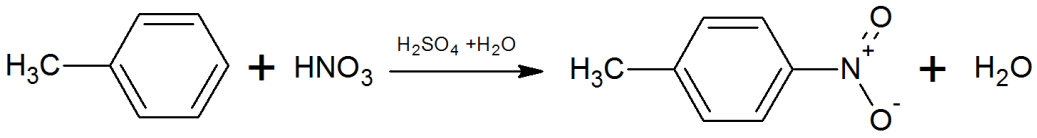
3.1 SYNTHESIS AND STRUCTURE CHARACTERIZATION

3.1.1 Methods of synthesis

3.1.1.1 Initial compounds for further synthesis

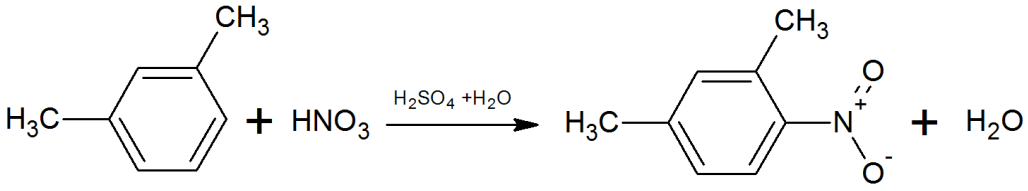
Initial alkyl- and methoxy-benzene derivatives were purchased from Sigma-Aldrich with a purity of not less than 99%. The initial mono-nitro derivatives of benzene were prepared by nitration of toluene, meta-xylene and mesitylene by the following procedures:

Preparation of 1-methyl-4-nitrobenzene



290 g of nitrating mixture (22,3% HNO_3, 65,6% H_2SO_4 and 12,1% H_2O) was dropwise added to toluene (30 g) under constant stirring at 60°C. The process was carried out for 40 minutes. The organic layer was separated by filtration, washed with solution of sodium carbonate (10%) and dried over Na_2SO_4. The reaction products were distilled through a high-performance rectification column [1]. The yield of *para*-isomer was 30% (yellow crystals, m.p. = 51 °C).

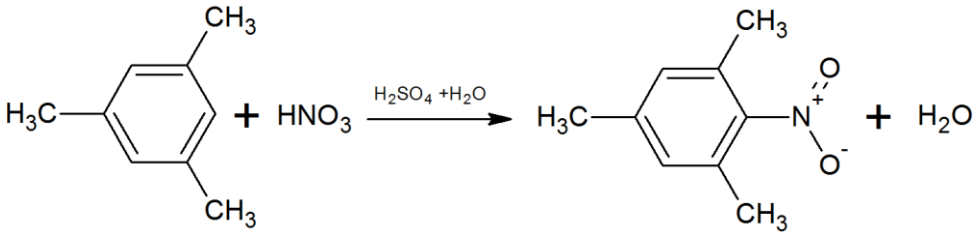
Preparation of 2,4-dimethyl-1-nitrobenzene



Nitration was carried out as follows: one mole of *m*-xylene at 30 °C was added to a mixture of 1.08 mole of H_2SO_4 (81%) and 1.1 mole of HNO_3. The reaction was continued for one hour. Then the mixture was poured onto ice. The organic layer was separated with a separating funnel, washed with of sodium carbonate solution (10%), and dried over Na_2SO_4. The product was separated from

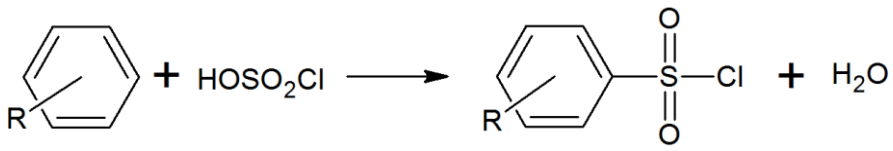
m-xylene by distillation with water vapor[2]. Yield of 2,4-dimethyl-1-nitrobenzene was 98% (yellow liquid, m.p. = 7 °C).

Preparation of 1,3,5-trimethyl-2-nitrobenzene



Concentrated nitric acid (specific gravity 1.38) was dropwise added to mesitylene (1 mole) at 30 °C for two hours. The mixture was then washed with water. The organic layer was filtered, washed with solution of sodium carbonate (10%) and distilled with water vapor to remove the remaining mesitylene. The product was recrystallized from alcohol. Under cooling nitro-mesitylene was released from the alcoholic solution, and was dried in air [3].Yield of mono 1,3,5-trimethyl-2-nitrobenzene was 80% (pale yellow prismatic crystals, m.p. = 44 °C).

3.1.1.2 Arenesulfonyl chlorides



Arenesulfonyl chlorides were synthesized by sulfochlorination of the corresponding derivatives of benzene with chlorosulfonic acid, according to [4]. Compounds (4-*t*-Bu-benzenesulfonyl chloride, 2,4,6-Me_3-benzenesulfonyl chloride, 2,4,6-Et_3-benzenesulfonyl chloride, 2,4,6-*i*-Pr_3-benzenesulfonyl chloride, 2-Me-benzenesulfonyl chloride, 4-Me-benzenesulfonyl chloride, 2,4-Me_2-benzenesulfonyl chloride, 2,5-Me_2-benzenesulfonyl chloride, 2-Me-5-*t*-Bu-benzenesulfonyl chloride, 2,6-Me_2-4-*t*-Bu- benzenesulfonyl chloride and 2,3,5,6-Me_4-benzenesulfonyl chloride, 2,4,6-OMe_3-benzenesulfonyl chloride)

were synthesized as follows. One mole of hydrocarbon, dissolved in 450 mL of an inert solvent ($CHCl_3$, CCl_4, hexane), was added to crystalline NaCl (one mole) under constant stirring at 0 °C, and then chlorosulphonic acid (five mol) was slowly added dropwise over half an hour. After 3 - 4 hours, the reaction mixture was poured onto ice, treated with chloroform, the extract dried, over $CaCl_2$ or Na_2SO_4, and filtered. The filtrate evaporated under vacuum. The resulting sulfonyl chloride was distilled under vacuum (2-5 mm Hg) with a reflux condenser, the middle fraction was collected and recrystallized from hexane (yield 65-70%).

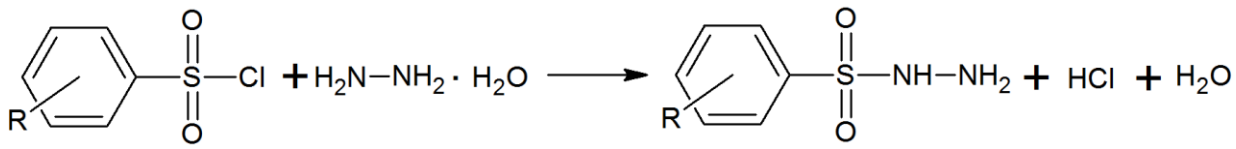
2-Me-5-NO_2-benzenesulfonyl chloride, 2,4-Me_2-5-NO_2-benzenesulfonyl chloride and 2,4,6-Me_3-3-NO_2-benzenesulfonyl chloride were synthesized analogously, but at a higher temperature (40-50 °C). The yield was 60-65%.

4-Br-benzenesulfonyl chloride, 4-Cl-benzenesulfonyl chloride, 3-NO_2-benzenesulfonyl chloride, 4-NO_2-benzenesulfonyl chloride and benzenesulfonyl chloride were purchased from a commercial supplier (Sigma-Aldrich) and recrystallized from hexane before use.

3.1.1.3 Arenesulfonyl bromides

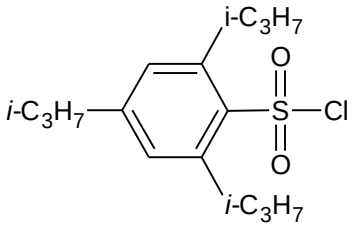
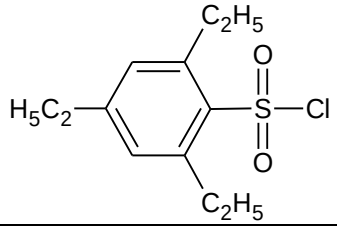
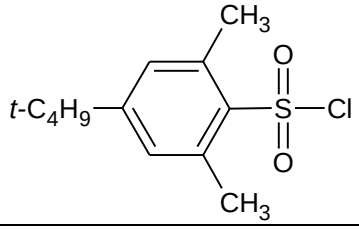
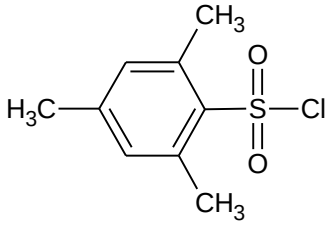
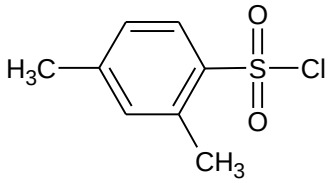
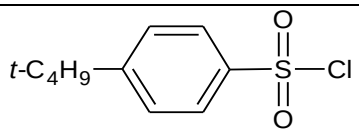
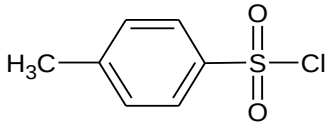
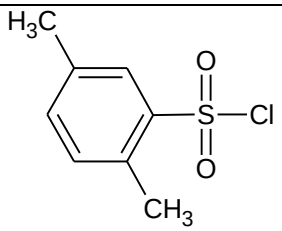
Arenesulfonyl bromides were prepared from the corresponding hydrazide under the method described in ref. [5].

Synthesis of arenesulfonohydrazide

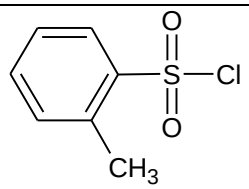
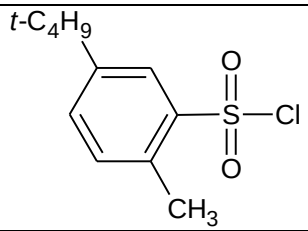
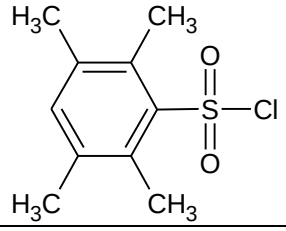
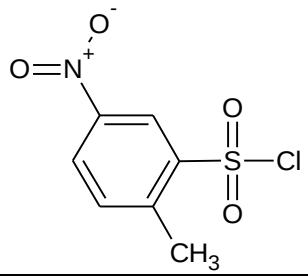
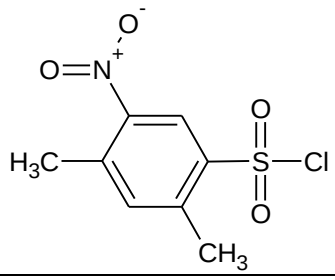
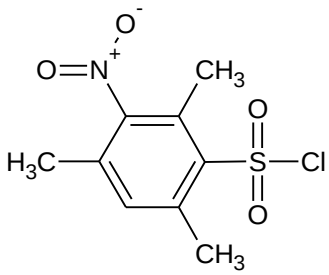
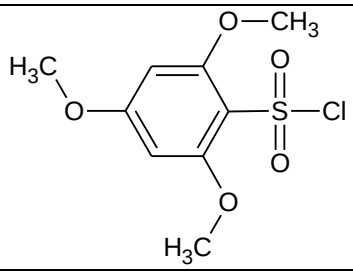


To obtain the initial hydrazide a concentrated solution of 0.1 g of the initial sulfonyl chloride in CH_2Cl_2 was added to 0.2 g of hydrazine hydrate, cooled to 5 °C, under strong stirring; temperature should not increase above 20°C. The mixture was stirred for 30 min. Then diluted with water to 1/3 ratio. The mixture was cooled to 0° C to precipitate the crystals of benzenesulfonyl hydrazide, which were filtered on a Buchner funnel.

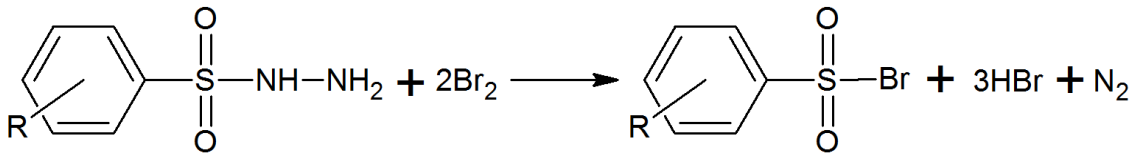
Table 3.1 Properties of synthesized arenesulfonyl chlorides

Formula	Gross formula	Appearance	m.p./ °C	Yield/ %
	$C_{15}H_{23}ClO_2S$	White powder	96-98	65
	$C_{12}H_{17}ClO_2S$	Oil	-	75
	$C_{12}H_{17}ClO_2S$	White crystals	66-67	85
	$C_9H_{11}ClO_2S$	White crystals	56.5-57	85
	$C_8H_9ClO_2S$	White crystals	33.5-34	83
	$C_{10}H_{13}ClO_2S$	White crystals	81.5-82	80
	$C_7H_7ClO_2S$	White crystals	70-71	50
	$C_8H_9ClO_2S$	White crystals	20	70

Continuation of Table 3.1

Formula	Gross formula	Appearance	m.p./ °C	Yield/ %
	$C_7H_7ClO_2S$	Oil	10	20
	$C_{11}H_{15}ClO_2S$	Oil	-	65
	$C_{11}H_{13}ClO_2S$	White crystals	97-101	85
	$C_7H_6ClNO_4S$	White crystals	44-46	60
	$C_8H_8ClNO_4S$	Light brown crystals	74.5-75,5	65
	$C_7H_6ClNO_4S$	Light gray crystals	60-61	65
	$C_9H_{11}ClO_5S$	Light pink crystals	134-136	65

Synthesis of arenesulfonyl bromides

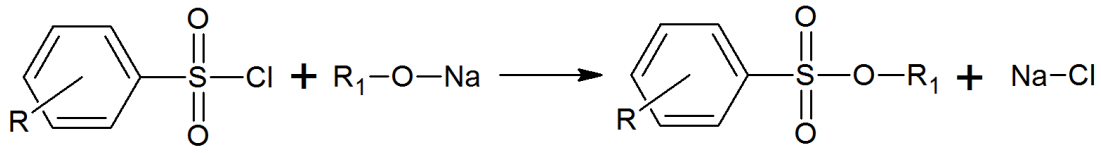


For the synthesis of arenesulfonyl bromides 0.01 g of the hydrazide were dissolved in $CHCl_3$ (80 mL), then 0.02 g of bromine were added. During bromination temperature should not rise above 10°C, so ice was periodically added to the reaction mixture. Bromine is added until the solution acquires a stable orange color (10-30 min.). The chloroform layer was separated by a separatory funnel, washed with water, dried with Na_2SO_4, and then the residual solvent was removed in vacuo. The dry residue was recrystallized from hexane.

(2,4,6-tri(propan-2-yl)benzenesulfonyl bromide) m.p.=82-83° C.

(4-methylbenzenesulfonyl bromide) m.p.=95-96° C.

3.1.1.4 Reaction products



R_1 = Me, Et, Pr, i-Pr

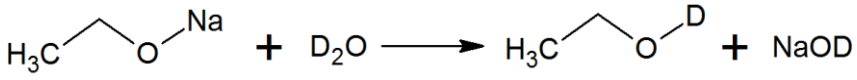
For X-ray analysis the reaction products were prepared from the appropriate sulfonyl chloride and sodium alkoxides [6]. To this end, 0.01 mole of sulfonyl chloride was added to a concentrated solution of 0.02 mol of the corresponding alkoxide in alcohol. The mixture was heated at 25 °C for two days, and then the mixture was poured onto ice. After repeated washing with water, the organic layer was separated, dried using Na_2SO_4 (in case of oil), or under vacuum. The product was recrystallized from hexane.

To confirm the structure of the reaction products by NMR-analysis the sulfonates were obtained by leaving the initial sulfonyl chloride for 3-4 days in the

corresponding alcohol at room temperature, after the excess of the alcohol was removed under vacuum.

3.1.1.5 Deuterated ethanol

Deuterated ethanol was obtained by reaction of sodium ethoxide with heavy water:



Initial ethoxide was prepared by dissolving sodium metal in ethanol. Then, the alcohol was distilled off and the remaining residue dried under vacuum. Heavy water in a 4-fold excess was added to the ethoxide. The reaction mixture was boiled under reflux for 30 minutes and distilled with a reflux condenser. Further purification was made according to standard methods of alcohols cleaning and drying.

3.1.2 Solvents purification

Alcohols were purchased from commercial products (Sigma-Aldrich) of analytical grade. Molecular sieves (3Å) were used for dehydration. All alcohols were redistilled immediately before the kinetic experiments at the temperatures specified in the literature ($b.p._{MeOH}$ =64.4° C; $b.p._{EtOH}$ = 78.32° C; $b.p._{PrOH}$ =97.15° C; $b.p._{i\text{-}PrOH}$ =82.6° C at 760 mm Hg). Immediately prior to kinetic studies alcohols were tested for water content by titration with Fischer reagent [7]. It was considered acceptable when water content < 0.002%.

The distillate obtained from the distiller Auga ELIX-Q was used for the hydrolysis.

Hexane was purified as follows [8]. The hydrocarbon was washed with concentrated sulfuric acid and then with water and dried, and finally distilled from sodium metal (b.p. = 68 °C). The distillate was stored over 3Å molecular sieves.

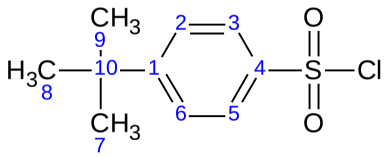
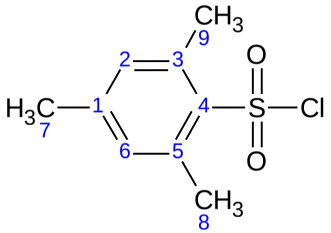
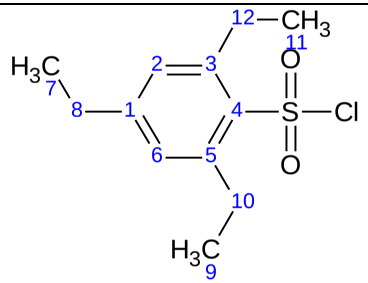
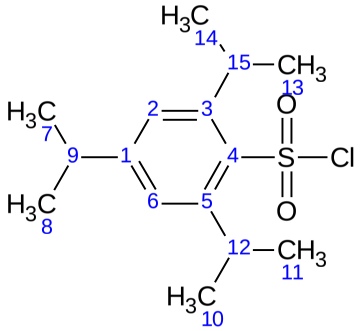
3.1.3 Structure determination

3.1.3.1 NMR-spectroscopy

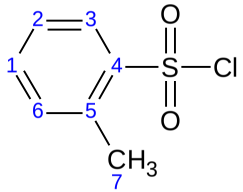
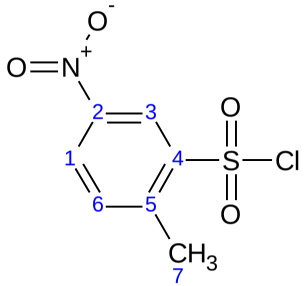
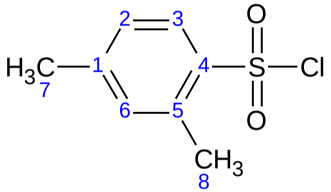
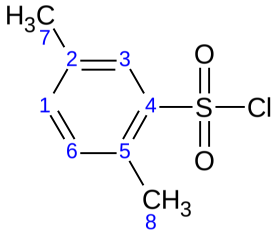
To confirm the structure and purity of the obtained compounds ^{1}H and ^{13}C NMR spectroscopy were used. The spectra were recorded on the 300 MHz NMR spectrometer (Bruker) at the University of Coruña, Spain. Structure determination was done using the program's MestReNova 10.0.2-15465.

Sample preparation for NMR analysis: the sample (about 10 mg) was dissolved in 500 μL of solvent ($CDCl_3$). Tables 3.2 and 3.3 describe the ^{1}H and ^{13}C NMR spectra for the studied arenesulfonyl chlorides and solvolysis products. From there it follows that all those NMR spectra correspond to the claimed structures and that all compounds are pure enough for it use in chemical kinetic studies.

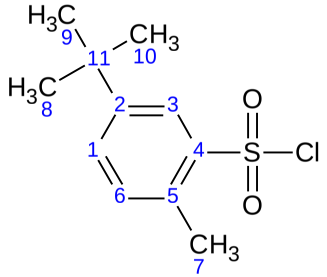
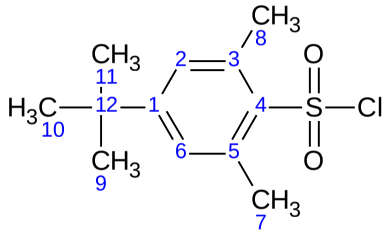
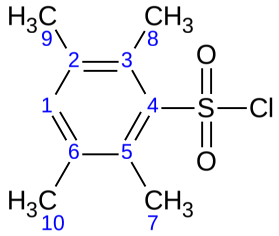
Table 3.2 - ^{1}H and ^{13}C NMR spectra of the obtained arenesulfonyl chlorides

Arenesulfonyl chloride	Formula	NMR-spectra
4-*tert*-butylbenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,48 (s, *J = 7,5 Hz*, 9 $H_{7,8,9}$), 8,37 (d,*J = 7,5 Hz*, 2 $H_{3,5}$), 8,76 (d, *J = 7,5 Hz*, 2 $H_{2,6}$), ppm.
2,4,6-trimethylbenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =2,75 (s, *J = 7,5 Hz*, 6 $H_{9,8}$), 2,37 (s,*J = 7,5 Hz*, 3 H_7), 7,04 (s, *J = 7,5 Hz*, 2 $H_{2,6}$), ppm.
2,4,6-triethylbenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,28 (m, *J = 7,5 Hz*, 3 H_7), 1,35 (m,*J = 7,5 Hz*, 6 $H_{9,11}$), 2,70 (d,*J = 7,5 Hz*, 2 H_8), 3,20 (d,*J = 7,5 Hz*, 4 $H_{12,\ 10}$), 7,31 (s,*J = 7,5 Hz*, 2 $H_{2,6}$), ppm.
2,4,6-tri(propan-2-yl)benzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,29 (m, *J = 7,5 Hz*, 12 $H_{10,\ 11,\ 13,14}$), 1,35 (m,*J = 7,5 Hz*, 6 $H_{7,8}$), 2,95 (m,*J = 7,5 Hz*, 1 H_9), 4,25 (m,*J = 7,5 Hz*, 2 $H_{12,\ 15}$), 7,50 (s,*J = 7,5 Hz*, 2 $H_{2,6}$), ppm.

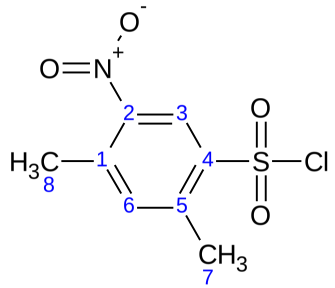
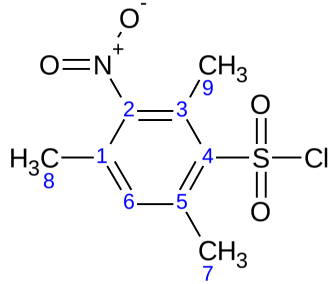
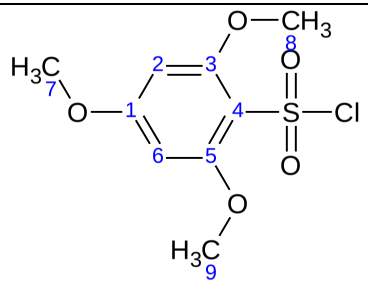
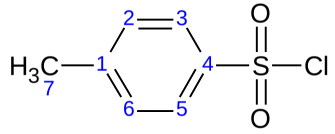
Continuation of Table 3.2

Arenesulfonyl chloride	Formula	NMR-spectra
2-methylbenzenesulfonyl chloride:		^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2,81 (s,*J = 7,5 Hz*, 3 H_7), 7,42 (s,*J = 7,5 Hz*, 1 H_2)7,61 (s,*J = 7,5 Hz*, 1 H_1),7,81(s,*J = 7,5 Hz*, 1 H_6), 8,07 (s,*J = 7,5 Hz*, 1 H_3), ppm.
2-methyl-5-nitrobenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =3,20(s,*J = 7,5 Hz*, 3 H_7), 8,50 (d,*J = 7,5 Hz*, 1 H_6),9,38(d,*J = 7,5 Hz*, 1 H_1), 9,88(s,*J = 7,5 Hz*, 1 H_3), ppm.
2,4-dimethylbenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =2,45(s,*J = 7,5 Hz*, 3 H_7), 2,75 (s,*J = 7,5 Hz*, 3 H_8),7,18(d,*J = 7,5 Hz*, 1 H_6), 7,25(s,*J = 7,5 Hz*, 1 H_2), 7,95(d,*J = 7,5 Hz*, 1 H_3), ppm.
2,5-dimethylbenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =2,42(s,*J = 7,5 Hz*, 3 H_7), 2,75 (s,*J = 7,5 Hz*, 3 H_8),7,31(d,*J = 7,5 Hz*, 1 H_1), 7,42(m,*J = 7,5 Hz*, 1 H_6), 7,87(s,*J = 7,5 Hz*, 1 H_3), ppm.

Continuation of Table 3.2

Arenesulfonyl chloride	Formula	NMR-spectra
5-*tert*-butyl-2-methylbenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,36(s,*J = 7,5 Hz*, 9 $H_{8, 9, 10}$), 2,75 (s,*J = 7,5 Hz*, 3 H_7),7,38(d,*J = 7,5 Hz*, 1 H_1), 7,68(m,*J = 7,5 Hz*, 1 H_6), 8,07(s,*J = 7,5 Hz*, 1 H_3), ppm.
4-*tert*-butyl-2,6-dimethylbenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,33(s,*J = 7,5 Hz*, 9 $H_{9, 10, 11}$), 2,76 (s,*J = 7,5 Hz*, 6 $H_{7,8}$),7,20(s,*J = 7,5 Hz*, 2 $H_{2,6}$), ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 23,44(C_7=C_8), 30,94 (C_9=C_{10}=C_{11}), 35,85 (C_{12}), 128,94 (C_2=C_6), 139,41 (C_1), 140,54 (C_3=C_5), 158,165 (C_4).
2,3,5,6-tetramethylbenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =2,31(s,*J = 7,5 Hz*, 6 $H_{9,10}$), 2,63 (s,*J = 7,5 Hz*, 6 $H_{8,7}$),7,27(s,*J = 7,5 Hz*, 1 H_1), ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 18,28 (C_9=C_{10}), 20,97(C_7= C_8), 135,78 (C_2= C_6), 136,82 (C_3= C_5), 138,00 (C_1), 144,86 (C_4).

Continuation of Table 3.2

Arenesulfonyl chloride	Formula	NMR-spectra
2,4-dimethyl-5-nitrobenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =2,70(s,*J = 7,5 Hz*, 3 H_8), 2,81 (s,*J = 7,5 Hz*, 3 H_7),7,47(s,*J = 7,5 Hz*, 1 H_7), 8,70(s,*J = 7,5 Hz*, 1 H_3), ppm.
2,4,6-trimethyl-3-nitrobenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,92(s,*J = 7,5 Hz*, 3 H_9), 2,23 (s,*J = 7,5 Hz*, 3 H_7),2,37(s,*J = 7,5 Hz*, 3 H_8), 7,03(s,*J = 7,5 Hz*, 1 H_6), ppm.
2,4,6-Trimethoxybenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =3,89(s,*J = 7,5 Hz*, 3 H_7), 3,96 (s,*J = 7,5 Hz*, 6 $H_{8,9}$),6,12(s,*J = 7,5 Hz*, 2 $H_{2,6}$), ppm.
4-methylbenzenesulfonyl chloride		^{1}H NMR ($CDCl_3$, 300 MHz): δ =2,49(s,*J = 7,5 Hz*, 3 H_7), 7,4 (s,*J = 7,5 Hz*, 2 $H_{2,6}$),7,91(s,*J = 7,5 Hz*, 2 $H_{3,5}$), ppm.

Continuation of Table 3.2

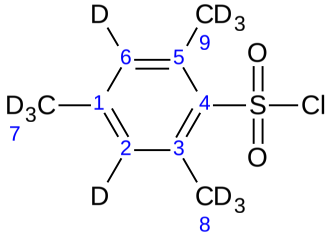
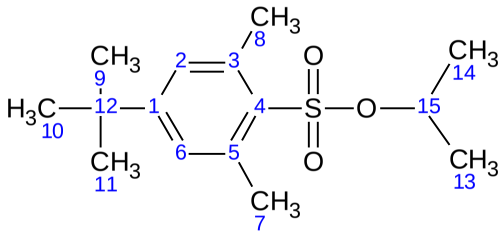
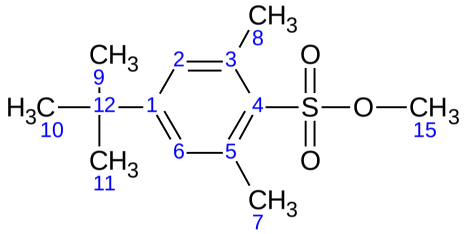
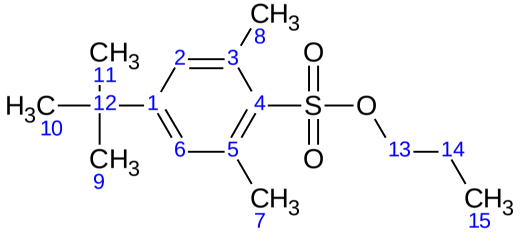
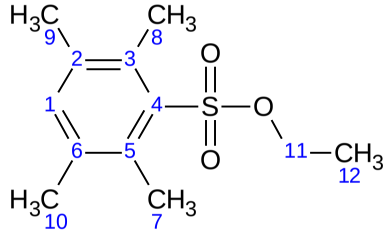
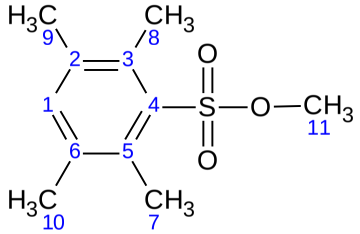
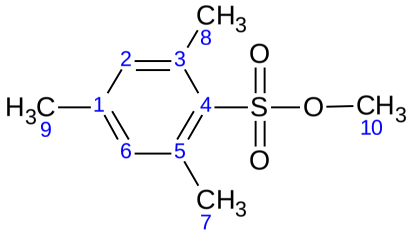
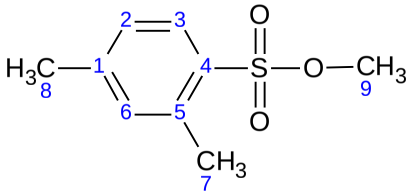
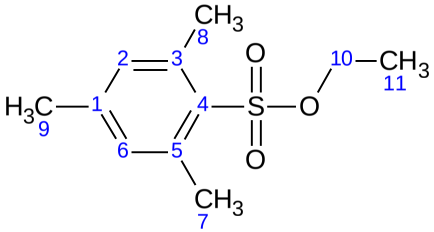
Arenesulfonyl chloride	Formula	NMR-spectra
2,4,6-tris [($^2H_3$)methyl]($^2H_2$) benzenesulfonyl chloride		^{13}C NMR (300 MHz, $CDCl_3$): δ = 22,11 (C_7), 22,63 (C_8=C_9), 132,27 (C_2= C_6), 139,37(C_3=C_5), 140,07(C_1), 145,29(C_4).

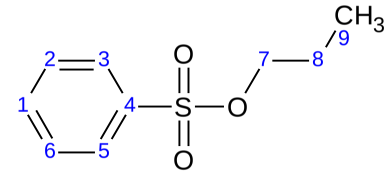
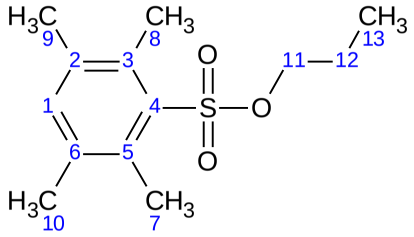
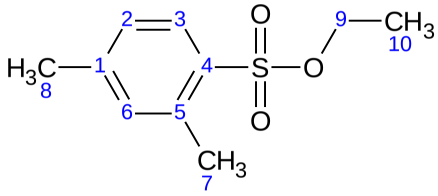
Table 3.3 – ^{1}H and ^{13}C NMR-spectra of the obtained solvolysis products

Benzenesulfonate	Formula	NMR-spectra
Propan-2-yl 4-tert-butyl-2,6-dimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,29(d,*J = 7,5 Hz*, 6 $H_{13,14}$), 1,31 (s,*J = 7,5 Hz*, 9 $H_{9,10,11}$),2,67(s,*J = 7,5 Hz*, 6 $H_{7,8}$), 4,72(m,*J = 7,5 Hz*, 1 H_{15}), 7,13(s,*J = 7,5 Hz*, 2 $H_{2,6}$), ppm.
Methyl 4-tert-butyl-2,6-dimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,13 (s,*J = 7,5 Hz*, 9 $H_{9,10,11}$),2,66(s,*J = 7,5 Hz*, 6 $H_{7,8}$), 3,72(s,*J = 7,5 Hz*, 3 H_{15}), 7,15(s,*J = 7,5 Hz*, 2 $H_{2,6}$), ppm.
Propyl 4-tert-butyl-2,6-dimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0,94(t,*J = 7,5 Hz*, 3 H_{15}), 1,3 (s,*J = 7,5 Hz*, 9 $H_{9,10,11}$),1,69(m,*J = 7,5 Hz*, 2 H_{14}), 2,67(s,*J = 7,5 Hz*, 6 $H_{7,8}$), 3,96(t,*J = 7,5 Hz*, 2 H_{13}), 7,14(s,*J = 7,5 Hz*, 2 $H_{2,6}$), ppm.
Ethyl 2,3,5,6-tetramethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1,31 (t,*J = 7,5 Hz*, 3 H_{12}),2,28(s,*J = 7,5 Hz*, 6 $H_{9,10}$), 2,55(s,*J = 7,5 Hz*, 6 $H_{7,8}$), 4,06(q,*J = 7,5 Hz*, 2 H_{11}), 7,18(s,*J = 7,5 Hz*, 1 H_1), ppm.

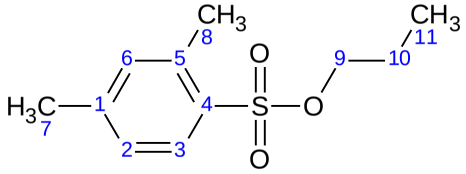
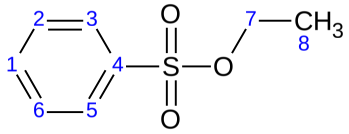
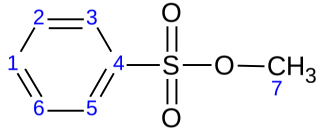
Continuation of Table 3.3

Benzenesulfonate	Formula	NMR-spectra
Methyl 2,3,5,6-tetramethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2,28(s,*J = 7,5 Hz*, 6 $H_{9,10}$), 2,54(s,*J = 7,5 Hz*, 6 $H_{7,8}$), 3,71(s,*J = 7,5 Hz*, 3 H_{11}), 7,19(s,*J = 7,5 Hz*, 1 H_1), ppm.
Methyl 2,4,6-trimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2,32(s,*J = 7,5 Hz*, 3 H_{10}), 2,63(s,*J = 7,5 Hz*, 6 $H_{7,8}$), 3,7(s,*J = 7,5 Hz*, 3 H_9), 6,98(s,*J = 7,5 Hz*, 2 $H_{2,6}$), ppm.
Methyl 2,4-dimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2,27(s,*J = 7,5 Hz*, 3 H_8), 2,49(s,*J = 7,5 Hz*, 3 H_7), 3,42(s,*J = 7,5 Hz*, 3 H_9), 6,88(d,*J = 7,5 Hz*, 1 H_6), 6,97(s,*J = 7,5 Hz*, 1 H_2), 7,71(d,*J = 7,5 Hz*, 1 H_3), ppm.
Ethyl 2,4,6-trimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,3(t,*J = 7,5 Hz*, 3 H_{11}), 2,31(s,*J = 7,5 Hz*, 3 H_9), 2,63(s,*J = 7,5 Hz*, 6 $H_{7,8}$), 4,04(q,*J = 7,5 Hz*, 2 H_{10}), 6,97(s,*J = 7,5 Hz*, 2 $H_{2,6}$), ppm.

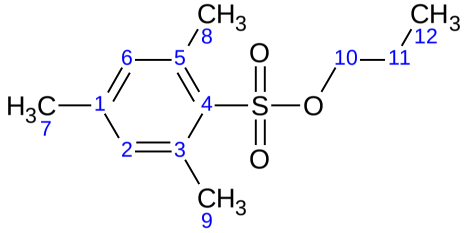
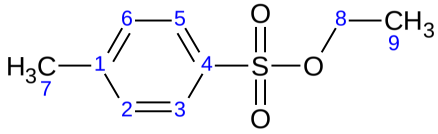
Continuation of Table 3.3

Benzenesulfonate	Formula	NMR-spectra
Propyl benzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =0,89 (t,*J = 7,5 Hz*, 3 H_9), 1,69(q,*J = 7,5 Hz*, 2 H_8), 4,02(t,*J = 7,5 Hz*, 2 H_7), 7,56(t,*J = 7,5 Hz*, 2 $H_{2,6}$), 7,64(t,*J = 7,5 Hz*, 1 H_1), 7,91(d,*J = 7,5 Hz*, 2 $H_{3,5}$), ppm.
Propyl 2,3,5,6-tetramethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0,94 (t,*J = 7,5 Hz*, 3 H_{13}), 1,67(m,*J = 7,5 Hz*, 2 H_{12}), 2,28(s,*J = 7,5 Hz*, 6 $H_{2,6}$), 2,55(s,*J = 7,5 Hz*, 6 $H_{7,8}$), 3,95(t,*J = 7,5 Hz*, 2 H_{11}), 7,17(s,*J = 7,5 Hz*, 1 H_1), ppm.
Ethyl 2,4-dimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,3(t,*J = 7,5 Hz*, 3 H_{10}), 2,39(s,*J = 7,5 Hz*, 3 H_8), 2,61(s,*J = 7,5 Hz*, 3 H_7), 4,06(q,*J = 7,5 Hz*, 2 H_9), 7,12(d,*J = 7,5 Hz*, 1 H_6), 7,15(s,*J = 7,5 Hz*, 1 H_2), 7,85(d,*J = 7,5 Hz*, 1 H_4), ppm.

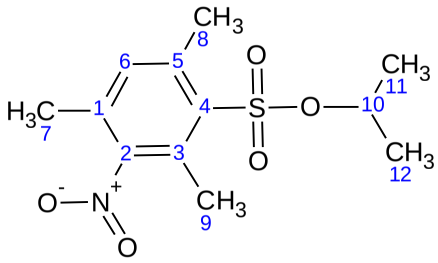
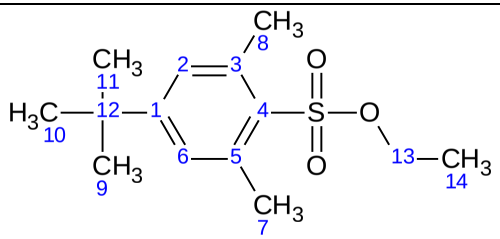
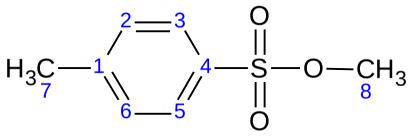
Continuation of Table 3.3

Benzenesulfonate	Formula	NMR-spectra
Propyl 2,4-dimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0,91 (t,*J = 7,5 Hz*, 3 H_{11}), 1,66(m,*J = 7,5 Hz*, 2 H_{10}), 2,38(s,*J = 7,5 Hz*, 3 H_7), 2,6(s,*J = 7,5 Hz*, 3 H_8), 3,94(t,*J = 7,5 Hz*, 2 H_9), 7,11(d,*J = 7,5 Hz*, 1 H_6), 7,16(s,*J = 7,5 Hz*, 1 H_2), 7,85(d,*J = 7,5 Hz*, 1 H_3), ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 10,2 (C_{11}), 20,23 (C_7), 21,49(C_8), 72,00 (C_9), 22,46(C_{10}), 126,8(C_3), 130,24(C_6), 131,79(C_2), 133,38(C_5), 138,22(C_1), 144,58(C_4).
Ethyl benzenesulfonate:		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,31(t,*J = 7,5 Hz*, 3 H_8), 4,13(q,*J = 7,5 Hz*, 2 H_7), 7,55(t,*J = 7,5 Hz*, 2 $H_{2,6}$), 7,64(t,*J = 7,5 Hz*, 1 H_1), 7,92(d,*J = 7,5 Hz*, 2 $H_{3,5}$), ppm.
Methyl benzenesulfonate		^{13}C NMR (300 MHz, $CDCl_3$): δ = 56,43 (C_7), 125,44 (C_3=C_5), 128,19(C_1), 129,87(C_2=C_6), 129,41(C_4).

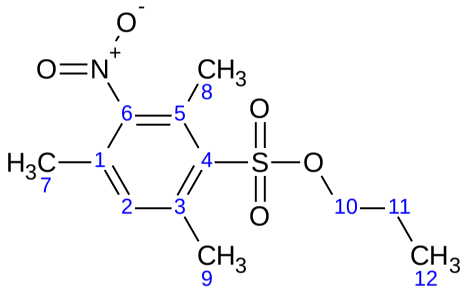
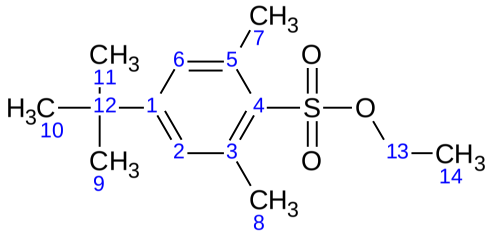
Continuation of Table 3.3

Benzenesulfonate	Formula	NMR-spectra
Propyl 2,4,6-trimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =0,93 (t,*J = 7,5 Hz*, 3 H_{12}), 1,67(m,*J = 7,5 Hz*, 2 H_{11}), 2,31(s,*J = 7,5 Hz*, 3 H_7), 2,63(s,*J = 7,5 Hz*, 6 $H_{8,9}$), 3,93(t,*J = 7,5 Hz*, 2 H_{10}), 6,97(s,*J = 7,5 Hz*, 2 H2,6), ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 10,27 (C_{12}), 21,14 (C_7), 22,47(C_{11}), 22,71(C_8=C_9), 71,23 (C_{10}), 130,97(C_2=C_6), 131,80(C_3=C_5), 139,97(C_1), 143,22(C_4).
Ethyl 4-methylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,3(t,*J = 7,5 Hz*, 3 H_9), 2,45(s,*J = 7,5 Hz*, 3 H_7), 4,1(q,*J = 7,5 Hz*, 2 H_8), 7,34(d,*J = 7,5 Hz*, 2 $H_{2,6}$), 7,79(d,*J = 7,5 Hz*, 2 $H_{3,5}$), ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 14,87 (C_9), 27,76 (C_7), 66,92 (C_8), 128,00(C_2=C_6), 130,04(C_3=C_5), 144,78(C_4).

Continuation of Table 3.3

Benzenesulfonate	Formula	NMR-spectra
Propan-2-yl 2,4,6-trimethyl-3-nitrobenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,24(d,*J = 7,5 Hz*, 6 $H_{11,12}$), 2,25(s,*J = 7,5 Hz*, 3 H_7), 2,5(s,*J = 7,5 Hz*, 3 H_8), 2,61(s,*J = 7,5 Hz*, 3 H_9), 4,16(m,*J = 7,5 Hz*,1 H_{10}), 7,04(s, *J = 7,5 Hz*, 1 H_6), ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 16,16 (C_{11}=C_{12}), 17,26 (C_9), 23,09 (C_7), 24,34(C_8), 66,88(C_{10}), 129,31(C_6), 131,64(C_5), 132,98(C_6), 138,23(C_3), 139,64(C_4), 152,27(C_2).
Ethyl 4-tert-butyl-2,6-dimethylbenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =1,31 (s, 9 $H_{9,10,11}$), 1,98 (s,*J = 7,5 Hz*, 3 H_{14}), 2,67 (s, *J = 7,5 Hz*, 6 $H_{7,8}$), 4,09 (q, *J = 7,5 Hz*, 2 H_{13}), 7,14 (s, *J = 7,5 Hz*, 2 $H_{2,6}$), ppm.
Methyl 4-methylbenzenesulfonate		^{13}C NMR (300 MHz, $CDCl_3$): δ = 20,96 (C_7), 56,27 (C_8), 125,60 (C_3=C_5), 128,23(C_2=C_6), 129,32(C_1), 130,01(C_4).

Continuation of Table 3.3

Benzenesulfonate	Formula	NMR-spectra
Propyl 2,4,6-trimethyl-3-nitrobenzenesulfonate		^{1}H NMR ($CDCl_3$, 300 MHz): δ =0,96 (t, 3 H_{12}), 1,72 (m,*J = 7,5 Hz*, 2 H_{11}), 2,3 (s, *J = 7,5 Hz*, 3 H_7), 2,56 (s, *J = 7,5 Hz*, 3 H_9), 2,69 (s, *J = 7,5 Hz*, 3 H_8), 4,03 (t, *J = 7,5 Hz*, 2 H_{13}), 7,14 (s, *J = 7,5 Hz*, 1 H_2), ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 20,96 (C_7), 56,27 (C_8), 125,60 (C_3=C_5), 128,23(C_2=C_6), 129,32(C_1), 130,01(C_4).
Ethyl 4-tert-butyl-2,6-dimethylbenzenesulfonate		^{13}C NMR (300 MHz, $CDCl_3$): δ = 14,88 (C_{14}), 23,11 ($C_{7,8}$), 31,05 (C_9=C_{10}=C_{11}), 34,81(C_{12}), 65,78(C_{13}), 128,26(C_2=C_6), 131,58(C_1), 139,69($C_{5=3}$), 156,00(C_4).

3.1.3.2 Monocrystal X-ray diffraction

Chemical structures were also confirmed by single crystal X-ray diffraction. Radiographs recorded on the diffractometer at the University of Coruña, Spain. Diffractometer: X8-Apex II (Manufacturer: Nonius-Bruker). Single crystal diffractometer with Kappa geometry, equipped with Mo source (λ = 0.7107 Å), a CCD detector and a cooling system (Kryoflex).

Structure determination was done using the following programs:

1. Data collection: "Apex2" suite v2010 (Bruker Instruments)
2. Cell refinement: "SAINT" v8.34A (Bruker, 2013)
3. Data reduction: "SAINT and XPREP" version 2008/2 (Sheldrick, Bruker AXS Inc.)
4. Structure solution: "XS" version 2008/1 (George M. Sheldrick, Acta Cryst. (2008). A64, 112-122)
5. Structure refinement: "XL" Version 2008/4 (George M. Sheldrick, Acta Cryst. (2008). A64, 112-122). Note: the refinement process was carried out by means of "Olex2" (Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K; Puschmann, H.. J. Appl. Cryst., 42, 339-341 (2009))
6. Molecule drawing: PLATON (2011) (A.L. Speck (2009) Acta Cryst. D65, 148-155)

Sample preparation. The crystal was placed in a saturated solution, and then the solvent was evaporated. A mixture of benzene and hexane was used for arenesulfonyl chlorides, and acetone for sulfonates.

For measurements at room temperature, crystals were glued on the top of a glass fiber using a commercial cyanoacrylate adhesive. For low temperature measurement, commercial polyimide loops (kapton) from Mitegen (Ithaca, NY, USA) were used along with perfluoropolyether oil (Fomblin (R), Aldrich (USA)).

Crystal selection was made using a Leica microscope (model MZ75) with polarized filters. Whenever the crystals were too long, *i.e.* when the largest dimension exceeded 0.4 mm, a razor blade was used to cut them out.

3.1.3.3 Chloride analysis

All the sulfonyl chlorides were subjected to elemental analysis for chloride by Mohr method, *i.e.* argentometric titration. [9]. The samples of arenesulfonyl chlorides dissolved in aqueous 1,4-dioxane, were kept at least a day to ensure complete conversion of the sulfonyl chloride, then the resulting solution was titrated with a freshly prepared solution of $AgNO_3$ as follows.

Aliquot of chloride solution (2 - 10 mL) was poured into an Erlenmeyer flask and diluted with distilled water (about 10 mL), then 3 - 5 drops of 5% potassium chromate solution were added and titrate, under vigorous stirring, with 0.05N solution of $AgNO_3$ until the color of the flask content changes from lemon-yellow to dark pink.

As the sample solution became acidic, it should be neutralized with sodium bicarbonate.

All substances showed purity close to 99%.

3.2 CHEMICAL KINETICS

3.2.1 Monitoring of the reaction progress

UV-Vis spectrophotometry was used to determine the reaction rate constants. The choice of this method was determined by a very broad range of the reaction rates of alcoholysis and hydrolysis, as well as its comparative simplicity, availability and low cost of the test substances. UV-spectrophotometric measurements of the solvolysis rates were carried out using a spectrophotometer Cary 1E UV-Vis, equipped with a thermostated cuvette holder and a calibrated thermistor in the temperature range 303-323K (± 0.1 °C).

Spectrophotometrical monitoring of the reaction progress was carried out at the appropriate wavelength (λ_W) for consumption of the sulfonyl chloride, which was selected from the absorption spectra of the sulfo derivatives and of the solvolysis products (Figure 3.1), separately prepared as described in a preceding section (3.1.1.4). Time resolved optical density (OD) data were recorded at equal time intervals.

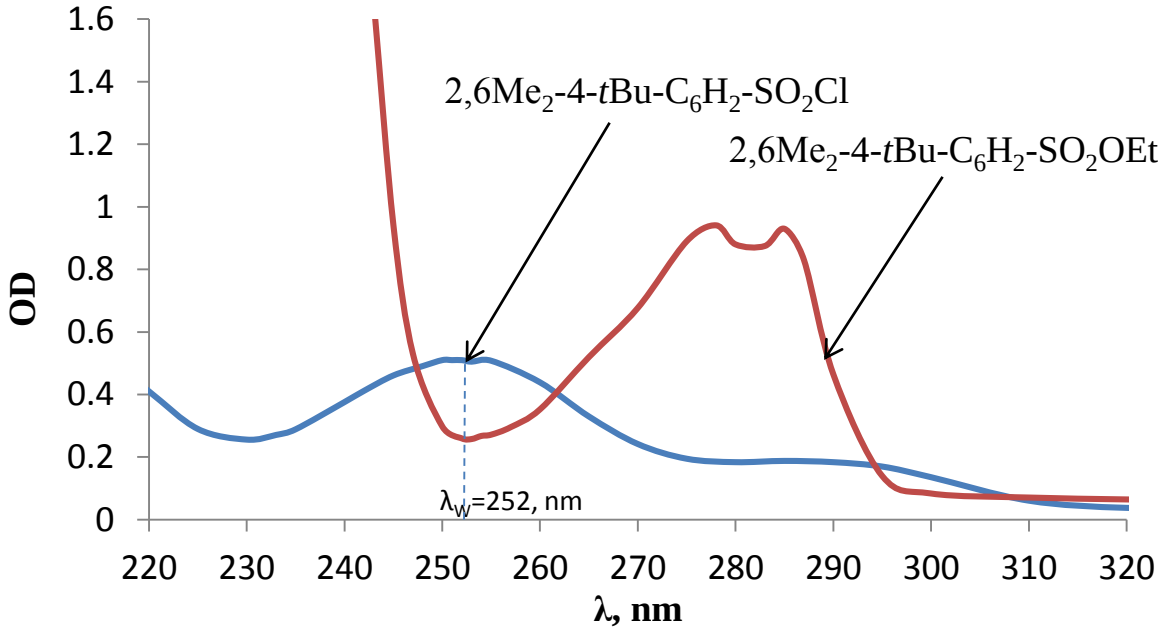


Figure 3.1 – UV spectra of the sulfonyl chloride dissolved in hexane ([2,6Me$_2$4-*t*Bu-C$_6$H$_2$-SO$_2$Cl] = $1.0 \cdot 10^{-4}$ M) and of the solvolysis product in ethanol ([2,6Me$_2$-4-*t*Bu-C$_6$H$_2$-SO$_2$OEt] = $4.7 \cdot 10^{-4}$ M).

The reaction was carried out under pseudo-first order conditions, with a significant excess of alcohol, [ROH] >> [sulfonyl chloride] (*c.a.* $1 \cdot 10^{-4}$ mol·dm^{-3}). The chloride was dissolved in dry hexane, and, after 0.04 mL were injected by a microsyringe in 3.5 mL of the alcohol previously thermostated in a quartz cuvette (*vide supra*). Before carrying out of a chemical kinetics experiment the cuvette, filled with the corresponding alcohol, was thermostated for 20 min. The same alcohol was used as reference in the solvolysis studies.

A solution of the sulfonyl chloride ($3.5 \cdot 10^{-4}$ mol/L) in hexane was prepared to determine the order relative to the alcohol. For each experimental point, the content of the cuvette was 0.25 mL of the sulfonyl chloride solution and a mixture of hexane and alcohol in accordance with Table. 3.4. The composition of the alcohol-hexane mixtures varied for each alcohol. For methanolysis were used next volume ratios of hexane to alcohol (**H:A**=0.00:3.50; 1:2.50; 1.25:2.25; 1.50:2.00; 1.75:1.75; 2.00:1.50). For ethanolysis was used another raw of volume ratios of hexane to alcohol (**H:A**=0.00:3.50; 1:2.50; 1.25:2.25; 1.50:2.00; 1.75:1.75) that was extended for few compounds by next experimental points: (**H:A**=0.75:2.75; 2.00:1.50; 2.25:1.25). In case of *iso*-propanolysis were used volume ratios of hexane to alcohol (**H:A**=0.00:3.50; 0.75:2.75; 1:2.50; 1.25:2.25; 1.50:2.00) that was also extended by additional next experimental points (**H:A**=1.75:1.75; 2.00:1.50; 2.25:1.25; 2.5:1.00) for most distrustful compounds.

The alcohol, at the working temperature, was added to the thermostated solution of the sulfonyl chloride in hexane.

3.2.2 Chemical kinetics data handling

The selection of the obtained optical density-time data for subsequent processing is of great importance. The optimal range is $0.3 < \alpha < 0.7$, where α is the degree of conversion. At the initial part of the kinetic curve ($\alpha < 0.3$) there are often a large number of temperature and concentration of errors, particularly in the case of fast processes with $t_{1/2}$ = 1-2 min, where $t_{1/2}$ is the half-life. At the final part of the kinetic curve ($\alpha > 0.8$), the influence of noise leads to noticeable oscillations of the measured magnitude (e.g. optical density**)**. Experience shows that if the reaction is carried out by more than 3-4 half lives, the linearity of the equations is greatly disturbed, so the "excess" part of the kinetic curve should be neglected.

The studied reaction involves two reactants A_1 and A_2:

$$A_1 + A_2 \xrightarrow{k} P$$

where A_1 – arenesulfonyl chloride; A_2 – alcohol; P – product; k – rate constant.

Alcohol is in large excess; therefore its concentration remains practically constant during the reaction.

Assuming $[A_2]_0 >> [A_1]_0$ the rate equation simplifies and takes the form:

$$\frac{d[P]}{dt} = k([A_1]_0 - [P])([A_2]_0 - P), \qquad \text{(Eq. 3.1)}$$

$$\frac{d[P]}{dt} = k \cdot [A_2]_0 \cdot ([A_1]_0 - [P]) = k_{\text{obs}} \cdot ([A_1]_0 - [P]), \qquad \text{(Eq. 3.2)}$$

where k_{obs} is the observed rate constant.

$$k_{\text{obs}} = k \cdot [A_2]_0 \qquad \text{(Eq. 3.3)}$$

Equation (3.2) represents a pseudo-first-order rate equation relative to A_1; therefore to obtain the value k_{obs} all methods of the first order reaction kinetics are applicable. Since the pseudo-first-order rate constant does not depend on the initial concentration of the reactant, any change in the concentration of A_1 has no effect on k_{obs}[10].

For the calculation of k_{obs} the following formula could apply:

$$k_{\text{obs}} = \frac{1}{t} \cdot ln \frac{(OD_0 - OD_t)}{(OD_t - OD_\infty)} \qquad \text{(Eq. 3.4)}$$

Graphical methods could be used to reduce experimental error. Graphs were constructed by plotting $\ln((OD_0\text{-}OD_t)/(OD_t\text{-}OD_\infty))$ versus time as shown in Fig. 3.2; the slope of the straight line being k_{obs}.

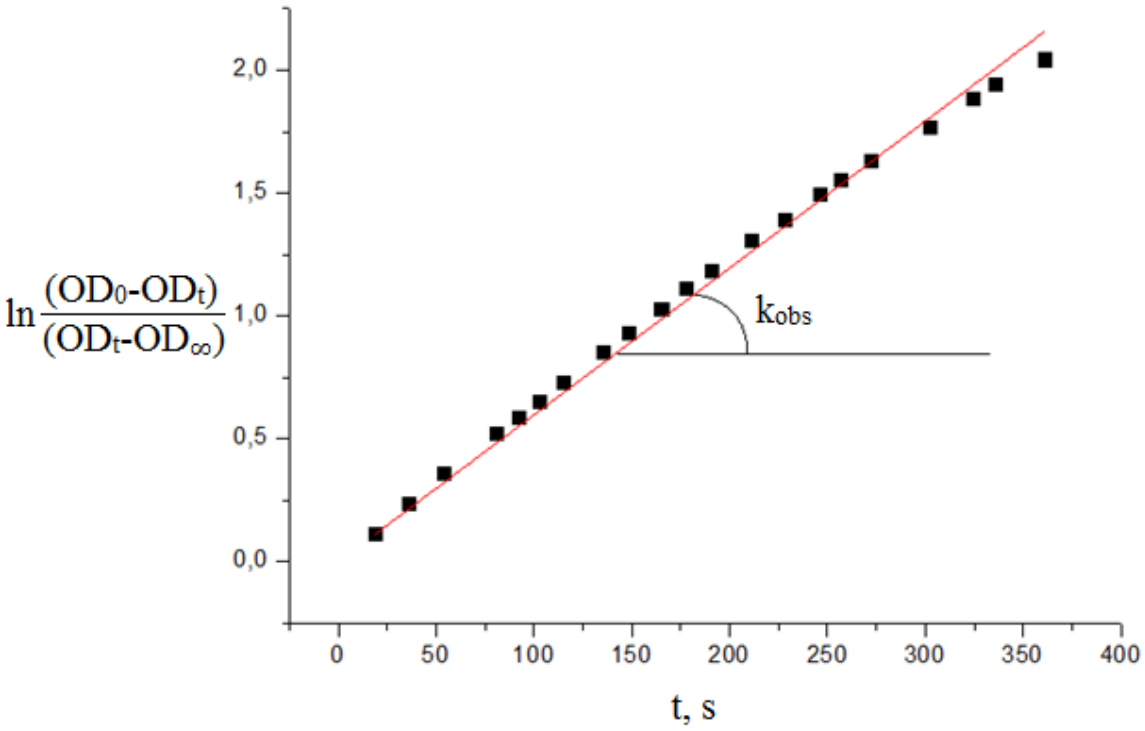


Figure 3.2 – Graphical calculation of the observed rate constant (k_{obs}) for the methanolysis of 2,6-Me_2-4-tBu-C_6H_2-SO_2Cl at 323 K .

Observed rate constants were finally calculated fitting the linear form of equation (3.4) to kinetic data by linear least squares. Calculations were carried out using OriginPro 8 SR4 v8.0951.

Second order rate constants k (units: $dm^3 \cdot mol^{-1} \cdot s^{-1}$) were obtained dividing the observed first order rate constant, *i.e.* k_{obs}, by the concentration of alcohol in the reaction mixture [10].

3.2.3 Activation parameters

Reaction rate constants were measured at three temperatures to obtain the thermodynamic values of the solvolysis state; the temperature range was not less than 20K.Values of the activation parameters for the solvolysis of arenesulfonyl chlorides were calculated using the Arrhenius (3.5) and the Eyring (3.6) equations[10].

$$k = A \cdot e^{\frac{-E_a}{RT}} \quad \text{(Eq. 3.5)}$$

$$k = \frac{k_B \cdot T}{h} \cdot e^{\frac{\Delta S^{\ddagger}}{R}} \cdot e^{-\frac{\Delta H^{\ddagger}}{RT}} \quad \text{(Eq. 3.6)}$$

Where k - observed rate constant; k_B - Boltzmann constant; h - Planck constant; $\Delta S^{\ddagger}$ - entropy of activation, $J \cdot mol^{-1} \cdot K^{-1}$; $\Delta H^{\ddagger}$ - enthalpy of activation, J/mol; R - universal gas constant.

For the calculation of activation parameters k values were used, which are linearly related to k_{obs}, see eq. (3.3). Arrhenius parameters were calculated from the linearlized Arrhenius equation: ln k = ln A – $(E_a/R) \cdot (1/T)$, *i.e.*, by plotting ln k as dependent variable and (1/T) as independent variable, so according to the equation of the straight line ($y = a \cdot x + b$), $a = -E_a/R$ and b = ln A. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated at 313K using a combination of Arrhenius and Eyring equations (3.5 & 3.6):

$$A = e^b, \quad \text{(Eq. 3.7)}$$

$$E_a = (\ln A - ln k_{313}) \cdot R \cdot T, \quad \text{(Eq. 3.8)}$$

$$\Delta H^{\ddagger} = E_a - R \cdot T, \quad \text{(Eq. 3.9)}$$

$$\Delta S^{\ddagger} = ln\left(\frac{\frac{k_{313}}{313}}{\frac{k_b}{h}}\right) \cdot R - \frac{\Delta H^{\ddagger}}{313} \quad \text{(Eq. 3.10)}$$

Entropy and enthalpy of activation allow the calculation of the Gibbs free energy of activation, this time also at 313K:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \cdot \Delta S^{\ddagger} \quad \text{(Eq. 3.11)}$$

The uncertainty in the enthalpy of activation is less than 4 $kJ \cdot mol^{-1}$, whereas that of the entropy of activation is less than 10 $J \cdot mol^{-1} \cdot K^{-1}$.

3.3 REFERENCES

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4 RESULTS AND DISCUSSION

4.1 ALCOHOLYSIS OF ARENESULFONYL CHLORIDES

Despite the rather large number of publications in the literature on the nucleophilic substitution at the sulfur atom by solvolysis of arenesulfonyl chlorides in alcohols, some peculiarities for hindered arenesulfonyl chlorides still remain open since it was regarded as secondary.

To clarify the issue of the substitution at the hindered sulfonyl center we investigated the structural effects in the alcoholysis of arenesulfonyl chlorides in methanol, ethanol, propanol, and *iso*-propanol at 303, 313 and 323 K.

The used compounds, general formula X-ArSO_2Cl were divided in two sets as follows:

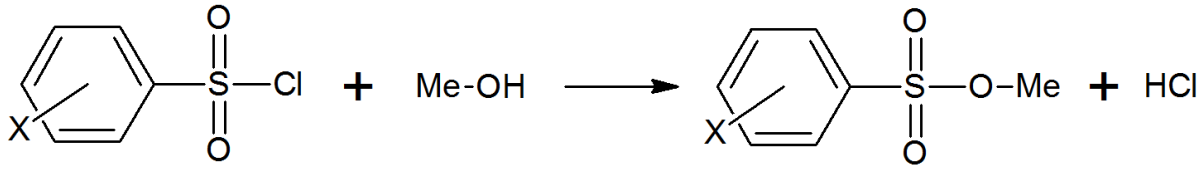
A: X=H-; 4-Me-; 4-*t*-Bu-; 4-Cl-; 4-Br-; 3-NO_2-; 4-NO_2-.

B: X=2,4,6-Me_3-; 2,4,6-Et_3-;2,4,6-*i*-Pr_3-; 2-Me-; 2,4-Me_2-; 2,5-Me_2-; 2-Me-5-*t*-Bu-; 2,6-Me_2-4-*t*-Bu-; 2,3,5,6-Me_4-; 2-Me-5-NO_2-; 2,4-Me_2-5-NO_2-; 2,4,6-Me_3-3-NO_2-; 2,4,6-$(OMe)_3$-.

To unravel the reaction mechanism it is necessary to carry out a chemical kinetic study to evaluate the influence of the following factors on the rate of solvolysis:

- the structure of the substituent in the sterically hindered substrate;
- the temperature;
- the nucleophile;
- the polarity of the medium (alcohol);
- the nature of the leaving group;
- the kinetic isotope effects: solvent and substrate;

4.1.1 **Methanolysis of arenesulfonyl chlorides**



The neutral methanolysis of aromatic sulfonyl chlorides was investigated. Methanolysis reactions were adequately fitted by a first-order kinetic model, the corresponding rate constants are collected in Table 4.1; from there it follows that the reaction is sensitive to the nature and position of the substituents in the sulfonyl chloride. The electronic nature of the *X* substituent has ambiguous effect. An increase of electron withdrawing properties of the *X* substituents in the model *A* series leads to lower reactivity, which is contrary to the behaviour predicted for typical S_N2 reactions.

Hammett's correlation shows reasonable linearity for the extended model series (Figure 4.1), with a negative slope ($\rho < 0$) for some substrates of the *A* series (X=H-; 4-Cl-; 4-Br-; 3-NO_2) and some representatives of the hindered *B* series (2-Me-; 2,4-Me_2-; 2,5-Me_2-; 2-Me-5-*t*-Bu-; 2,4-Me_2-5-NO_2-; 2,4,6-*i*-Pr_3-) irrespective of the temperature.

The rather low reactivity relative to the regression line of 4-*t*-Bu- and 4-Me-derivative is not easily explained; while the observed reactivity of 4-nitro-derivative is clearly above of the line. On the other hand, the following sterically hindered compounds: X=2,4,6-Me_3-; 2,4,6-Et_3-; 2,6-Me_2-4-*t*-Bu-; 2,3,5,6-Me_4-; 2-Me-5-NO_2-; 2,4,6-Me_3-3-NO_2-; 2,4,6-$(OMe)_3$- show anomalous acceleration (see Figure 4.1). The most reactive compounds include all those substituted in both *ortho*-positions by -Me groups; surprisingly, the sterically-hindered 2,4,6-*i*-Pr_3-derivative behaves as unhindered compounds, lying well in the linear correlation, so that its behavior can be explained in accordance with the electronic effects of substituents. ρ-values less than zero imply a not negligible decrease in electron density at the reaction site.

Table 4.1 Observed rate constants for the methanolysis of X-$ArSO_2Cl$

X	$k_{obs}\cdot10^4$ / s^{-1}		
	303 K	313 K	323 K
	A series		
4-*t*-Bu-	0.900±0.010	2.05±0.02	4.32±0.07
4-Me-	1.63±0.01	3.80±0.02	7.57±0.05
H-	1.64±0.01	3.76±0.01	8.16±0.01
4-Br-	1.45±0.01	3.24±0.02	7.11±0.03
4-Cl-	1.21±0.01	2.89±0.02	6.34±0.04
3-NO_2-	1.03±0.04	2.25±0.04	4.00±0.10
4-NO_2-	2.68±0.01	6.42±0.01	11.8±0.1
	B series		
2,4,6-$(OMe)_3$-	27.8±0.1	51.2±0.1	102±1
2,4,6-*i*-Pr_3-	3.64±0.01	7.94±0.04	16.7±0.1
2,6-Me_2-4-*t*-Bu-	13.7±0.1	28.1±0.2	58.5±0.6
2,4,6-Me_3-	13.2±0.1	29.1±0.2	51.8±0.4
2,3,5,6-Me_4-	9.57±0.03	20.1±0.1	40.4±0.3
2,4,6-Et_3-	4.20±0.03	10.3±0.1	21.1±0.2
2,4-Me_2-	2.35±0.01	5.23±0.03	12.2±0.1
2-Me-5-*t*-Bu-	2.03±0.01	5.12±0.02	10.6±0.1
2,5-Me_2-	2.28±0.01	5.34±0.02	11.4±0.1
2-Me-	1.93±0.01	4.70±0.02	10.3±0.1
2,4,6-Me_3-3-NO_2-	5.74±0.02	12.8±0.2	24.4±0.3
2,4-Me_2-5-NO_2-	1.07±0.01	2.58±0.02	5.59±0.04
2-Me-5-NO_2-	1.27±0.01	3.00±0.05	7.20±0.10

On classical grounds[1] it suggests a possible "loosening" of the S-Cl bond and a S_N1-like transition state. By the same reason it is consistent with the lack of steric limitations for nucleophile attack at the sulfonyl center in the 2,4,6-*i*-Pr_3-derivative.

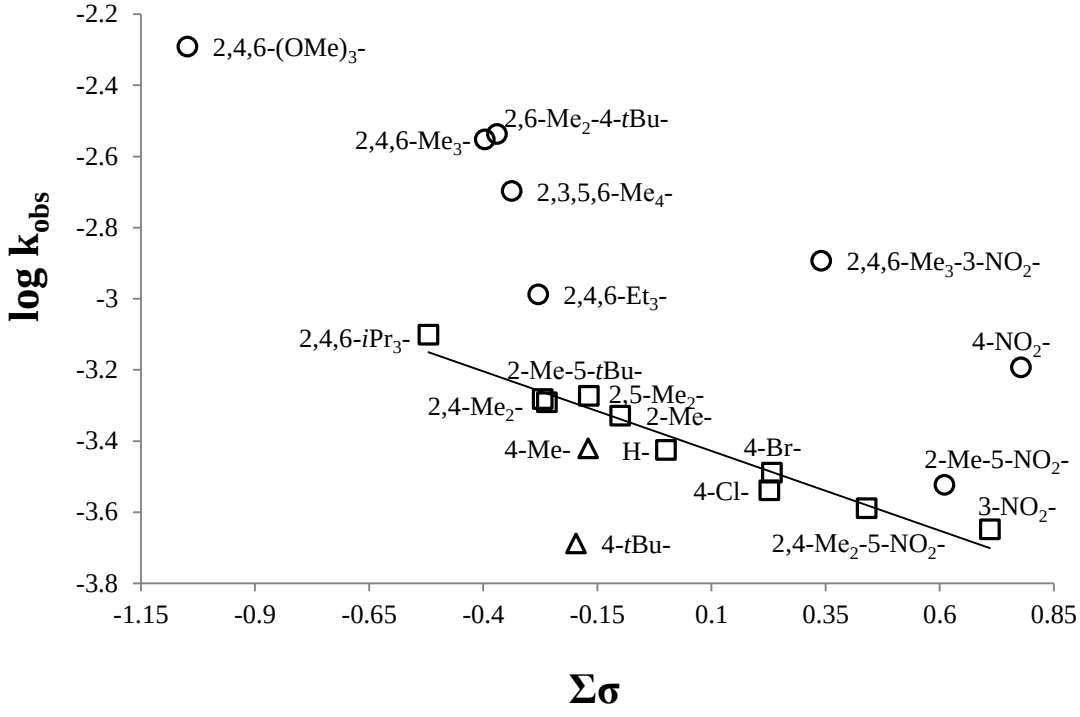


Figure 4.1 Hammett correlation for the methanolysis of X-ArSO_2Cl at 313K.
□ extended model series; ○ compounds showing enhanced reactivity;
Δ compounds with reduced reactivity.

Although alternative substrate groupings might be proposed, the tendency would always imply a negative value for ρ.The values obtained for Hammett's ρ at different temperatures (Table 4.2) are consistent with obtained data for bimolecular nucleophilic substitutions in hindered substrates containing sulfur.[2, 3]

Table 4.2 Parameters from Hammett correlation analysis at different temperatures of the methanolysis of X-ArSO_2Cl for the extended model series

T / K	-*log* k_0	-ρ	r	n*
303	3.75±0.02	0.44±0.05	0.90	10
313	3.38±0.01	0.45±0.03	0.95	10
323	3.05±0.01	0.43±0.04	0.93	10

*n- sample size

The existence of a $logk_{T1}$ *vs.* $logk_{T2}$ isokinetic dependence (r=0.994-0.997) for all substrates (Figure 4.2), and the homogeneity of mechanistic criteria for the methanolytic process involving arenesulfonyl chlorides: similar secondary solvent KIE [4,5] effect of the change of nucleophile [3, 2, 6-7] and solvent effect [3, 6] point to a typical S_N2-nucleophilic substitution mechanism, but with the possible non-classical deviations of the TS structure for a number of hindered substrates.[8-21].

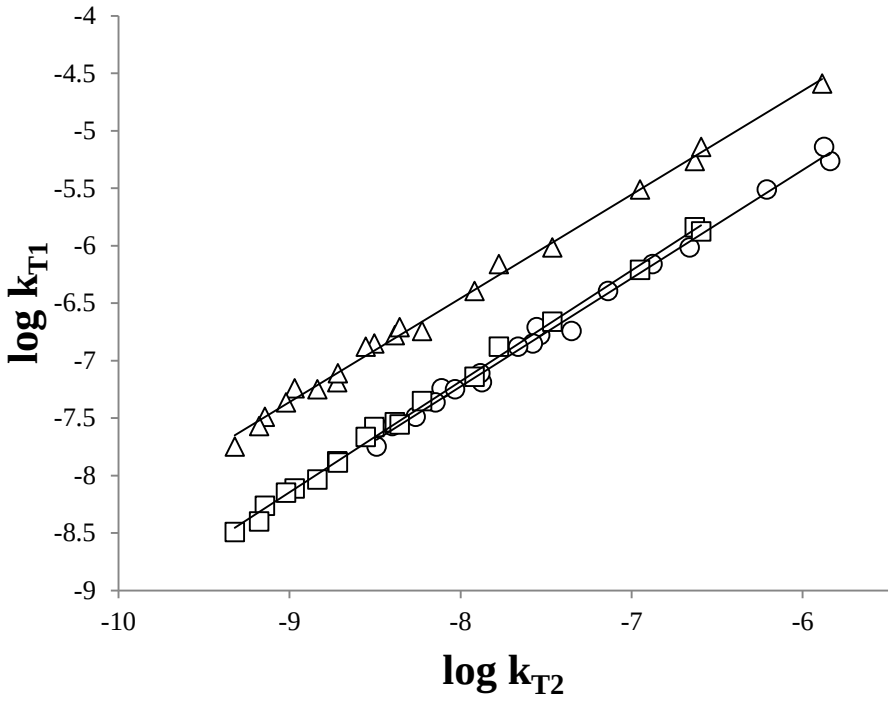


Figure 4.2 Log k_{T1}-log k_{T2} isokinetic dependence for X-$ArSO_2Cl$ methanolysis at 303-323K.

□ T_1=303K; T_2=313K; Δ T_1=303K; T_2=323K; ○ T_1=313K; T_2=323 K.

Activation parameters are collected in Table 4.3 and in Figure 4.3.The effect of the *ortho*- substituents on $\Delta H^{\ddagger}$ is ambiguous. For the *A* series enthalpy of activation does not change, $\Delta H^{\ddagger}_{mean}$ = 62 ± 3 kJ·mol^{-1}, *i.e.*, it may considered an isoenthalpic series.

Table 4.3 Activation parameters for the methanolysis of X-$ArSO_2Cl$

X	$\Delta H^{\ddagger}$* / kJ·mol^{-1}	$-\Delta S^{\ddagger}$ */ J·mol^{-1}·K^{-1}	$\Delta G^{\ddagger}$ *,**/ kJ·mol^{-1}
	A series		
4-*t*-Bu-	62±1	143±3	107±2
4-Me-*	61±1	146±4	106±3
H-*	65±2	133±5	106±3
4-Br-	63±1	137±2	106±2
4-Cl-*	61±3	146±8	107±5
3-NO_2-	62±4	144±14	107±8
4-NO_2-*	60±3	145±10	105±6
	B series		
2,4,6-$(OMe)_3$-	51±3	152±9	99±5
2,4,6-*i*-Pr_3-	60±1	138±1	104±1
2,6-Me_2-4-*t*-Bu-	57±2	137±5	100±3
2,4,6-Me_3-	54±4	148±13	100±8
2,3,5,6-Me_4-	57±1	141±1	101±1
2,4,6-Et_3-	64±3	124±10	103±6
2,4-Me_2-	65±2	126±7	105±5
2-Me-5-*t*-Bu-	66±3	125±11	105±7
2,5-Me_2-	64±1	131±8	105±2
2-Me-	67±1	123±4	105±2
2,4,6-Me_3-3-NO_2-	57±3	144±8	103±5
2,4-Me_2-5-NO_2-	66±1	131±4	107±3
2-Me-5-NO_2-	69±2	120±5	106±3

* An additional point at 25^0 C, ref [22], has been included in the calculation

** Estimated considering the second order constant k_2, *i.e.*$k_{obs} = k_2 \cdot [solvent]$).

*** Value calculated at 40ºC.

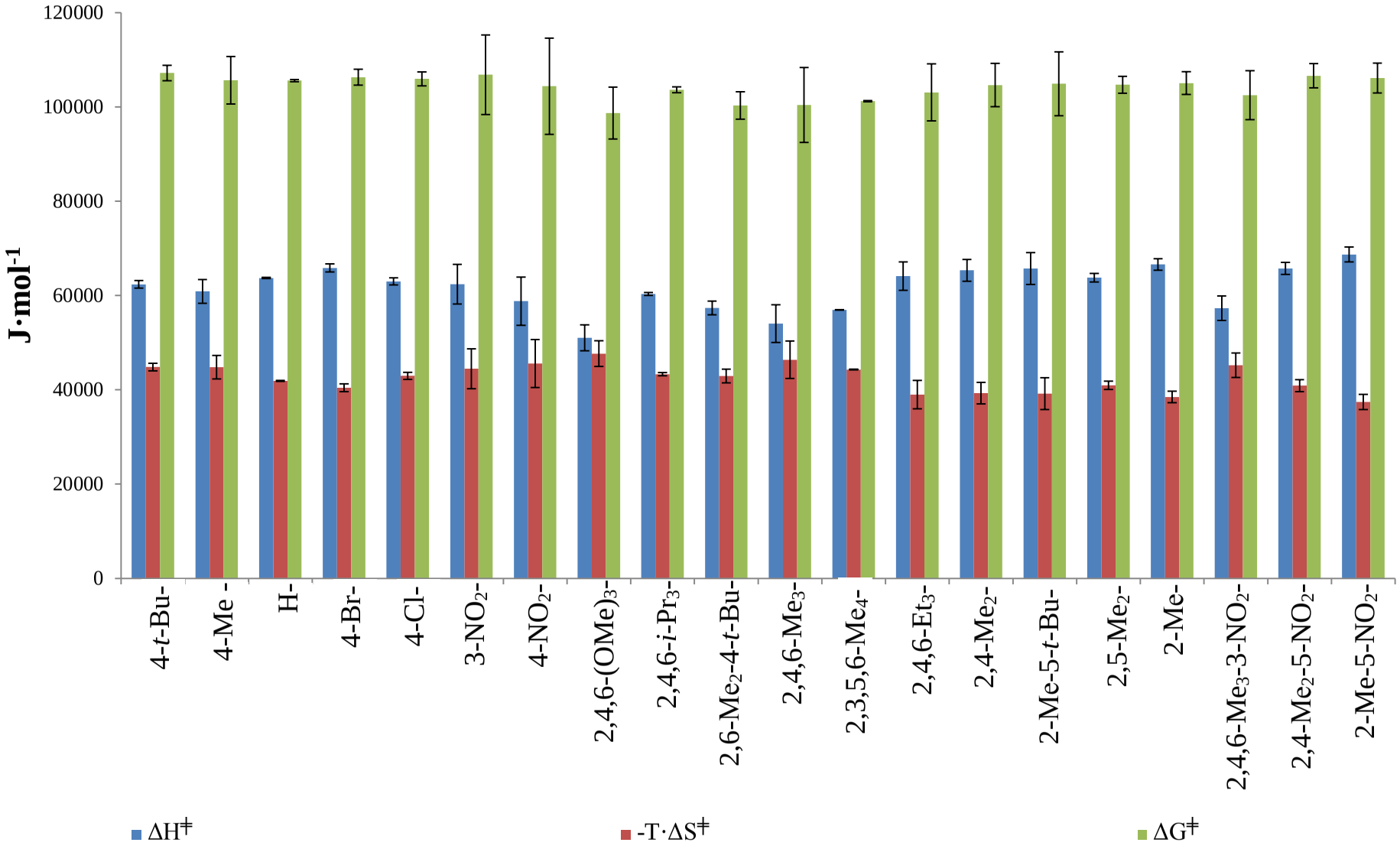


Figure 4.3 Activation parameters for X-ArSO$_2$Cl methanolysis.

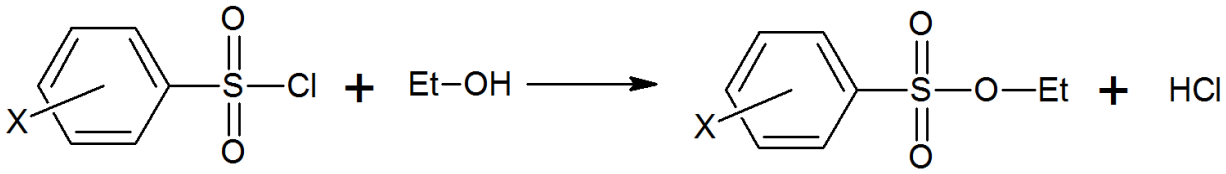
For *B* set the situation is more complicated; di-*ortho*-alkylated substrates show a slightly lower values of the activation enthalpy, where as for mono-*ortho*-alkylated compounds those values are rather disperse, which likely is due to the effect of substituents other than *ortho*. Values of entropy of activation do not show a clear pattern.

When only methyl substituents are considered, $\Delta H^{\ddagger}$ slightly decreases in going from unsubstituted or mono-*ortho*-methylated compounds to di-*ortho*-methylated, the same is observed for $\Delta G^{\ddagger}$, the contrary happens to $\Delta S^{\ddagger}$.

The similarity of the activation parameters for both series supports the same methanolysis mechanism for all the studied substrates; the transition from S_N2 to S_N1 mechanism should be accompanied by a sharp change of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

The bad correlation result of the isokinetic ratio $\delta\Delta H^{\ddagger} = \beta\delta\Delta S^{\ddagger}$ ($R^2 = 0.76$) indicates some degree of heterogeneity in the reaction series.

4.1.2 Ethanolysis of arenesulfonyl chlorides



The neutral ethanolysis of aromatic sulfonyl chlorides is similar to that of methanolysis, the corresponding rate constants are collected in Table 4.4. As stated above, the nature and position of the substituents have noticeable effect on the reaction rate.

Hammett's correlation (Eq. 2.1) also shows a reasonable linearity (Table 4.5), again with a negative slope ($\rho<0$) for some substrates of *A* series (X=H-; 4-Cl-; 4-Br-) and individual representatives of hindered *B* series (X=2,4-Me_2-; 2-Me-5-*t*-Bu-; 2,4-Me_2-5-NO_2-; 2,4,6-*i*-Pr_3-) irrespective of the working temperature (Figure 4.4). The same comments of the previous section apply here.

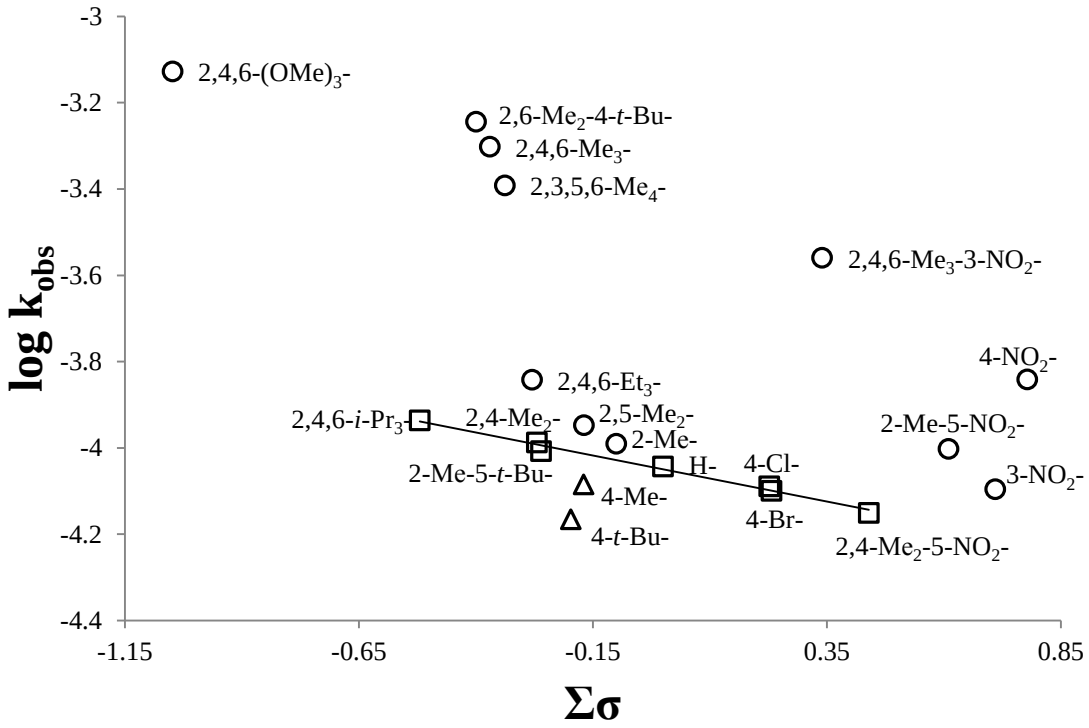


Figure 4.4 Hammett correlation for the ethanolysis of X-$ArSO_2Cl$ at 313K.

□ the extended model series; ○ compounds showing enhanced reactivity;

Δ compounds with reduced reactivity.

Table 4.4 Observed rate constants for the ethanolysis of X-$ArSO_2Cl$.

X	$k_{obs}\cdot10^4$ / s^{-1}		
	303 K	313 K	323 K
	A series		
4-*t*-Bu-	0.21±0.01	0.50±0.08	0.93±0.03
4-Me-	0.36±0.01	0.82±0.01	1.91±0.01
H-	0.36±0.01	0.91±0.01	1.87±0.01
4-Br-	0.33±0.01	0.67±0.01	1.75±0.01
4-Cl-	0.35±0.01	0.82±0.01	1.65±0.01
3-NO_2-	0.39±0.02	0.80±0.02	1.65±0.04
4-NO_2-	0.66±0.02	1.44±0.02	3.35±0.04
	B series		
2,4,6-$(OMe)_3$-	1.62±0.01	4.41±0.01	8.74±0.01
2,4,6-*i*-Pr_3-	0.51±0.02	1.16±0.01	2.58±0.01
2,6-Me_2-4-*t*-Bu-	2.25±0.01	5.7±0.8	11.3±0.03
2,4,6-Me_3-	2.24±0.01	4.99±0.02	10.2±0.03
2,3,5,6-Me_4-	1.67±0.01	4.05±0.05	8.2±0.2
2,4,6-Et_3-	0.67±0.01	1.44±0.01	3.47±0.01
2,4-Me_2-	0.47±0.03	1.03±0.01	2.40±0.01
2-Me-5-*t*-Bu-	0.43±0.01	0.98±0.02	2.10±0.04
2,5-Me_2-	0.47±0.01	1.13±0.01	2.58±0.01
2-Me-	0.44±0.01	1.02±0.01	2.40±0.02
2,4,6-Me_3-3-NO_2-	1.34±0.01	2.76±0.01	5.57±0.01
2,4-Me_2-5-NO_2-	0.30±0.01	0.71±0.01	1.61±0.01
2-Me-5-NO_2-	0.45±0.01	1.00±0.01	2.19±0.02

It is noticeable that the most reactive substrates are those having two methyl or methoxy substituents at the *ortho*-position.

Table 4.5 Parameters derived from Hammett correlation analysis at different temperatures in the ethanolysis of X-$ArSO_2Cl$ for the extended model series

T / K	-*log* k_0	-ρ	r	n*
303	4.42±0.01	0.24±0.02	0.947	7
313	4.05±0.01	0.21±0.01	0.985	7
323	3.71±0.01	0.23±0.03	0.917	7

*n- sample size

As before (*vide supra*), the existence of a $logk_{T1}$ *vs.* $logk_{T2}$ isokinetic dependence (r=0,994-0,997) for all substrates (Figure 4.5), and the homogeneity of mechanistic criteria for the ethanolytic process involving arenesulfonyl chlorides: effect of the change of nucleophile [3, 2, 6-7] and solvent effect [3, 6] point to a S_N2-nucleophilic substitution mechanism for all the substituents *X* (Fig. 4.5).

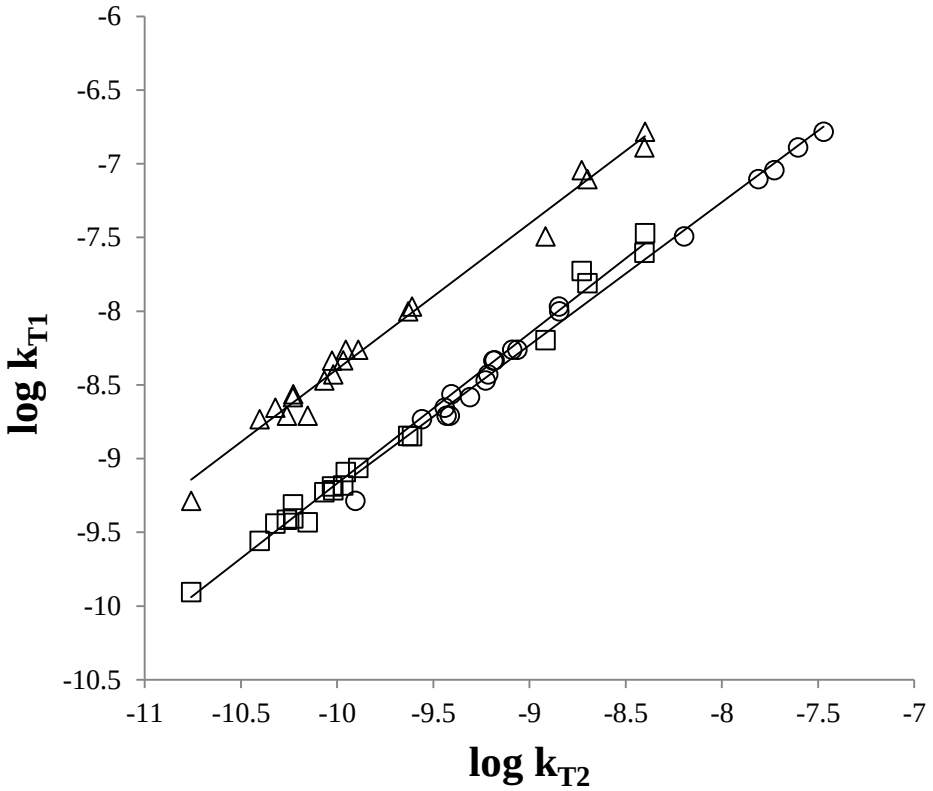


Figure 4.5 Log k_{T1}-log k_{T2} isokinetic dependence for X-$ArSO_2Cl$ ethanolysis at 303-323K.□ T_1=303K; T_2=313K; Δ T_1=303K; T_2=323K; ○ T_1=313K; T_2=323 K.

Activation parameters are collected in Table 4.6 and Figure 4.6. Again comments of the previous section apply here; in this case empirical data also support the same ethanolysis mechanism for all the studied substrates.

Table 4.6 Activation parameters for the ethanolysis of X-$ArSO_2Cl$

X	$\Delta H^{\ddagger *,**}$ / kJ·mol^{-1}	$-\Delta S^{\ddagger *,**}$/ J·mol^{-1}·K^{-1}	$\Delta G^{\ddagger *,**}$/ kJ·mol^{-1}
	A series		
4-*t*-Bu-	58±4	165±14	110±9
4-Me-	66±2	136±6	109±4
H-	65±3	138±11	109±7
4-Br-	62±2	151±7	109±4
4-Cl-	66±1	136±3	109±2
3-NO_2-	57±1	165±4	109±2
4-NO_2-	65±3	136±8	107±5
	B series		
2,4,6-$(OMe)_3$-	67±6	119±19	104±12
2,4,6-*i*-Pr_3-	65±1	138±2	108±1
2,6-Me_2-4-*t*-Bu-	64±4	126±14	104±9
2,4,6-Me_3-	57±3	150±8	104±5
2,3,5,6-Me_4-	63±3	132±10	105±6
2,4,6-Et_3-	65±4	134±13	107±8
2,4-Me_2-	65±3	138±9	108±5
2-Me-5-*t*-Bu-	63±1	143±2	108±1
2,5-Me_2-	67±1	129±1	108±1
2-Me-	67±2	131±5	108±3
2,4,6-Me_3-3-NO_2-	56±1	157±2	105±1
2,4-Me_2-5-NO_2-	66±1	136±3	109±2
2-Me-5-NO_2-	63±1	144±3	108±2

* Estimated considering the second order constant k_2, *i.e.* $k_{obs} = k_2 \cdot [solvent]$.

** Value calculated at 40ºC.

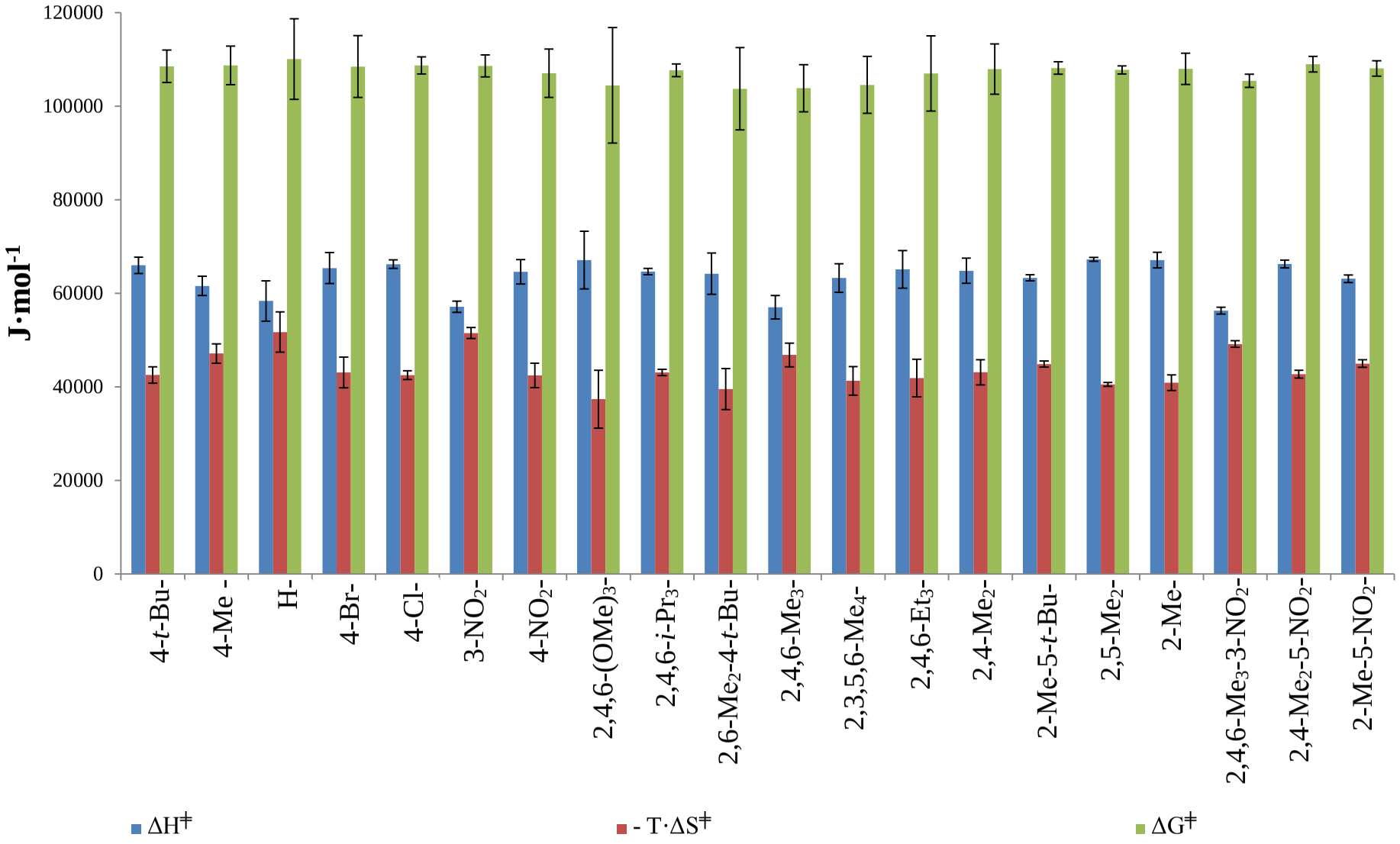
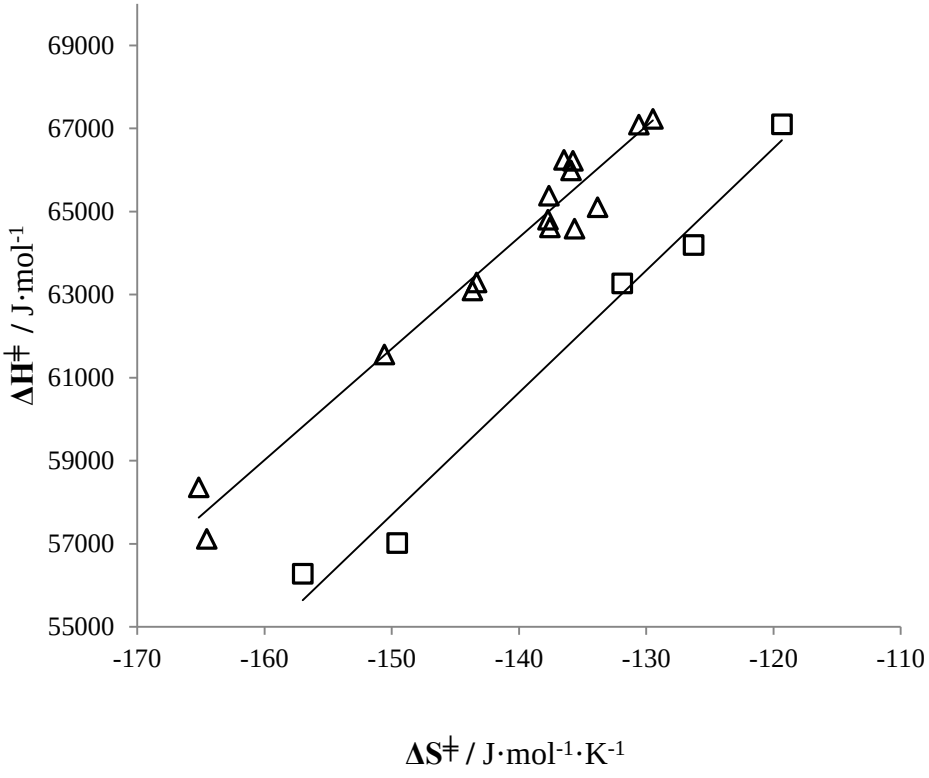


Figure 4.6 Activation parameters for X-ArSO$_2$Cl ethanolysis.

The isokinetic relation $\delta\Delta H^{\ddagger} = \beta\delta\Delta S^{\ddagger}$ also shows bad correlation ($R^2 = 0{,}670$) indicating the heterogeneity of the reaction series. Satisfactory correlations are obtained breaking data in two groups (Figure 4.7):

Group 1 ($\Delta H^{\ddagger}=262\cdot\Delta S^{\ddagger} + 101039$; $R^2=0.964$) includes: X=H-; 4-Me-; 4-*t*-Bu-; 4-Cl-; 4-Br-; 3-NO_2-; 4-NO_2-; 2,4,6-Et_3-; 2,4,6-*i*-Pr_3-;2-Me-; 2,4-Me_2-; 2,5-Me_2-; 2-Me-5-*t*-Bu-; 2-Me-5-NO_2-; 2,4-Me_2-5-NO_2-.

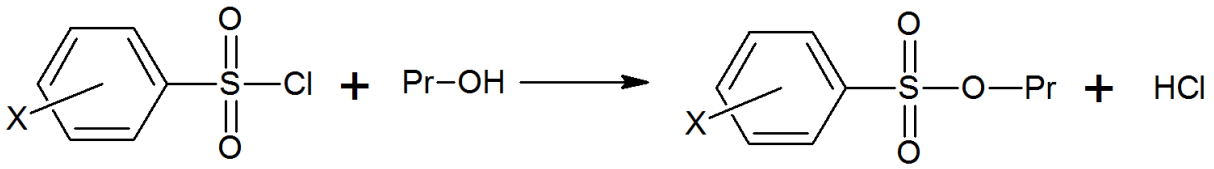
Group 2 ($\Delta H^{\ddagger}=294\cdot\Delta S^{\ddagger} + 101835$; $R^2=0.983$) contains: X=2,4,6-Me_3-; 2,6-Me_2-4-*t*-Bu-; 2,3,5,6-Me_4-; 2,4,6-Me_3-3-NO_2-; 2,4,6-$(OMe)_3$-.



Δ *Group 1;* □ *Group 2.*

Figure 4.7 $\Delta H^{\ddagger}$ *vs*. $\Delta S^{\ddagger}$ for the ethanolysis of X-$ArSO_2Cl$

4.1.3 Propanolysis of arenesulfonyl chlorides



The neutral propanolysis of aromatic sulfonyl chlorides was also adequately fitted by a first-order kinetic model, the corresponding rate constants are collected in Table 4.7. As with methanolysis and ehtanolyisis, this solvolysis is also sensitive to the nature and position of the substituents and shows a complex and ambiguous influence of the electronic nature of the *X* substituent (Figure 4.8).

Hammett's correlation shows a reasonable linearity, again with a negative slope ($\rho < 0$) for some substrates of *A* series (X=H-; 4-Me-; 4-Cl-; 4-Br-) and some of representatives of hindered *B* series (2-Me-5-*t*-Bu-; 2,4,6-*i*-Pr_3-) irrespective of the working temperature (Fig. 4.8)

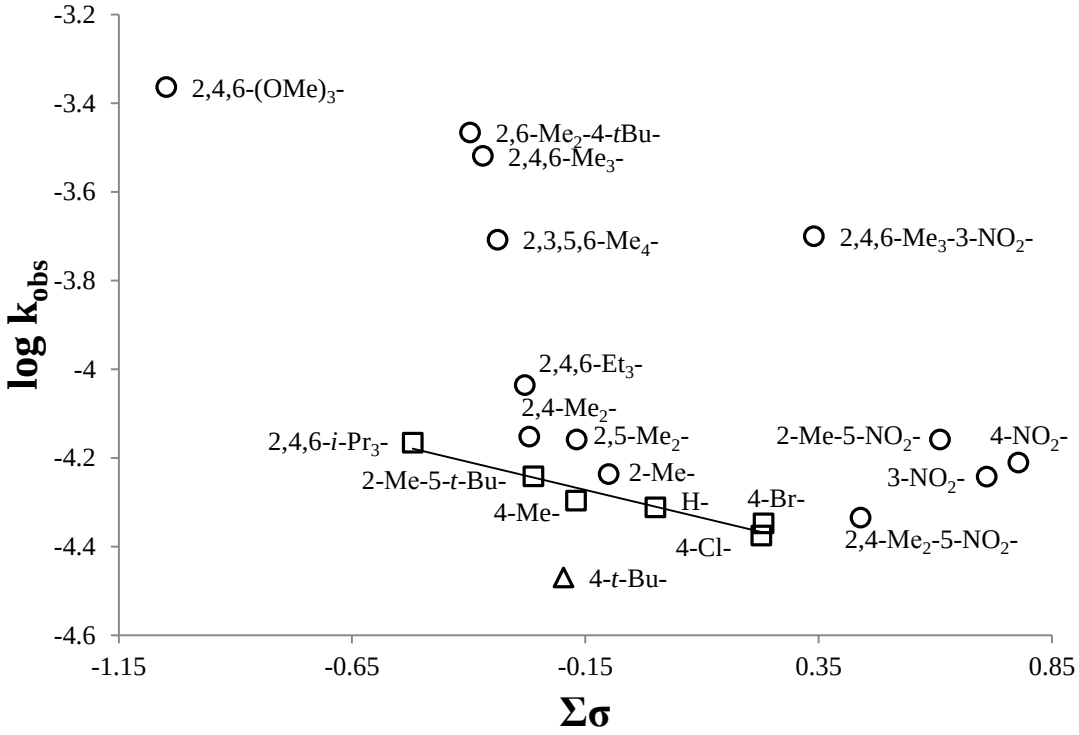


Figure 4.8 Hammett correlation for the propanolysis of X-$ArSO_2Cl$ for the extended model series at 313K.

□ the extended model series; ○ compounds showing enhanced reactivity;

Δ compounds with reduced reactivity.

Table 4.7 Observed rate constants for propanolysis of X-$ArSO_2Cl$ at 303-323K

X	$k_{obs}\cdot10^4$ / s^{-1}		
	303 K	313 K	323 K
	A series		
4-*t*-Bu-	0.138±0.001	0.339±0.003	0.573±0.007
4-Me-	0.224±0.001	0.506±0.002	1.16±0.01
H-	0.203±0.001	0.488±0.003	1.09±0.01
4-Br-	0.185±0.004	0.450±0.007	0.975±0.005
4-Cl-	0.170±0.005	0.422±0.006	0.946±0.005
3-NO_2-	0.267±0.006	0.57±0.01	1.24±0.02
4-NO_2-	0.255±0.007	0.62±0.04	1.26±0.06
	B series		
2,4,6-$(OMe)_3$-	1.42±0.01	2.95±0.01	5.06±0.01
2,4,6-*i*-Pr_3-	0.312±0.002	0.684±0.001	1.36±0.01
2,6-Me_2-4-*t*-Bu-	1.50±0.01	3.43±0.01	6.33±0.03
2,4,6-Me_3-	1.39±0.01	3.03±0.01	6.13±0.02
2,3,5,6-Me_4-	1.00±0.01	1.96±0.01	4.07±0.03
2,4,6-Et_3-	0.408±0.002	0.923±0.004	1.91±0.01
2,4-Me_2-	0.281±0.001	0.705±0.003	1.43±0.01
2-Me-5-*t*-Bu-	0.255±0.001	0.574±0.004	1.24±0.01
2,5-Me_2-	0.315±0.004	0.695±0.005	1.36±0.01
2-Me-	0.255±0.001	0.581±0.001	1.27±0.01
2,4,6-Me_3-3-NO_2-	0.869±0.005	2.00±0.02	3.66±0.02
2,4-Me_2-5-NO_2-	0.202±0.003	0.463±0.005	1.08±0.01
2-Me-5-NO_2-	0.316±0.006	0.695±0.004	1.49±0.02

ρ-values less than zero imply a not depreciable decrease in electron density at the reaction site in the transition state.

Table 4.8 Parameters derived from Hammett correlation analysis at different temperatures in the propanolysis of X-$ArSO_2Cl$ for the extended model series

T / K	-*log* k_0	-ρ	r	n*
303	4.68±0.01	0.32±0.03	0.961	6
313	4.31±0.01	0.25±0.03	0.932	6
323	3.97 ±0.01	0.20±0.01	0.985	6

*n- sample size

The following *ortho*-substituted compounds display anomalous acceleration: X=2,4,6-Me_3-; 2,4,6-Et_3-; 2,6-Me_2-4-*t*-Bu-; 2,3,5,6-Me_4-; 2-Me-5-NO_2-; 2,4-Me_2-5-NO_2-; 2,4,6-Me_3-3-NO_2; 2,4,6-$(OMe)_3$-; 2-Me-; 2,4-Me_2-; 2,5-Me_2-; 4-NO_2-; 3-NO_2-.(Figure 4.8). The most reactive compounds include all those substituted in both *ortho* positions by -Me groups (Figure 4.8). As in previous sections the highly sterically-hindered 2,4,6-*i*-Pr_3-derivative follows the same behavior as unhindered compounds, lying well in the linear correlation, so that its behavior can be explained in accordance with the electronic effects of the substituents.

The existence of a $logk_{T1}$ *vs.* $logk_{T2}$ isokinetic dependence (r=0.992-0.995) for all substrates (Figure 4.9), point to a single mechanism for the whole series. [9-21]

Activation parameters are collected in Table 4.9 and Figure 4.10. Enthalpy of activation decreases as the steric hindrance of the substrate increases. The unsubstituted *A* series is isoenthalpic as $\Delta H^{\ddagger}$ depends weakly on the *X* substituent, only nitro compounds show a slight decrease. The entropy of activation shows no pattern when the all compounds are considered.

The absence of significant fluctuations among activation parameters for both series can serve as an additional demonstration of the same mechanism of solvolysis for all the studied substrates in propanol.

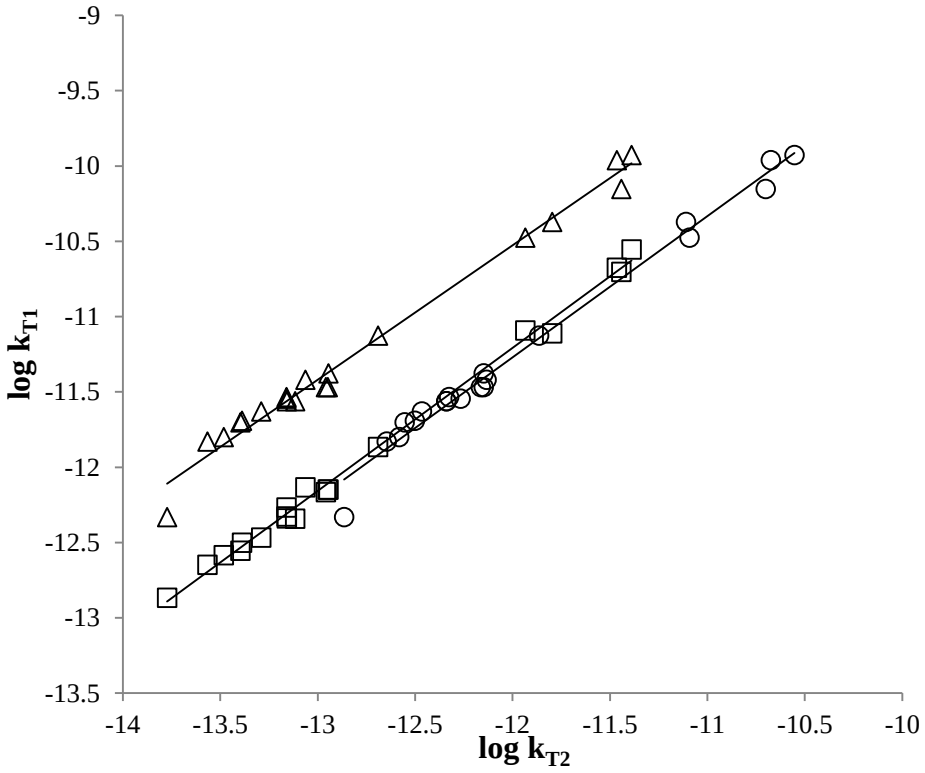


Figure 4.9 Log k_{T1} *vs.* log k_{T2} isokinetic dependence for the X-$ArSO_2Cl$ propanolysis at 303-323K. □ T_1=303K; T_2=313K; Δ T_1=303K; T_2=323K; ○ T_1=313K; T_2=323 K.

As in the ethanolysis, nice isokinetic relations, $\delta\Delta H^{\ddagger} = \beta\delta\Delta S^{\ddagger}$, are found when the sulfonyl chlorides are divided in two groups (Figure 4.11):

Group 1 ($\Delta H^{\ddagger}$= 362·$\Delta S^{\ddagger}$ + 116135; R^2=0.981) contains X=H-; 4-Me-; 4-*t*-Bu-; 4-Cl-; 4-Br-; 3-NO_2-; 4-NO_2-; 2,4,6-Et_3-; 2,4,6-*i*-Pr_3-;2-Me-; 2,4-Me_2-; 2,5-Me_2-; 2-Me-5-*t*-Bu-; 2-Me-5-NO_2-; 2,4-Me_2-5-NO_2-.

Group 2 ($\Delta H^{\ddagger}$= 303·$\Delta S^{\ddagger}$ + 103378; R^2=0.964) includes X=2,4,6-Me_3-; 2,6-Me_2-4-*t*-Bu-; 2,3,5,6-Me_4-; 2,4,6-Me_3-3-NO_2-; 2,4,6-$(OMe)_3$-.

Table 4.9 Activation parameters for the propanolysis of X-$ArSO_2Cl$

X	$\Delta H^{\ddagger *,**}$ / kJ·mol^{-1}	$-\Delta S^{\ddagger *,**}$/ J·mol^{-1}·K^{-1}	$\Delta G^{\ddagger *,**}$/ kJ·mol^{-1}
	A series		
4-*t*-Bu-	56±4	173±13	111±9
4-Me-	65±2	141±5	109±3
H-	66±1	137±2	109±1
4-Br-	68±1	133±3	110±2
4-Cl-	66±1	140±5	110±3
3-NO_2-	61±1	154±4	109±3
4-NO_2-	63±3	146±9	109±6
	B series		
2,4,6-$(OMe)_3$-	50±3	175±11	104±7
2,4,6-*i*-Pr_3-	58±1	161±4	109±2
2,6-Me_2-4-*t*-Bu-	57±4	151±12	104±8
2,4,6-Me_3-	59±1	147±2	105±1
2,3,5,6-Me_4-	55±2	161±7	106±5
2,4,6-Et_3-	61±1	149±3	108±2
2,4-Me_2-	64±4	141±12	109±8
2-Me-5-*t*-Bu-	62±1	148±1	109±1
2,5-Me_2-	58±2	162±6	109±4
2-Me-	64±1	145±1	109±1
2,4,6-Me_3-3-NO_2-	57±4	157±13	106±8
2,4-Me_2-5-NO_2-	66±2	138±5	109±3
2-Me-5-NO_2-	61±1	151±2	108±1

* Estimated considering the second order constant k_2, *i.e.* $k_{obs} = k_2 \cdot [solvent]$.

** Value calculated at 40ºC.

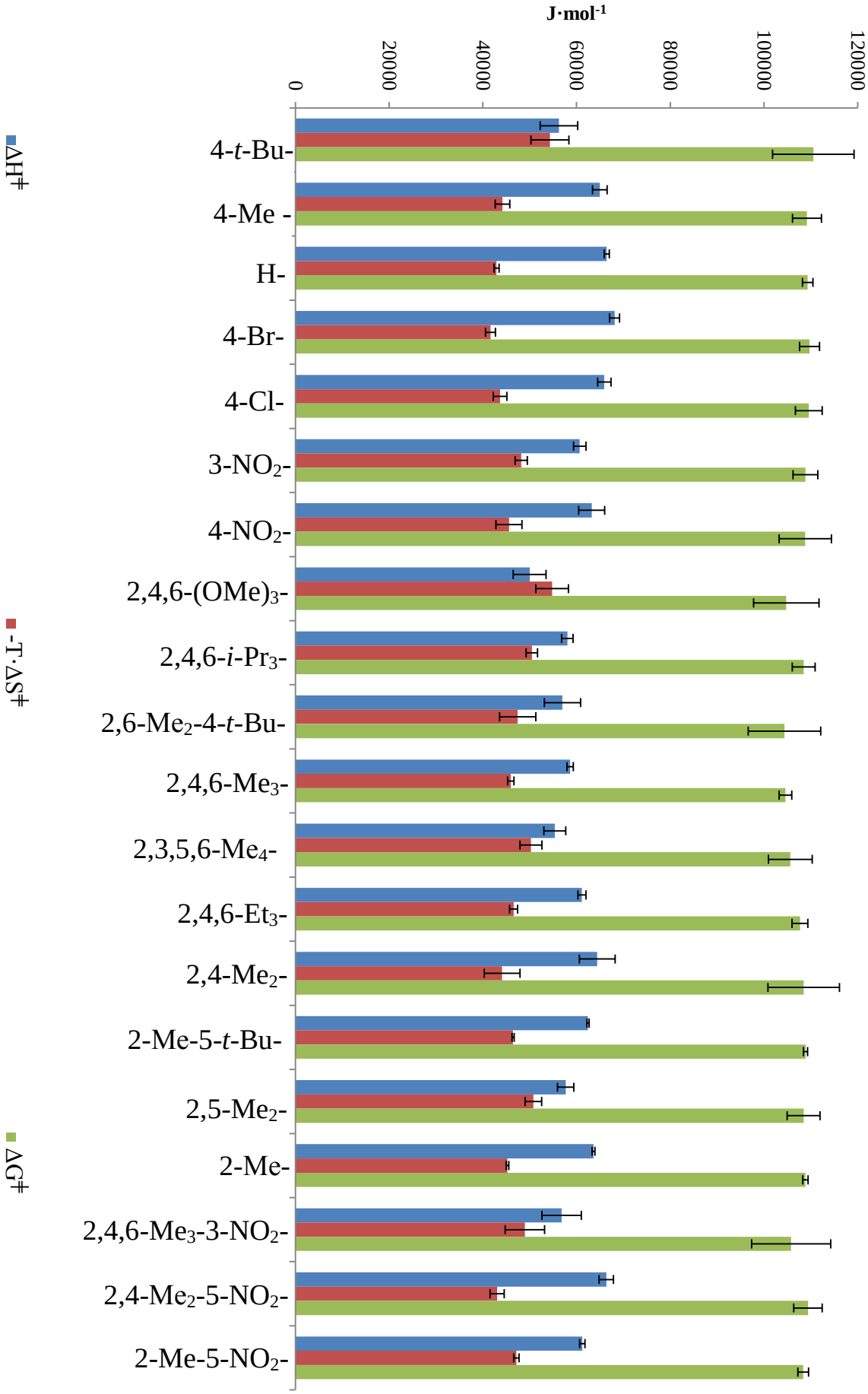
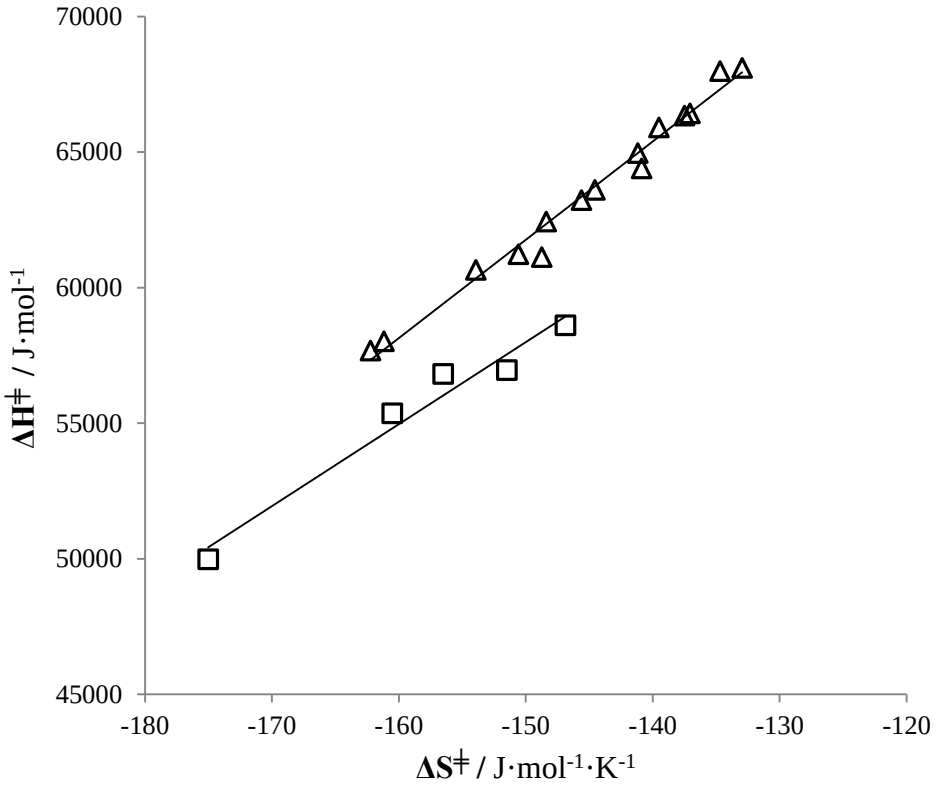


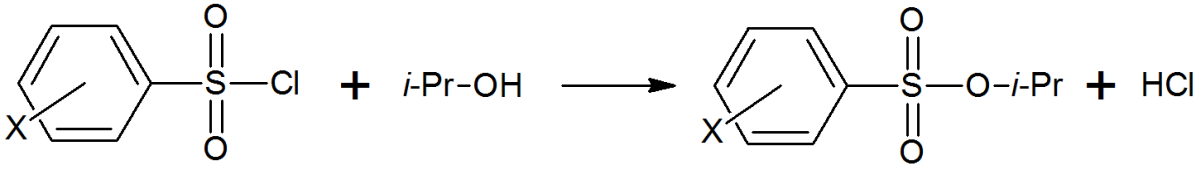
Figure 4.10 Activation parameters for the X-ArSO$_2$Cl propanolysis.



Δ *Group 1;* □ *Group 2.*

Figure 4.11 $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ for the propanolysis of X-ArSO_2Cl

4.1.4 *Iso*-propanolysis of arenesulfonyl chlorides



The kinetics of the neutral *iso*-propanolysis of aromatic sulfonyl chlorides shows several unusual features relative to unbranched alcohols. *Iso*-propanolysis reaction rates were adequately fitted by a first-order kinetic model. The values of the observed rate constants are given in Table 4.10; this time the reaction rate is weakly sensitive to the electronic nature of the substituents *X* that demonstrates an ambiguous effect (Figure 4.12).

Hammett correlation (Table 4.11) for the solvolysis by *iso*-propyl alcohol shows a reasonable linearity with a positive slope ($\rho > 0$) for substrates of the *A* series (X=H-; 4-Me-; 4-*t*-Bu-; 4-Br-; 4-NO_2), see Figure 4.12.

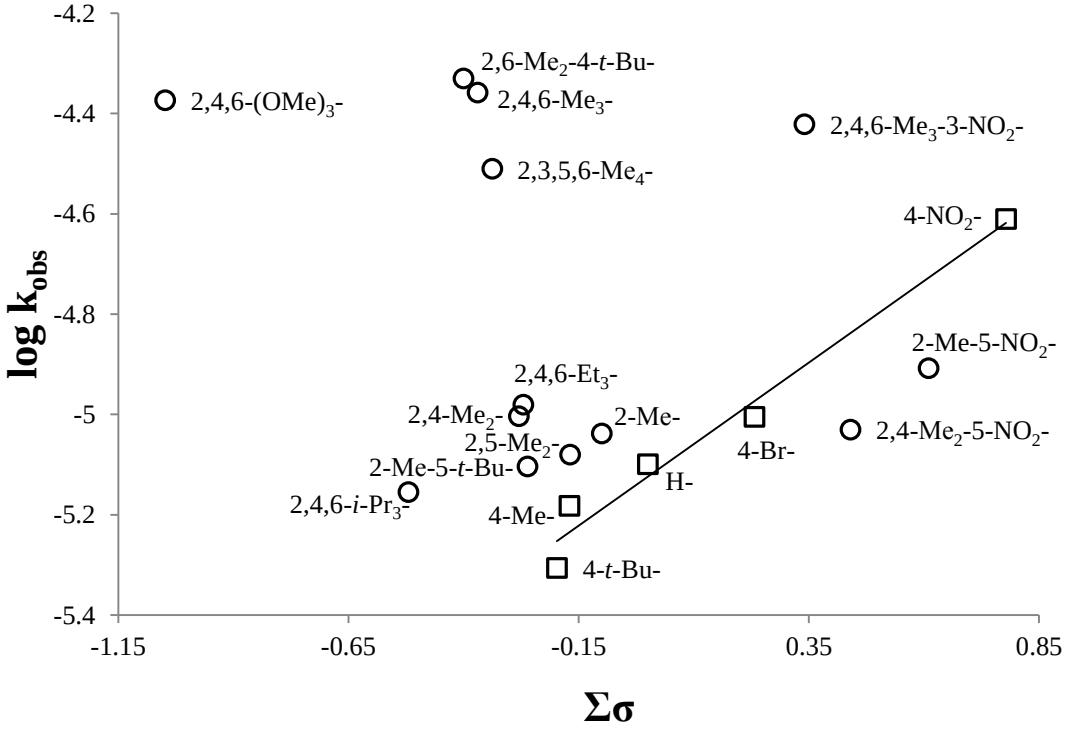


Figure 4.12 Hammett correlation for the *iso*-propanolysis of X-$ArSO_2Cl$ at 313 K.

□ A series; ○ B series.

Table 4.10 Observed rate constants for *iso*-propanolysis of X-$ArSO_2Cl$ at 303-323 K.

X	$k_{obs}\cdot10^5$ / s^{-1}		
	303 K	313 K	323 K
	A series		
4-*t*-Bu-	0.239±0.006	0.490±0.01	0.965±0.006
4-Me-	0.33±0.01	0.657±0.008	1.52±0.03
H-	0.33±0.01	0.800±0.01	1.84±0.02
4-Br-	0.457±0.001	0.989±0.001	2.42±0.001
4-NO_2-*	1.07±0.01	2.45±0.01	5.32±0.01
	B series		
2,4,6-$(OMe)_3$-	2.16±0.01	4.23±0.01	8.67±0.01
2,4,6-*i*-Pr_3-	0.32±0.01	0.700±0.005	1.25±0.01
2,6-Me_2-4-*t*-Bu-	2.58±0.07	4.67±0.01	8.90±0.03
2,4,6-Me_3-	2.06±0.02	4.38±0.01	8.37±0.03
2,3,5,6-Me_4-	1.55±0.02	3.09±0.01	5.96±0.02
2,4,6-Et_3-	0.512±0.005	0.992±0.001	2.00±0.02
2,4-Me_2-	0.46±0.01	1.05±0.01	2.47±0.01
2-Me-5-*t*-Bu-	0.305±0.003	0.788±0.008	1.66±0.01
2,5-Me_2-	0.368±0.007	0.83±0.01	1.87±0.01
2-Me-	0.401±0.009	0.92±0.02	2.03±0.01
2,4,6-Me_3-3-NO_2-	1.91±0.03	3.79±0.03	7.17±0.02
2,4-Me_2-5-NO_2-	0.43±0.01	0.933±0.005	1.93±0.02
2-Me-5-NO_2-	0.53±0.01	1.24±0.01	2.52±0.02

*Data taken from [23]

Table 4.11 Parameters derived from Hammett correlation analysis at different temperatures of the *iso*-propanolysis of X-$ArSO_2Cl$, *A* series

T / K	-*log* k_0	ρ	r	n*
303	5.45±0.03	0.61±0.07	0.961	5
313	5.12±0.02	0.65±0.06	0.974	5
323	4.77±0.04	0.70±0.10	0.937	5

*n- sample size

Compounds of the *B* series show increased reactivity, but 2,4-Me_2-5-NO_2- and 2-Me-5-NO_2- derivatives demonstrate lower reactivity then it was expected from Hammett's correlations for *A* set. Sterically hindered compounds display anomalous acceleration: X=2,4,6-Me_3-; 2,4,6-Et_3-; 2,6-Me_2-4-*t*-Bu-; 2,3,5,6-Me_4-; 2-Me-5-NO_2-; 2,4,6-Me_3-3-NO_2-; 2,4,6-$(OMe)_3$-(Figure 4.12). The most reactive compounds include all those substituted in both *ortho* positions by -Me groups (Figure 4.12).

As in the solvolysis with other alcohols, the existence of a $logk_{T1}$ *vs.* $logk_{T2}$ isokinetic dependence (r=0.975-0.990) for all substrates (Figure 4.13) points to a common substitution mechanism for all compounds.

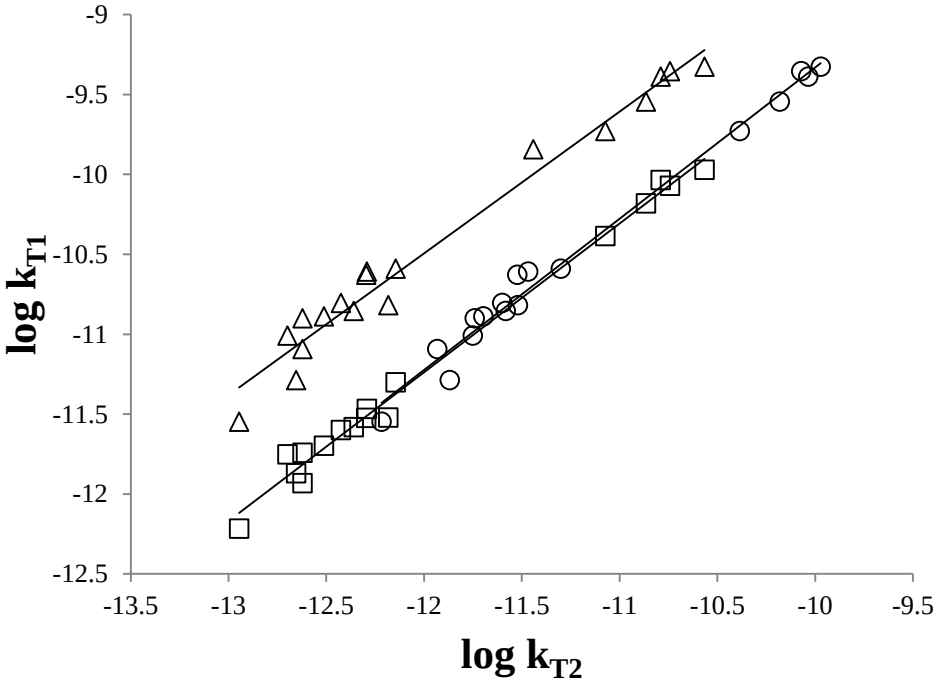
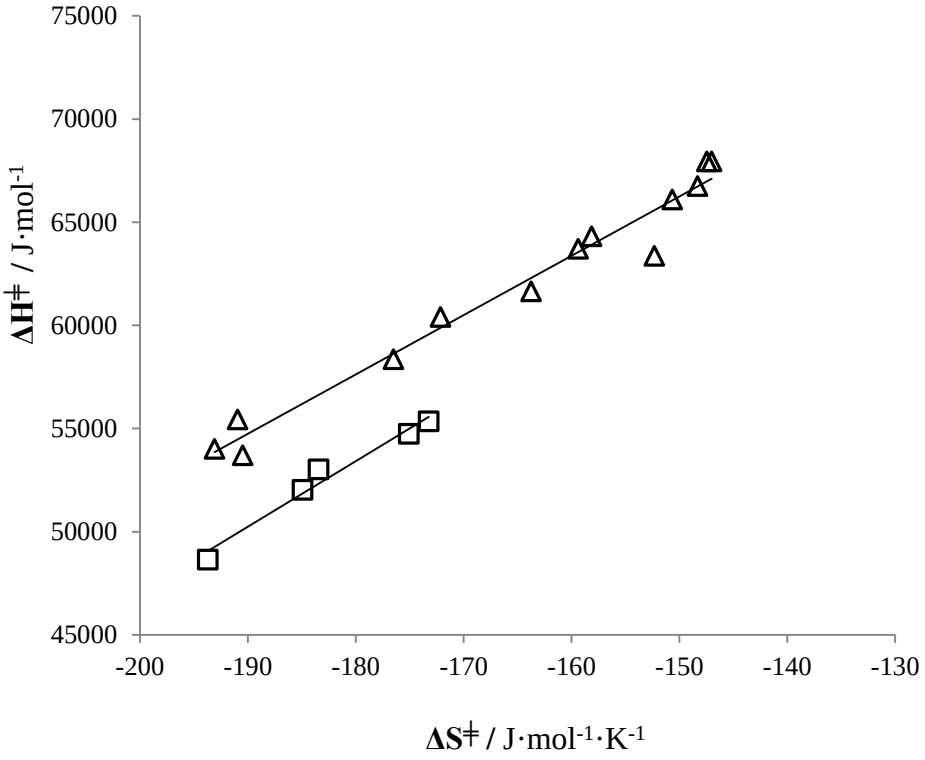


Figure 4.13 Log k_{T1}-log k_{T2} isokinetic dependence for the X-$ArSO_2Cl$ *iso*-propanolysis at 303-323K. □ T_1=303K; T_2=313K; Δ T_1=303K; T_2=323K; ○ T_1=313K; T_2=323 K.

Good isokinetic relations, $\delta\Delta H^{\ddagger} = \beta\delta\Delta S^{\ddagger}$, (Figure 4.14) are obtained when the studied compounds are divided into two groups:

Group1 ($\Delta H^{\ddagger} = 288 \cdot \Delta S^{\ddagger} + 109428$; $R^2=0.970$) contains X=H-; 4-Me-; 4-*t*-Bu-; 4-Cl-; 4-Br-; 3-NO_2-; 4-NO_2-; 2,4,6-Et_3-; 2,4,6-*i*-Pr_3-; 2-Me-; 2,4-Me_2-; 2,5-Me_2-; 2-Me-5-*t*-Bu-; 2-Me-5-NO_2-; 2,4-Me_2-5-NO_2-.

Group2 ($\Delta H^{\ddagger} = 317 \cdot \Delta S^{\ddagger} + 110500$; $R^2=0.973$) includes X=2,4,6-Me_3-; 2,6-Me_2-4-*t*-Bu-; 2,3,5,6-Me_4-; 2,4,6-Me_3-3-NO_2-; 2,4,6-$(OMe)_3$-.



Δ *Group 1;* □ *Group 2*

Figure 4.14 $\Delta H^{\ddagger}$ *v.s.* $\Delta S^{\ddagger}$ for the *iso*-propanolysis of X-$ArSO_2Cl$

Table 4.12 and Figure 4.15 show the values of the obtained activation parameters; from there it follows that enthalpy of activation decreases with introduction of *ortho*-alkyl substituting groups in the aromatic ring. On the other hand, the values of the entropy of activation do not show any pattern.

Table 4.12 Activation parameters for the *iso*-propanolysis of X-$ArSO_2Cl$

X	$\Delta H^{\ddagger}$* / kJ·mol^{-1}	$-\Delta S^{\ddagger}$ */ J·mol^{-1}·K^{-1}	$\Delta G^{\ddagger}$ *,**/ kJ·mol^{-1}
	A series		
4-*t*-Bu-	55±1	191±3	115±2
4-Me-	60±5	172±15	114±9
H-	68±1	147±2	114±2
4-Br-	66±4	150±13	113±8
4-NO_2-***	63±1	152±1	111±1
	B series		
2,4,6-$(OMe)_3$-	55±2	175±7	110±4
2,4,6-*i*-Pr_3-	54±4	193±12	114±8
2,6-Me_2-4-*t*-Bu-	49±2	194±7	109±4
2,4,6-Me_3-	55±2	173±5	110±3
2,3,5,6-Me_4-	53±1	183±1	110±1
2,4,6-Et_3-	54±2	190±6	113±4
2,4-Me_2-	67±2	148±6	113±4
2-Me-5-*t*-Bu-	68±3	147±10	114±6
2,5-Me_2-	64±1	158±3	114±2
2-Me-	64±1	159±4	114±2
2,4,6-Me_3-3-NO_2-	52±1	184±1	110±1
2,4-Me_2-5-NO_2-	58±3	176±8	114±5
2-Me-5-NO_2-	62±1	164±4	113±3

* Estimated considering the second order constant k_2, *i.e.* $k_{obs} = k_2 \cdot [solvent]$.

** Value calculated at 40ºC.

***Data taken from ref. [23]

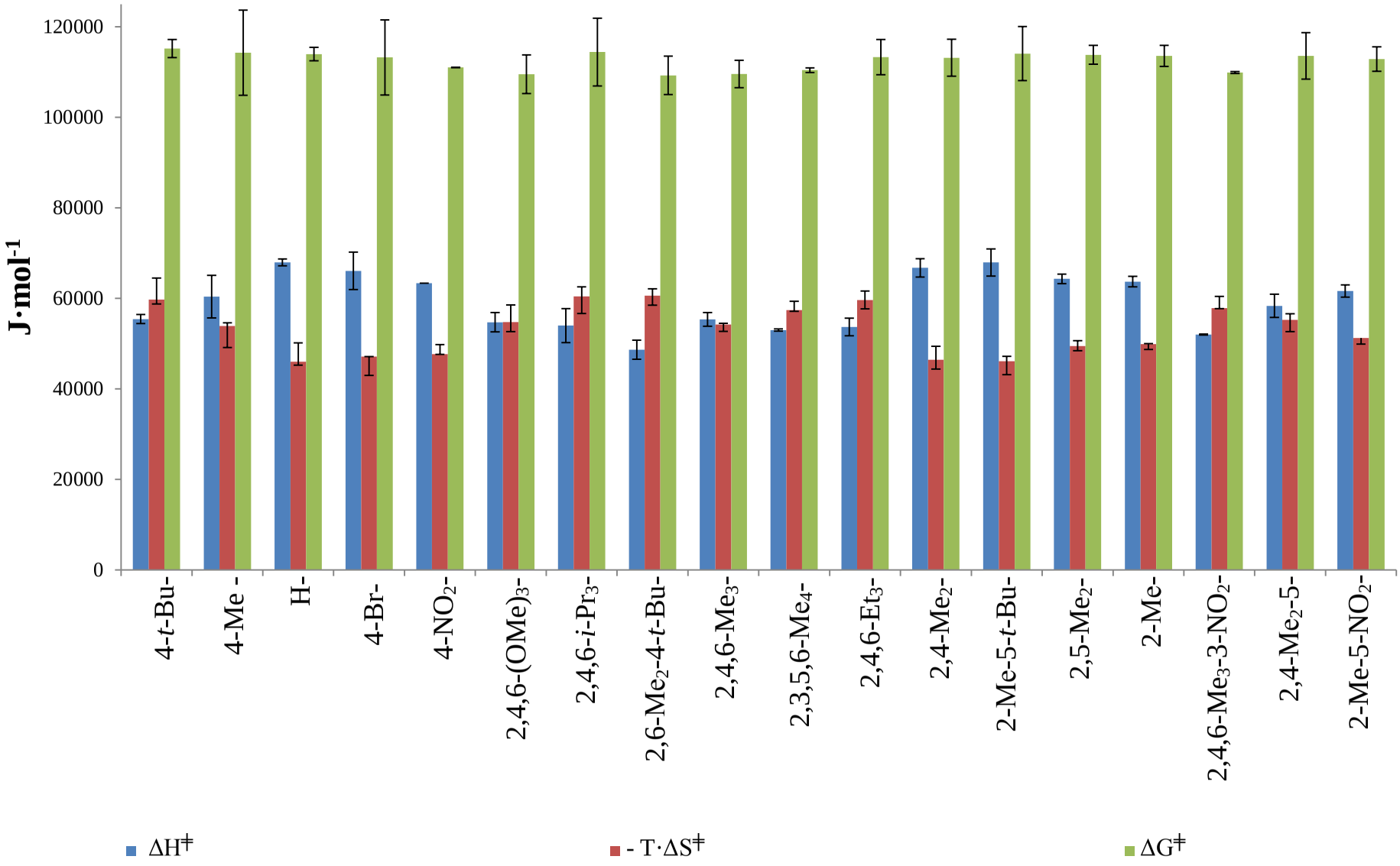
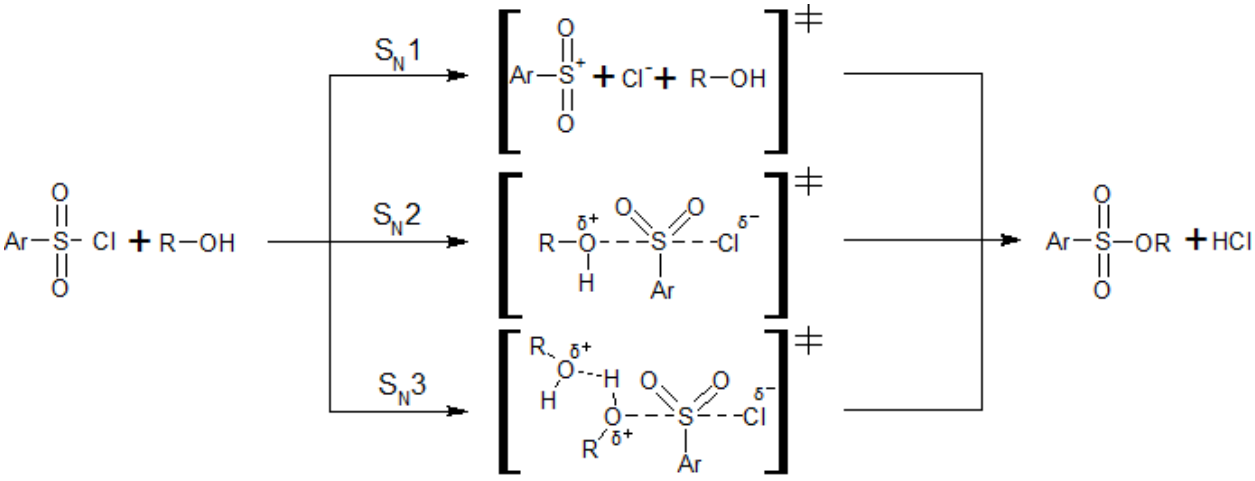


Figure 4.15 Activation parameters for X-ArSO$_2$Cl *iso*-propanolysis

4.2 KINETIC ISOTOPE EFFECTS

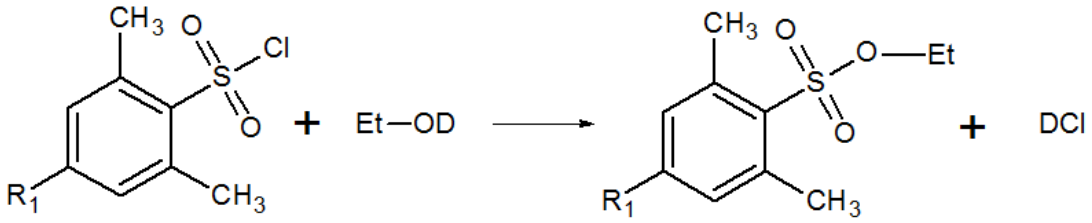
As indicated above, despite the existence of a large corpus of research on solvolytic processes at sulfonyl centers, details on this nucleophilic substitution mechanism remain unclear. Sterically hindered derivatives of aromatic sulfonic acids that contain *ortho*-alkyl groups show kinetic features that pose questions on the classical view of bimolecular substitution mechanism. [2, 8, 18, 25] *o*-alkyl derivatives of benzenesulfonyl chlorides show increased reactivity in solvolysis processes. In this respect, as shown in Scheme 4.1, the feasibility of uni-[18] and bimolecular mechanisms,[26] structural modifications of the S_N2-type transition state (TS) involving a second molecule of nucleophile (S_N3-mechanism),[10] the stabilization of the bimolecular TS by intramolecular interactions, hyperconjugation effects[8, 27] or stereochemical rearrangements during the nucleophilic attack[8, 25] is discussed here.



Scheme 4.1 Mechanistic possibilities for solvolytic processes at a sulfonyl centre

Here, we analyze the mechanism of solvolysis, hydrolysis and alcoholysis, of sterically hindered arenesufonyl chlorides in the light of the results of solvent isotope effects (SIE) and secondary kinetic isotope effects (SKIE) in the temperature range 303-323 K.

4.2.1 Solvent isotope effect of sterically hindered arenesulfonyl chlorides



Scheme 4.2 SIE on the ethanolysis of sterically hindered arenesulfonyl chlorides (R_1=Me, *t*-Bu)

SIE were studied to check the catalytic assistance of the solvent as nucleophile [10] in the ethanolysis of X-$ArSO_2Cl$ in the range 303-323 K; the observed rate constants and the corresponding SIE are collected in Table 4.13.

Table 4.13 SIE observed in the ethanolysis of X-$ArSO_2Cl$

X-	T / K	$k_{Et\text{-}OD}\cdot10^4$/ s^{-1}	$k_{Et\text{-}OH}\cdot10^4$/ s^{-1}	SIE=($k_{Et\text{-}OH}/k_{Et\text{-}OD}$)
(**1**) 2,6-Me_2-4-*t*-Bu-	303	1.78±0.01	2.25±0.01	1.26±0.02
	313	4.00±0.02	5.70±0.04	1.42±0.06
	323	8.04±0.05	11.3±0.1	1.41±0.06
(**2**) 2,4,6-Me_3-	303	1.63±0.01	2.24±0.01	1.37±0.02
	313	3.57±0.01	4.99±0.01	1.40±0.02
	323	7.60±0.04	10.2±0.1	1.34±0.02
(**3**) 4-Me-	303	0.261±0.007	0.36±0.01	1.39±0.02
	313	0.66±0.07	0.82±0.01	1.24±0.02
	323	1.42±0.01	1.91±0.01	1.35±0.02

Ortho-methylated substrates show increased reactivity toward solvolysis in all cases (Table 4.13). Change from protonated to deuterated solvent causes a slight decrease in the observed rate constants. For compound **3**, adopted as model compound, SIE ranges between 1.24 and 1.39. SIE for hindered substrates **1** & **2** shows a similar range of SIE (1.26-1.42) in agreement with previous observations for the methanolysis of sulfonyl chlorides.[21,4] The observed SIEs are comparable when considering different compounds and temperatures. For the methanolysis of **2** and **3** SIE ($k_{Me\text{-}OH}/k_{Me\text{-}OD}$) are, respectively, 1.68 and 1.72, in good agreement with those observed here.[4,21] Similar SIE, ranging from 1.2 to 1.6, are typical for S_N2 processes at sulfonyl centers.[4, 5, 21, 28, 29] These results point to a SIE of the alcoholic proton, the proton transfer between the oxygen of the attacking alcohol and that of a solvent molecule not taking place in the rate-determining step. Analysis of the SIE could be done in terms of fractionation factors:

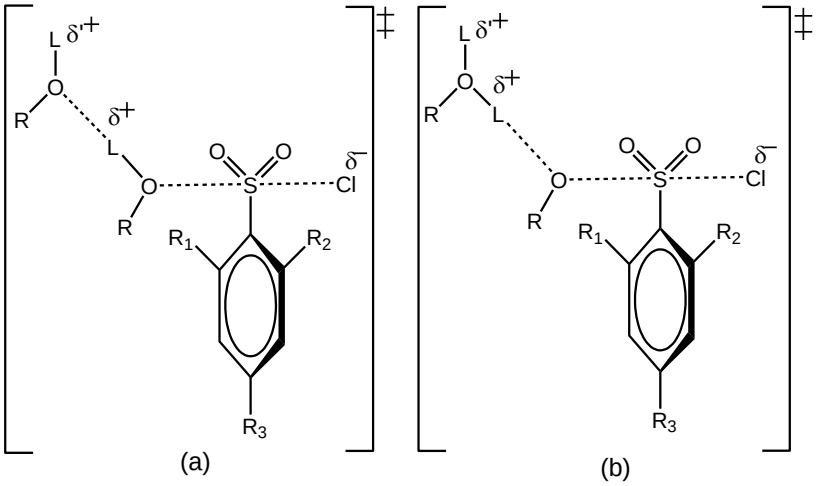
$$SIE = \frac{k_{EtoH}}{k_{EtOD}} = \frac{\phi_{EtOL}}{\prod_i \phi_i^{\ddagger}} \qquad \text{(Eq. 4.1)}$$

where ϕ_{EtOL} is the fractionation factor of the alcoholic hydrogen/deuterium of ethanol, whereas $\phi^{\ddagger}_i$s are the fractionation factors of the alcoholic hydrogen/deuterium atoms involved in the TS.

The value of the solvent isotope effect could be consistent, regardless of the position of the hydrogen/deuterium, with both ‘early’ (Scheme 4.3(a)) or ‘late’ (Scheme 4.3(b)) S_N2 TS’s, where L designates either H or D.

When the extreme ‘early’ TS is considered, where the hydrogen/deuterium is only starting to be transferred to another solvent molecule and an almost complete typical S-O bond has been formed and the hydrogen/deuterium bears a positive charge, and assuming the fractionation factor of the alcoholic hydrogen/deuterium should be similar to that of $MeOL_2^+$ ($\phi_L{}^+$ *c.a.* 0.60 relative to MeOL)[30], a SIE=(k_{EtOH}/k_{EtOD}) *ca.* 1.7 would be expected. Under the same assumption,

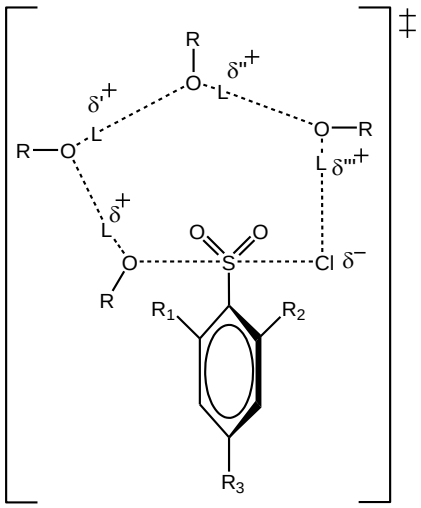
SIE=(k_{EtOH}/k_{EtOD}) *ca.* 2.7 would be expected for the extreme 'late' TS, where the hydrogen/deuterium has been almost fully transferred to another solvent molecule.



Scheme 4.3 'Early' (a) and 'late' (b) TS's for the S_N2 mechanism of arenesulfonyl chlorides solvolysis with general base catalysis by a second solvent molecule.

The observed SIE is *ca.* 1.35 (Table 4.13) which implies the fractionation factor of the hydrogens/deuteriums involved in the transition state being ≈ 0.74, suggesting the S-O bond at the TS has not been fully formed and the H/D-OEt bond resembles to that of EtO-H/D bond. Such figure is compatible either with an 'early', even with a cyclic one involving several solvent molecules as shown in Scheme 4.4.

These results support the participation of, at least, a second solvent molecule in the TS, through a general-base catalysis mechanism.[10] There is strong evidence in the literature for this kind of mechanism, with participation of solvent-chains.[31, 32, 33] It has been found that there is an optimal number of solvent molecules that facilitates the mechanism, for example *via* linear proton transfer in the TS.[33]



Scheme 4.4 TS for the general-base catalyzed S_N2 mechanism for solvolysis of arenesulfonyl chlorides involving a chain of solvent molecules.

Activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$) are similar, within the statistical uncertainty, for both solvents (Table 4.14). Sterically hindered substrates **1** & **2** shows slightly lower $\Delta G^{\ddagger}$~(104-105kJ·mol^{-1}) in comparison with the less sterically hindered **3**,[30, 34, 35] which provides an additional evidence against proton transfer in the rate-determining step.

Table 4.14 Activation parameters for the ethanolysis X-ArSO_2Cl in EtOH and EtOD.

X-	Solvent	$\Delta H^{\ddagger}$*/ kJ·mol^{-1}	$-\Delta S^{\ddagger}$*/ J·mol^{-1}·K^{-1}	$\Delta G^{\ddagger}$*,**/ kJ·mol^{-1}
(**1**) 2,6-Me_2-4-*t*-Bu-	Et-OD	59±2	146±5	105±1
	Et-OH	64±4	126±14	104±9
(**2**) 2,4,6-Me_3-	Et-OD	60±1	143±2	105±3
	Et-OH	57±3	150±8	104±5
(**3**) 4-Me-	Et-OD	66±3	137±9	109±6
	Et-OH	66±2	137±6	109±3

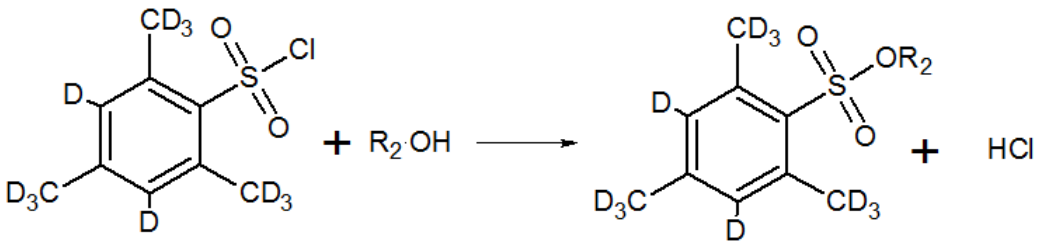
* Estimated considering the second order constant k_2, *i.e.*:$k_2=k_{obs}$/[solvent].

** Value calculated at 313 K.

On the other hand, the large negative values of the entropy of activation are consistent with a highly ordered TS, which supports the participation of solvent molecules in the TS, as shown in Scheme 4.4. The low and similar values of the enthalpy of activation point to a highly concerted TS, which would support the hypothesis of the formation of solvent chains (Scheme 4.4).

SIE in the ethanolysis of sterically hindered arenesulfonyl chlorides slows the reaction rate by *ca.* 35%. Such result rules out proton transfer in the rate-determining step, and the analysis of the SIE in terms of fractionation factors agrees with a S_N2 mechanism involving at least a second solvent molecule in the TS.

4.2.2 Secondary kinetic isotope effects (SKIE)



Scheme 4.5 SKIE on the solvolysis of sterically hindered arenesulfonyl chlorides (R_2=H-, Me-, Et-, Pr-, *i*-Pr-).

To check the effect of non-bonding intramolecular interactions between the hydrogens of the *ortho*-methyl groups and the oxygens of the sulfonyl groups, the activation parameters and the SKIE's (k_{2H}/k_{2D}) were determinated for the solvolysis of 2,4,6-$(CH_3)_3$-$C_6H_2SO_2Cl$ (**2**) and its deuterated analog 2,4,6-$(CD_3)_3$-$C_6D_2SO_2Cl$ (**2D**) using different solvents as nucleophiles. Comparable results were obtained in both cases (Tables 4.15 & 4.16).

The reactivity of **2** and **2D** is similar within statistical error for all solvolytic processes; similarly, activation parameters are statistically indistinguishable (Table 4.15), and values of SKIE are very close to unity in all cases, within statistical uncertainty, for all studied nucleophiles (Table 4.16). Thus no SKIE is observed when hydrogens of the *o*-alkyl groups are replaced by deuterium.

Table 4.15 Observed rate constants and activation parameters for solvolysis of **2** and **2D** using different solvents as nucleophiles.

Compound	Nucleophile	T / K	$k_{obs}\cdot10^4$/ s^{-1}	$\Delta H^{\ddagger}$*/ $kJ\cdot mol^{-1}$	$-\Delta S^{\ddagger}$*/ $J\cdot mol^{-1}\cdot K^{-1}$	$\Delta G^{\ddagger}$*,**/ $kJ\cdot mol^{-1}$
2	H_2O	293	505±8	49±2	134±7	91±5
		298	746±25			
		303	1090±42			
		308	1640±57			
		313	2000±31			
		318	2650±116			
	EtOH	303	2.24±0.01	57±3	150±8	104±5
		313	4.99±0.02			
		318	7.06±0.01			
		323	10.2±0.1			
		328	14.20±0.01			
	MeOH	303	13.2±0.1	54±4	148±13	100±8
	PrOH	323	6.13±0.02	59±1	147±2	105±1
	i-PrOH	323	0.84±0.01	55±2	173±5	110±3
2D	H_2O	293	493±2	51±2	128±5	91±3
		298	764±10			
		303	1120±35			
		308	1550±27			
		313	2140±37			
		318	2790±81			
	EtOH	303	2.23±0.01	59±2	143±7	104±4
		313	4.95±0.01			
		318	7.59±0.01			
		323	10.2±0.01			
		328	13.8±0.01			
	MeOH	303	12.5±0.1	-	-	-
	PrOH	323	5.83±0.01	-	-	-
	i-PrOH	323	0.87±0.01	-	-	-

* Estimated considering the second order constant k_2, *i.e.* $k_2 = k_{obs}/[solvent]$.

** Value calculated at 313 K.

Table 4.16 SKIE observed for solvolysis of **2** and **2D** at different temperatures using different solvents as nucleophiles

Nucleophile	T / K	SKIE (k_2/k_{2D})
H_2O	293	1.03±0.01
	298	0.98±0.01
	303	0.97±0.01
	308	1.06±0.02
	313	0.93±0.02
	318	0.95±0.02
EtOH	303	1.00±0.01
	313	1.01±0.01
	318	0.93±0.02
	323	1.00±0.01
	328	1.03±0.01
MeOH	303	1.06±0.01
PrOH	323	1.05±0.01
i-PrOH	323	0.96±0.02

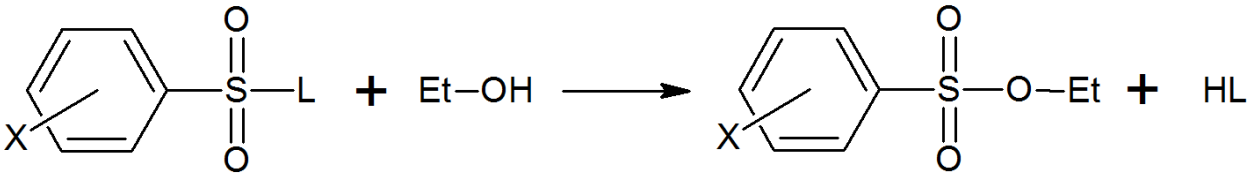
As stated before, activation parameters are similar regardless of the steric hindrance of the substrates, which points to a common reaction mechanism for the solvolysis of sulfonyl chlorides. Large negative activation entropy values, and low, and similar, activation enthalpy values are consistent with a S_N2 mechanism with participation of, at least, a second solvent molecule in the TS, and most possibly with a cyclic TS in which a reduced number of solvent molecules form chains, in a general-base catalysis mechanism. The reasons of the positive steric effect of compounds bearing two *o*-methyl groups might be attributed to structural features of the S_N2 transition state.

Obtained results pose serious doubts on the applicability of the idea of σ-π-hyperconjugation to this particular case.[18] It follows that non-covalent

intramolecular interactions between the *o*-methyl hydrogens and oxygen atoms of the sulfonyl group or/and solvent molecules do not stabilize the S_N2-transition state in the rate limiting step of the reaction. However, other factors might have influence on the reactivity as the cited interactions in the initial state as well as in the immediate vicinity to the reaction center.

4.3 LEAVING GROUP EFFECT

Solvolysis of arenesulfonyl bromides in ethanol at 303-323K was studied to determine the leaving group effect:



Scheme 4.6 Leaving group effect in the ethanolysis of X-$ArSO_2$-L
(X=4-Me-; 2,4,6-*i*-Pr_3-; 2,6-Me_2-4-*t*-Bu-; L= Br; Cl.)

The choice of the new leaving group was dictated by the extremely low solvolysis reaction rates of sulfonyl fluorides and the instability of sulfonyl iodides. Sulfonyl bromides react faster than sulfonyl chlorides (Table 4.17), the modest rate enhancement ($4 < k_{Br}/k_{Cl} < 6$) clearly indicates that the S-Halogen bond breaking does not occur in the rate limiting step. It rules out S_N1-like TS involving either a contact ion pair or a solvent-separated ion pair. Table 4.17 shows that rate constants increase with temperature with both leaving groups.

Analysis of the activation parameters is difficult because $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ reflect either different degrees of specific solvation of reactants and transition states or empirical errors cancelation. Closer inspection shows $\Delta H^{\ddagger}$ negligible fluctuations from which it can be concluded that the relative energy of halogen bond-breaking does not affect the difference in reactivity of both halides. It could also be evidence of a "late" TS for all sulfonyl halides. For bromine substituted sulfonyl derivatives $\Delta S^{\ddagger}$ varies in less than chlorine ones, which is not contrary to the principle of reactivity-selectivity. In spite of larger atomic radius of bromine, sulfonyl chlorides show larger $\Delta S^{\ddagger}$ values than bromides. Likely this is due to the more ordered structure of the solvated TS caused by the greater electronegativity and the lower size of the chlorine atom. Similar $\Delta G^{\ddagger}$ values have been found for both halides.

Table 4.17 Effect of the leaving group on observed rate constants and activation parameters in the ethanolysis of arenesulfonyl halides X-$ArSO_2$-L at 303-323 K.

X	L	303 K		313 K		323 K		$\Delta H^{\ddagger}$*/ kJ·mol^{-1}	$-\Delta S^{\ddagger}$ */ J·mol^{-1}·K^{-1}	$\Delta G^{\ddagger}$*,**/ kJ·mol^{-1}
		$k_{obs}\cdot10^4$/ s^{-1}	k_{Br}/k_{Cl}	$k_{obs}\cdot10^4$/ s^{-1}	k_{Br}/k_{Cl}	$k_{obs}\cdot10^4$/ s^{-1}	k_{Br}/k_{Cl}			
4-Me-	Br	2.20±0.01	6.1±0.2	5.06±0.07	6.2±0.2	12.00±0.09	6.29±0.08	67±2	116±6	104±4
	Cl	0.36±0.01		0.82±0.01		1.91±0.01		66±2	136±6	108±3
2,4,6-*i*-Pr_3-	Br	2.80±0.04	5.5±0.1	6.87±0.09	5.9±0.8	13.4±0.1	5.2±0.3	66.9±0.4	105±1	100±1
	Cl	0.506±0.024		1.16±0.01		2.58±0.01		64.6±0.7	138±2	108±1
2,6-Me_2-4-*t*-Bu-	Br	10.4±0.2	4.6±0.2	24.6±0.5	4.3±0.1	56±2	4.95±0.07	62±4	131±13	103±8
	Cl	2.25±0.01		5.7±0.8		11.3±0.3		64±4	126±14	104±9

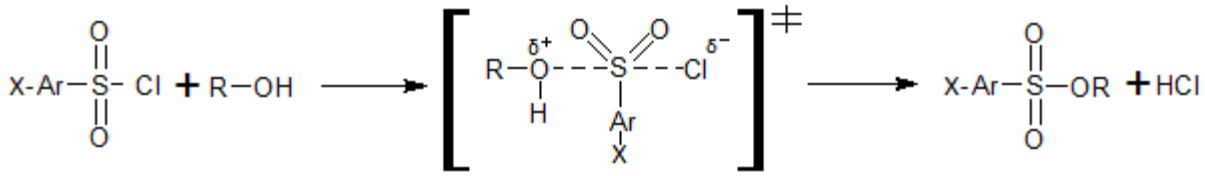
* Estimated considering the second order constant k_2, *i.e.* $k_{obs} = k_2\cdot$[solvent].

** Value calculated at 313K

The obtained results once again confirm the same bimolecular S_N2 mechanism for the solvolysis of hindered and unhindered arenesulfonyl halides. Relatively low values of k_{Br}/k_{Cl} = (4 – 6) indicate the asymmetry of the TS with the prevalence of bond-formation, which could be caused by the structural features of the substrates, as well as an important contribution of the specific solvation.

The coincidence of indirect criteria of reaction mechanism (KIE, change of the nucleophile, solvent), as well as the presence of isokinetic dependency and homogeneity of the thermodynamic parameters for all the investigated series of substrates favours to single mechanism of substitution similar to S_N2. Likely there is a spectrum of TS of S_N2-type that specificity caused by special solvent interaction with each of the substrates.

4.4 REACTION ORDER ON THE NUCLEOPHILE



Scheme 4.7 Alcoholysis of arenesulfonyl chlorides.

(R=Me-, Et-, *i*-Pr-.)

The study of the nucleophilic substitution processes at the sulfur atom of sulfonyl chlorides become more complicated when it involves *ortho*-alkyl substituents in the substrate; in this case the attack on the sulfur atom might be presumably hindered by the presence of such *o*-alkyl groups. [34-35] Nevertheless, it is clear that sterically hindered derivatives of aromatic sulfonic acids have a number of kinetic features that pose doubts about the classical mechanism of substitution at sulfonyl group, and assume the existence of the so called "positive steric effect" that labels those compounds as abnormally reactive.[34-36]

Previous results point to a cyclic TS in which solvent molecules form chains and take part in the reaction like in a general-base catalysis mechanism. Here we want to clarify the question about the catalytic assistance of the solvent as nucleophile in the alcoholysis of arenesulfonyl chlorides.[8] It is important to analyze the particularities of *o*-alkyl groups influence on the structure and molecularity of TS of arenesulfonyl chlorides solvolysis. It is also interesting to explore the influence of the nucleophile on the reaction order.

The goal is the identification of the fine structure of the transition state on the basis of determining the kinetic reaction order for the nucleophile in the presence of steric hindrance to nucleophilic attack.

The alcoholysis of arenesulfonyl chlorides X-$ArSO_2Cl$, where X=2,4,6-Me_3-; 2,4,6-Me_3-3-NO_2-; 2,6-Me_2-4-*t*-Bu-; 2,3,5,6-Me_4-; 2,4,6-*i*-Pr_3-; 2,4-Me_2-; 2,4,6-$(OMe)_3$-; H-; 4-Me-; 4-*t*-Bu- was studied.

The observed rate constants of solvolysis, k_{obs}, were determined by varying of the nucleophile concentration C_N at a fixed initial concentration of the sulfonyl substrate in alcohol-hexane mixtures at 323 K.A linear dependence was found (Figure 4.16) according to the following equation:

$$ln\, k_{obs} = ln\, k' + b \cdot ln\, C_N \qquad \text{(Eq. 4.2)}$$

The slope, *b*, corresponds to the kinetic reaction order relative to the nucleophile, *i.e.*, $k_{obs} = k' \cdot [\text{nucleophile}]^b$, the corresponding values are collected in Table 4.18.

The distribution of substrates in terms of chemical reactivity matches that of found previously; the presence of *ortho*-alkyl groups promotes the acceleration of the process (Table 4.18). The obtained kinetic data are consistent with earlier ones for the solvolysis of these substrates [6, 10, 34, 37, 38].

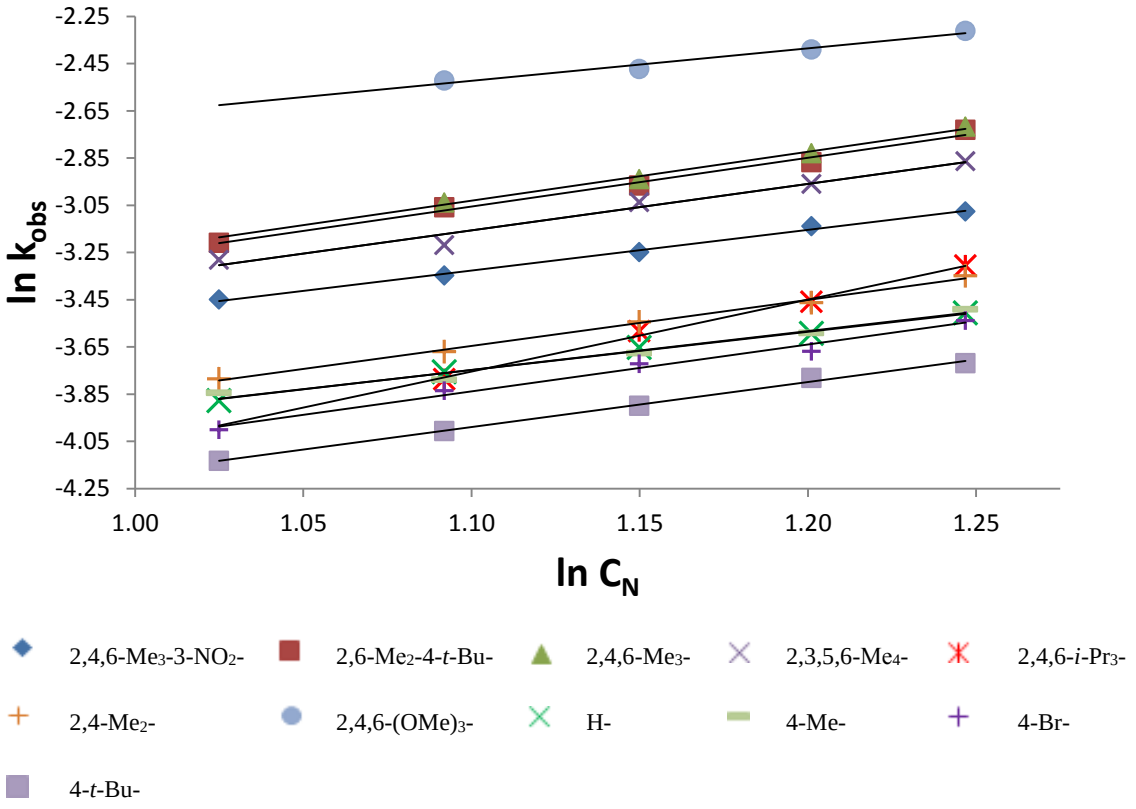


Figure 4.16 Lnk_{obs} *vs.* lnC_N for the methanolysis of X-$ArSO_2Cl$ in methanol-hexane mixtures at 323 K

Sterically unhindered substrates (**8-11**, Table 4.18) are characterized by order two relative to the methanol (b ~ 2). The order of all hindered *ortho*-methylated compounds also oscillates around the same value, but 2,4,6-*i*-Pr_3-benzenesulfonyl chloride (**5**), b=3.0, and 2,4,6-$(OMe)_3$-benzenesulfonyl chloride (**6**) b=1.3.

Table 4.18 Regression coefficients *ln k'* and b (Eq. 4.2) for the solvolysis of X-$ArSO_2Cl$ in methanol-hexane mixtures at 323 K

№	X	Intercept *ln k'*	Slope b	R^2	n*
1	2,4,6-Me_3-3-NO_2-	-5.8±0.2	2.3±0.2	0.968	5
2	2,3,5,6-Me_4-	-5.3±0.2	2.0±0.2	0.966	5
3	2,4,6-Me_3-	-5.3±0.1	2.1±0.1	0.991	4
4	2,6-Me_2-4-*t*-Bu-	-5.3±0.1	2.1±0.1	0.988	5
5	2,4,6-*i*-Pr_3-	-7.1±0.2	3.1±0.1	0.993	4
6	2,4,6-$(OMe)_3$-	-3.96±0.06	1.31±0.05	0.997	4
7	2,4 Me_2-	-5.79±0.08	1.95±0.07	0.995	5
8	H-	-6.1±0.2	2.1±0.2	0.972	5
9	4-Me-	-5.86±0.07	1.90±0.06	0.997	4
10	4-Br-	-6.0±0.2	2.0±0.1	0.979	5
11	4-*t*-Bu-	-6.09±0.07	1.91±0.06	0.996	5

* n - sample size

The general behavior is the same in ethanol-hexane mixtures (Figure 4.17), the corresponding reaction orders are listed in Table 4.19. Solvolysis in ethanol is characterized by orders of the reaction $2 < b < 3$ for all *ortho*-methylated substrates (**1-4, 7**). Unhindered substrates (**8, 10**) exhibit values around 2, and compounds (**5**) and (**6**) show the same dependence as in the methanolysis. Unexpectedly the reaction order relative to the ethanol of 4-Me-benzenesulfonyl chloride is 2.8.

The same study was carried out in *iso*-propanol-hexane mixtures (Figure 4.18); again the observed behavior could be described by Eq. 4.1, and the corresponding values are collected in Table 4.20. The reaction order on the nucleophile of almost all substrates varies around 3. The exceptions being 2,4,6-$(OMe)_3$-benzenesulfonyl chloride (**6**) and benzenesulfonyl chloride (**8**) for which b is slightly higher than two.

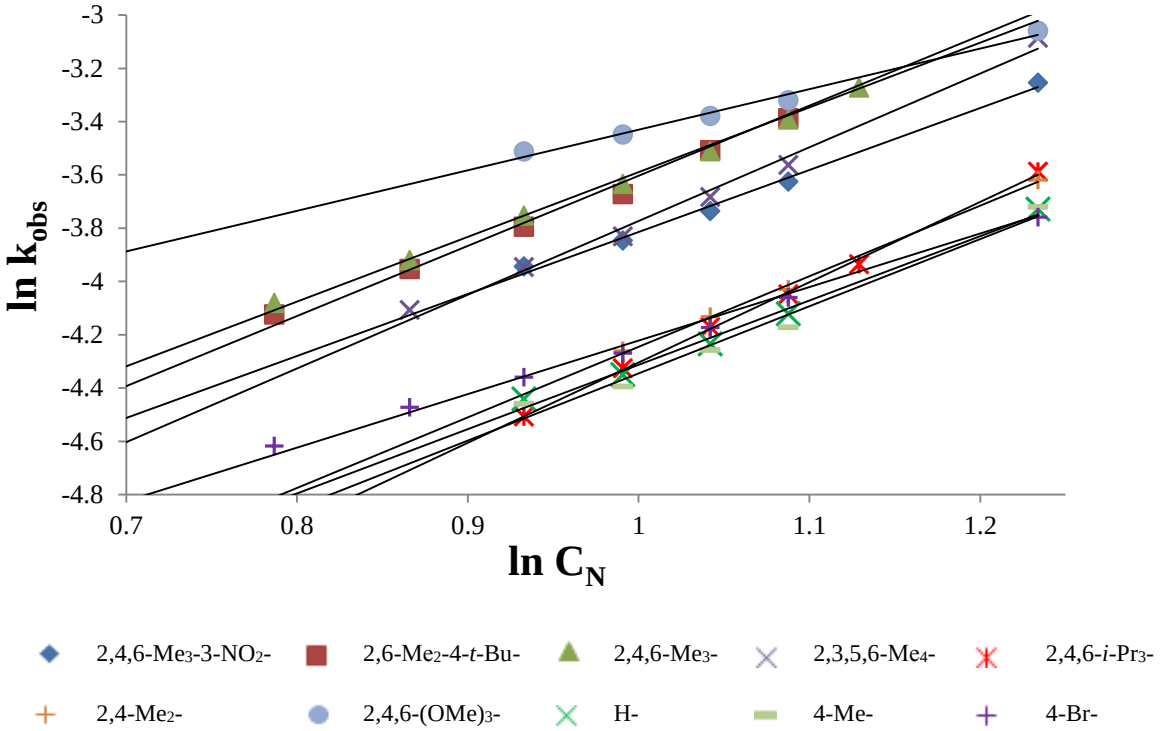


Figure 4.17 Lnk_{obs} *vs.* lnC_N for the ethanolysis of X-$ArSO_2Cl$ in ethanol-hexane mixtures at 323 K

Table 4.19 Regression coefficients *ln k'* and *b* (Eq. 4.2) for the solvolysis of X-$ArSO_2Cl$ in ethanol-hexane mixtures at 323 K

№	X	Intercept *ln k'*	Slope *b*	R^2	n*
1	2,4,6-Me_3-3-NO_2-	-6.1±0.1	2.3±0.1	0.994	5
2	2,3,5,6-Me_4-	-6.5±0.1	2.7±0.1	0.991	6
3	2,4,6-Me_3-	-6.28±0.04	2.66±0.03	0.999	5
4	2,6-Me_2-4-*t*-Bu-	-6.2±0.1	2.6±0.1	0.993	5
5	2,4,6-*i*-Pr_3-	-7.34±0.04	3.04±0.04	0.999	5
6	2,4,6-$(OMe)_3$-	- 5.0±0.1	1.52±0.09	0.989	5
7	2,4 Me_2-	-6.89±0.09	2.65±0.08	0.998	4
8	H-	-6.4±0.2	2.1±0.2	0.984	4
9	4-Me-	-7.2±0.2	2.8±0.2	0.994	4
10	4-Br-	-6.23±0.03	2.01±0.04	0.997	8

* n – sample size

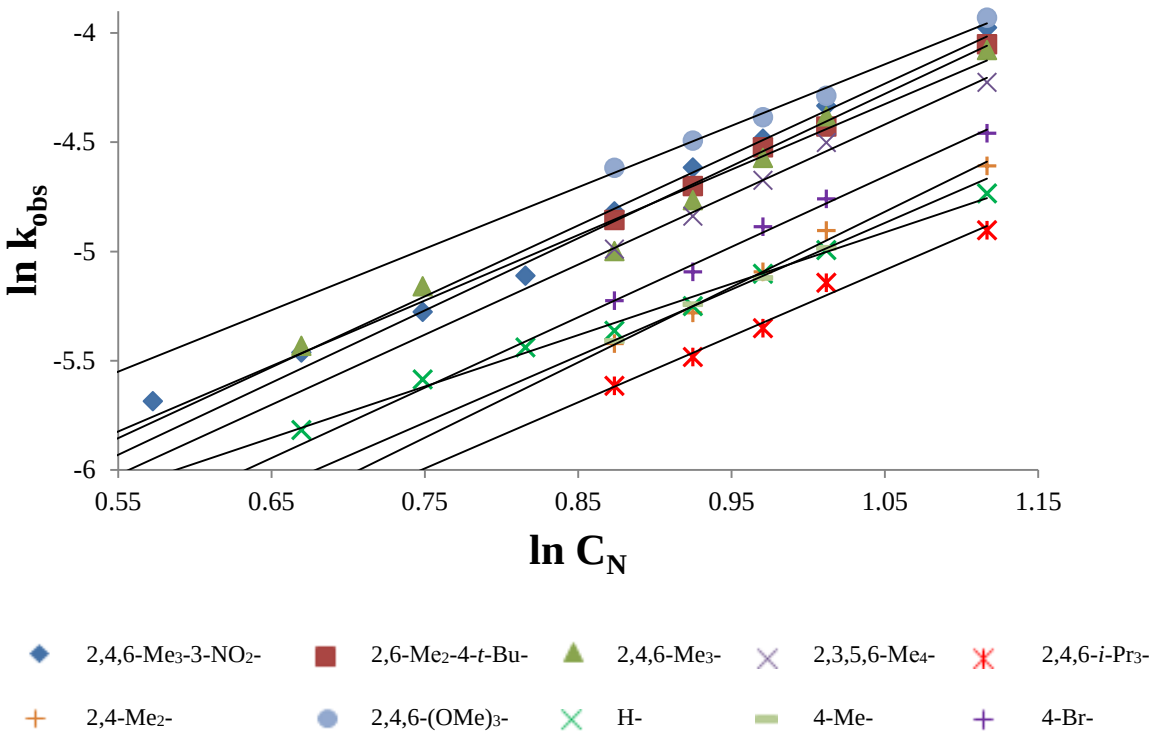


Figure 4.18 Lnk_{obs} *vs.* lnC_N for the *iso*-propanolysis of X-$ArSO_2Cl$ in *iso*-propanol-hexane mixtures at 323 K

Table 4.20 Regression coefficients *ln k'* and *b* (Eq. 4.2) for the solvolysis of X-$ArSO_2Cl$ in *iso*-propanol-hexane mixtures at 323 K

№	X	Intercept *ln k'*	Slope *b*	R^2	n
1	2,4,6-Me_3-3-NO_2-	-7.6±0.1	3.2±0.1	0.988	9
2	2,3,5,6-Me_4-	-7.48±0.08	3.04±0.08	0.996	7
3	2,4,6-Me_3-	-7.4±0.1	3.0±0.2	0.990	6
4	2,6-Me_2-4-*t*-Bu-	-7.8±0.2	3.2±0.2	0.991	5
5	2,4,6-*i*-Pr_3-	-8.3±0.2	3.0±0.2	0.981	5
6	2,4,6-$(OMe)_3$-	-6.57±0.05	2.25±0.05	0.997	5
7	2,4 Me_2-	-8.4±0.2	3.5±0.2	0.992	5
8	H-	-7.38±0.07	2.35±0.08	0.993	8
9	4-Me-	-8.07±0.09	3.1±0.1	0.997	4
10	4-Br-	-8.0±0.2	3.2±0.2	0.991	5

* n - sample size

To estimate the steric effect of the alcohol on the reaction order on the nucleophile (*b*), *b* was plotted *vs.* *v* (Charton's steric constant) as shown in Figure 4.19; from there it follows that *b* increases with bulkier nucleophiles. Satisfactory correlations were obtained only for alkylated derivatives of benzenesulfonyl chloride with $\Sigma\sigma_X < 0$ (Table 4.21) using the equation:

$$b = \delta \cdot \nu + c_1 \qquad \text{(Eq. 4.3)}$$

Alkylated derivatives of benzenesulfonyl chloride with steric hindrance show sensitivity of the reaction order to the steric bulkiness of the alcohol due to the steric packing of alcohol molecules at the TS. According to the reactivity-selectivity principle (RSP), the sensitivity coefficient (δ) should decrease for the more reactive substrates. Poor correlations for substrates with $\Sigma\sigma_X \geq 0$ can indicate a less ordered TS or may point out the TS destabilization by electron withdrawing substituents.

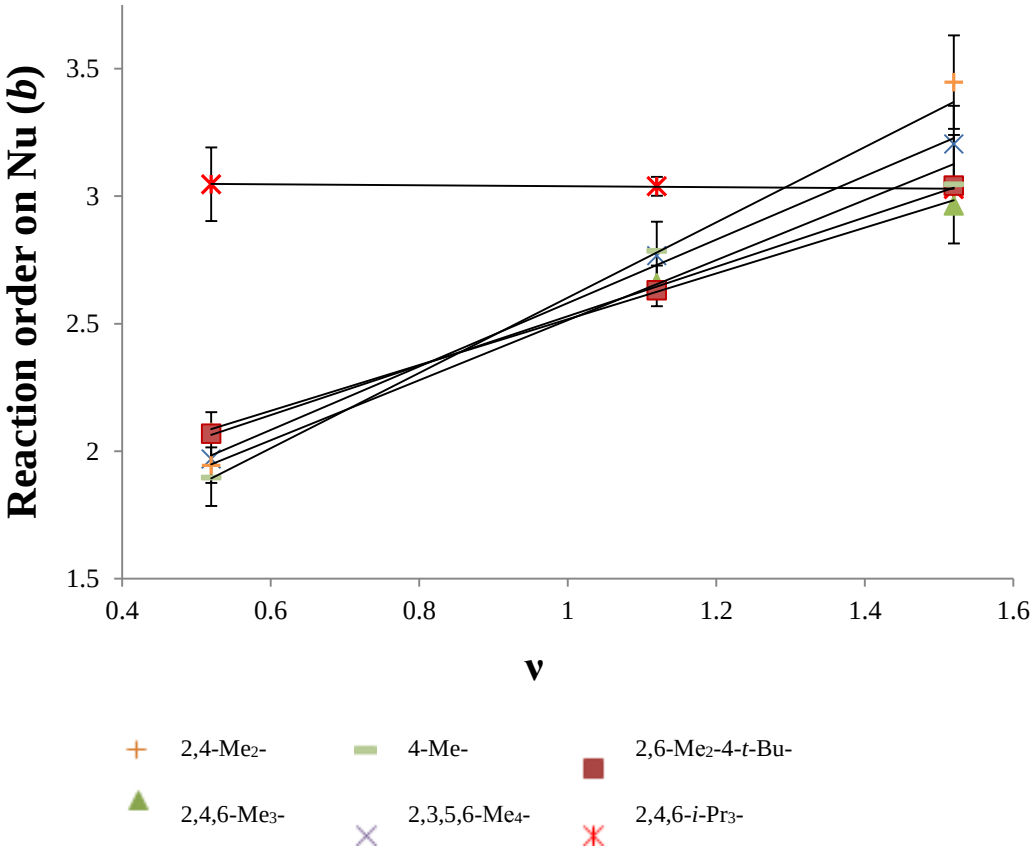


Figure 4.19 Reaction order with respect to Nu (*b*) *vs.* Charton's steric constant (ν) of the alcohol's hydrocarbon part

Table 4.21 Regression coefficients of Eq. 4.2

X	c_1	δ	R^2
2,6-Me_2-4-*t*-Bu-	1.56±0.03	0.70±0.02	0.999
2,4,6-Me_3-	1.62±0.07	0.90±0.06	0.996
2,3,5,6-Me_4-	1.34±0.07	1.24±0.06	0.997
2,4 Me_2-	1.1±0.3	1.5±0.2	0.977
4-Me-	1.3±0.3	1.2±0.2	0.964

The reactivity of sulfonyl chlorides significantly depends on the nucleophile concentration and confirms previous ideas about the classical bimolecular S_N2 process;[6, 7-10, 36-39] however, obtained results suggest that the TS involves two nucleophile molecules in methanol and ethanol, and three with *iso*-propanol. The change of space requirements for TS with increasing of steric bulk of the nucleophile may explain the participation of additional nucleophile molecules in *iso*-propanolysis. The fractional values of *b* for ethanolysis can be interpreted by change in the degree of solvation as the nucleophile changes, and simultaneous participation of an alcohol molecule of in multiple similar interactions with other molecules of the substrate and solvent.

X-ray diffraction studies of the sterically overloaded molecule 2,4,6-*i*-Pr_3-benzenesulfonyl chloride, have shown some distortion of the benzene ring plane (± 0.021 Å),[40] which takes the form of highly flattened "bath". Moreover the relative orientation of the *iso*-propyl *ortho*-substituents allows the occurrence of intramolecular nonbonded contacts between the oxygen atoms of sulfo groups and the protons of the central carbon atoms of *iso*-propyl *ortho*-groups. Spatially bulky *iso*-propyl *ortho*-substituents promote the spatial fixation of the $–SO_2Cl$ group and limit the nucleophile approach. Probably the combination of these factors contributes to the participation three solvent molecules in the TS in the case of all the tree alcohols. 2,4,6-$(OMe)_3$-benzenesulfonyl chloride exhibits too low reaction order relative to

the nucleophile and the maximum reactivity, which might be attributed to a large negative total electronic effect. For 2,4,6-$(OMe)_3$-substituents $\Sigma\sigma$ = -1,048, which promotes the separation of the leaving group and favours a more "loose" TS.

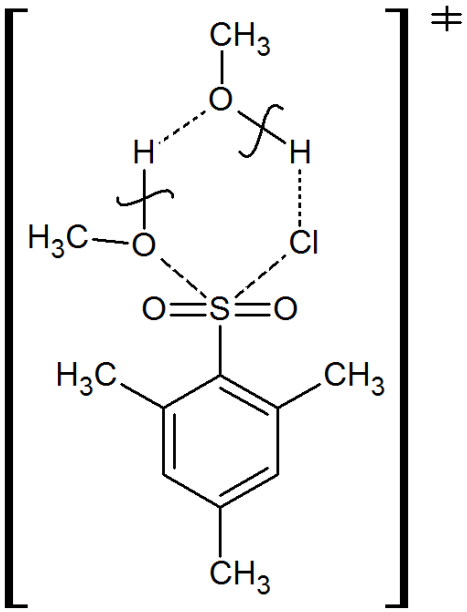
It has been demonstrated that nucleophilic substitution by alcohols at tetracoordinate hexavalent sulfur atom in arenesulfonic acids derivatives has the features related to variability of the structure of the TS S_N2-type and is more complicated than previously thought.

Small values obtained for solvent isotope effects (SIE), in turn, cast doubts on the catalytic effect of a second nucleophile molecule in the formation of the transition state.[4, 10, 37] In view of this, obtained data of the reaction order relative to the nucleophile (*b*) indicate that the structure of the TS is determined to a greater extent by solvation interactions.

The parameter *b* increases with the volume of the steric substituents and is not related uniquely to the electronic nature of the *X* substituent group (Tables 4.18-4.20).

Detailed features of the transition state of solvolytic processes involving the sulfur atom in sulfonyl compounds are now discussed. TS's of various structures and spatial features within a single S_N2 substitution mechanism is assumed, likely with the existence of a polymolecular cyclic TS (see Scheme 4.8). Ambiguous influence of the electronic nature of the substituent, interactions of sulfo group with *ortho*-alkyl substituents in initial state may explain the significant difference in the reactivity of substrates with different structures within the same mechanism of solvolysis. Strictly speaking the TS is trimolecular, *i.e.*, second order in alcohol, but in accordance with formal criteria it corresponds to a S_N2 mechanism.

Such TS explains low values of SIE, as in the cyclic TS the sum of the orders of bond-breaking and bond-forming is less than would be in the typical attack of the nucleophile with the assistance of a second molecule of solvent as it happens in general base catalysis, *i.e.*, the so-called S_N3-mecanism.[10]



Scheme 4.8 - Cyclic transition state involving of two solvent molecules (nucleophile) by example of mesitylene sulfonyl chloride methanolysis

This TS is formally in the boundary between three-and bimolecular; it retains the first order on the alcohol because the second solvent molecule is not directly involved in bond breaking/forming at the sulfur atom.

4.5 X-RAY ANALYSIS OF SOME DERIVATIVES OF ARENESULFONIC ACIDS

To understand the effect of steric factors on the solvolysis of hindered arenesulfonyl chlorides, it is necessary to identify the structural features of the investigated substrates and of the reaction products. X-ray analysis was carried out in solid crystals having in mind that such structure can differ from that of occurring in solution; nevertheless this information can be useful in the understanding of the TS structure.

Since most of the studied substrates were not in X-ray databases (*e.g.* Cambridge Structural Database), X-ray analysis of these compounds were carried out (see Annexes A.1). Sterically hindered substrates shown that oxygens of sulfo groups were oriented towards the *ortho*-methyl groups (Figure 4.20, Figure 4.21).

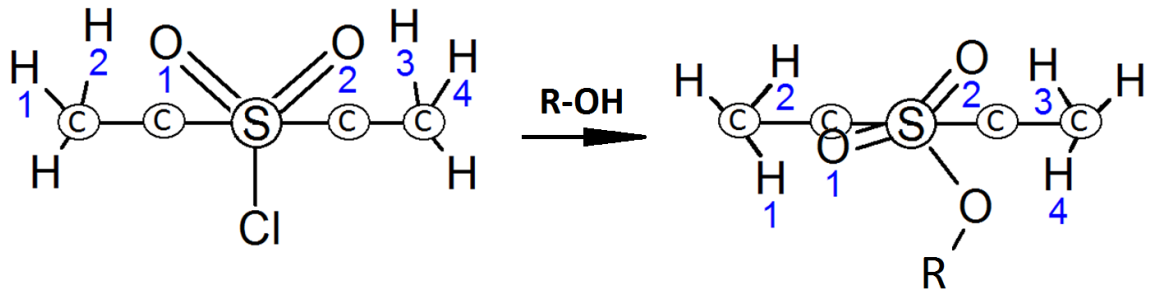


Figure 4.20 Sterical models of hindered arenesulfonyl chloride and arenesulfonate

The distance between the hydrogen atom of the *o*-alkyl group and the nearest oxygen of the sulfonyl group, $l_{(O\cdots H)}$, Table 4.22, is comparable to the length of typical hydrogen bonds (2.30-2.70 Å),[41, 42] thus a weak intramolecular interaction (C-H···O) may occur [43,44]. The value of the sum of Van der Waals radii [45] of oxygen and hydrogen atoms, Σr_W = 2.72 Å, also supports the idea about C-H···O intramolecular interactions in these compounds.

In the products the angle $\angle(O_1SO_2)$ between the oxygens of sulfo group is retained, whereas one of the oxygens of the sulfo group keeps its orientation towards the *ortho*-methyl group, as evidenced by the low values of torsion angles ∠(O(1)-S(1)-C(1)-C(2)) (see Annex A.1; Fig. 4.21); this may indicate that such

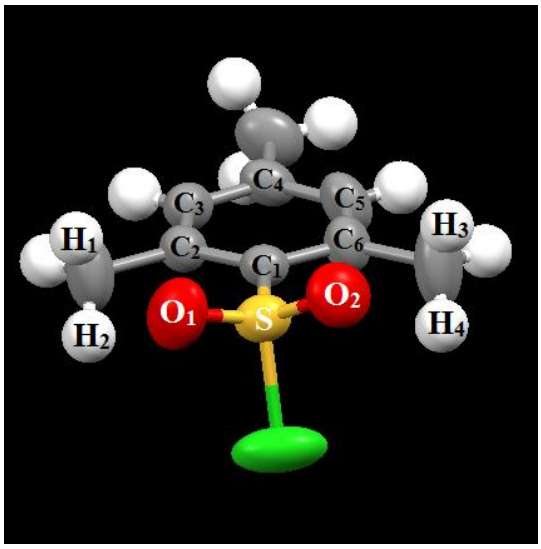
interactions are preserved in the products and may contribute to the rearrangement of the oxygens of the sulfo group in TS.

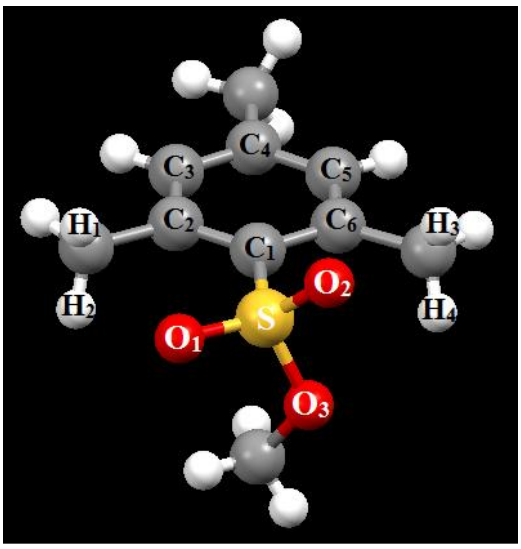
Table 4.22 Distances between the oxygens of the sulfo group and the hydrogens of *ortho*-methyl groups of some derivatives of hindered arenesulfonic compounds.

Compound	$l_{(O1\cdots H1)}$*, [Å]	$l_{(O1\cdots H2)}$*, [Å]	$l_{(O2\cdots H3)}$*, [Å]	$l_{(O2\cdots H4)}$*, [Å]	$\angle(O_1SO_2)$, [°]
4-*tert*-butyl-2,6-dimethylbenzenesulfonyl chloride	2.453	2.511	2.358	2.702	118.36
Ethyl 4-*tert*-butyl-2,6-dimethylbenzenesulfonate	2.456	2.515	2.551	3.096	118.46
Propan-2-yl 4-*tert*-butyl-2,6-dimethylbenzenesulfonate	2.48	2.483	2.486	3.202	118.55
Methyl 4-*tert*-butyl-2,6-dimethylbenzenesulfonate	2.438	2.490	2.475	3.198	118.06
Propyl 4-*tert*-butyl-2,6-dimethylbenzenesulfonate	2.437	2.470	2.586	2.890	118.74
2,4,6-trimethylbenzenesulfonyl chloride	2.443	2.531	2.453	2.603	117.67
Propan-2-yl 2,4,6-trimethylbenzenesulfonate	2.446	2.517	2.464	3.046	117.93
Methyl 2,4,6-trimethylbenzenesulfonate	2.473	2.540	2.475	2.903	118.30
Propan-2-yl 2,3,5,6-tetramethylbenzenesulfonate	2.281	2.660	2.538	2.887	118.61
Propyl 2,3,5,6-tetramethylbenzenesulfonate	2.732	2.632	2.425	3.762	118.20
2,4,6-trimethyl-3-nitrobenzenesulfonyl chloride	2.521	2.409	2.507	2.578	118.27
2,4,6-tri(propan-2-yl) benzenesulfonyl chloride **	2.732	-	2.425	-	118.06
3-chloro-2-methylbenzenesulfonyl chloride**	2.301	-	-	-	119.39

*Numeration of the atoms corresponds to Figures 4.20, 4.21

**Obtained from Cambridge Structural Database

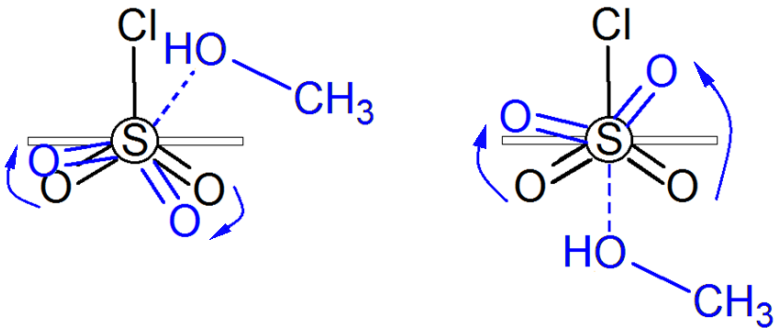




2,4,6-trimethylbenzenesulfonyl chloride Methyl 2,4,6-trimethylbenzenesulfonate

Figure 4.21 X-ray structure of arenesulfonyl derivatives

Ortho-alkyl groups may block the backside attack of the nucleophile through steric hindrance and fixing the oxygens of the sulfo group by intramolecular interactions. On the other hand, frontal axial attack may assist the cyclic TS as it decreases the bond lengths in the cycle (Figure 4.22).



a. b.

Figure 4.22 Different types of nucleophilic attack at the reaction center during arenesulfonyl chloride methanolysis.

a. axial attack; b. backside frontal attack.

Intramolecular interactions between the oxygens of the sulfo group and the hydrogens of *ortho*-methyl groups in the initial state may be the reason of the so called "positive steric effect" and explain the abnormal reactivity of those hindered compounds.

4.6 CONCLUSIONS

We suggest next interim conclusions:

- All considered substrates, in all alcohols, react through an unique mechanism of nucleophilic substitution that has been proved by $logk_{T1}$ *vs.* $logk_{T2}$ isokinetic dependencies and by the similarity of the activation parameters.
- The values of SIE, the leaving group effect, the effect of nucleophile change, the decreasing of reactivity with decreasing of nucleophile concentration point to S_N2 like TS for the solvolysis of arenesulfonyl.
- The reaction order with respect to nucleophile higher than one suggests the nucleophilic assistance of at least one additional molecule of alcohol at the TS.
- X-Ray analysis data for sterically hindered arenesulfonyl chlorides points to weak intramolecular interactions C-H···O between the hydrogen atom of the *o*-alkyl group and the nearest oxygen of the sulfonyl group in the corresponding sulfonyl chloride.

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5 FINAL DISCUSSION

5.1 COMPARATIVE ANALYSIS OF ALCOHOLYSIS OF SULFONYL CHLORIDES

5.1.1 Formal kinetics

There is an increase of selectivity toward the extended model series of substrates with increasing of hydrocarbonic "tail" of the alcohol series: MeOH – EtOH – PrOH, which agrees with the reactivity-selectivity principle, and is expected in terms of the stereochemical requirements of the TS. Sensitivity to electronic effects varies monotonically (Table 5.1), but in the case of *i*-PrOH the sensitivity coefficient ρ of the Hammett equation changes its sign.

Table 5.1 Correlation parameters of the Hammett equation for the extended model series of arenesulfonyl chlorides solvolysis at 313K

Alcohol	-*log* k_0	ρ	r	n^*
MeOH	3.38±0.01	-0.45±0.03	0.950	10
EtOH	4.05±0.01	-0.21 ±0.01	0.985	7
PrOH	4.31±0.01	-0.25±0.03	0.932	6
i-PrOH	5.12±0.02	0.65±0.06	0.974	5

*n – sample size

For unbranched alcohols solvolysis of sulfonyl chlorides with *X* electron-withdrawing substituents is slowed down and accelerated by electron-donating ones, not typical for bimolecular nucleophilic substitutions. I*so*-propanolysis shows an opposite behaviour. Also, di-*ortho*-methylated substrates show increased activity in comparison with unhindered derivatives in all alcohols. Thus such behaviour cannot be explained solely by the electronic effects in the substrates.

5.1.2 Thermodynamics of the solvolysis

To facilitate the discussion the obtained data were divided into three subgroups: sterically unhindered, mono- and di-*ortho*-alkylated. The tested substrates show that activation parameters are structure dependent. Enthalpy of activation of sterically unhindered substrates increases in the series MeOH – EtOH – PrOH, whereas for mono-*ortho*-alkylated sulfonyl chlorides it tends to decrease. In *iso*-propanol $\Delta H^{\ddagger}$ is an average of that of sterically unhindered and mono-*ortho*-alkylated, and becomes approximately equal to 62 $kJ \cdot mol^{-1}$. For di-*ortho*-alkylated substrates, in MeOH – EtOH – PrOH, the activation enthalpy does not change, while it decreases slightly in *i*-PrOH. Entropy of activation and activation Gibbs energy tends to increase with the size of the alkyl radical in the alcohol for all substrates.

Evaluation of isokinetic temperature (T_{iso}) is very complicated by the large variety of studied substrates and by the strong heterogeneity of the studied series. There is no common point of intersection of all kinetic curves. We should talk more properly about isokinetic areas for subgroups of substrates. T_{iso} was estimated by linear extrapolation of the experimental data using least squares (Table 5.2; Figure 5.1).[1] The effect of the substrate structure on the nature of the solvent-nucleophile is ambiguous. Just in the case of methanolysis there is enthalpy control in the reaction zone.

All hindered substrates (mono-*ortho*- and di-*ortho*-alkylated) show a sharp decrease of T_{iso} in going from methanol to other alcohols. TS of sterically hindered substrates in ethanol, propanol and *iso*-propanol possibly are less rigid; therefore T_{iso} does not vary. The substrates of unhindered group display a gradual decline of T_{iso} with the increase of the nucleophile steric bulkiness as the entropic contribution increases, which brings the TS to the entropy control zone already in the operating temperature region.

Solvolysis of all the groups of substrates in ethanol shows greater proximity of T_{iso}=315-328 K, within the experimental range.

Table 5.2 Isokinetic temperature (T_{iso}) for the alcoholysis of substrates of different subgroups

Substrate group	MeOH	EtOH	PrOH	*i*-PrOH
Sterically unhindered substrates	403±15	315±33	293±7	264±12
Mono-*ortho*-alkylated substrates	522±25	324±6	320±5	303±6
Di-*ortho*-alkylated substrates*	486±30	328±18	313±8	308±7

* 2,4,6-Et_3-benzenesulfonyl chloride and 2,4,6-*i*-Pr_3-benzenesulfonyl chloride were not used in the calculations

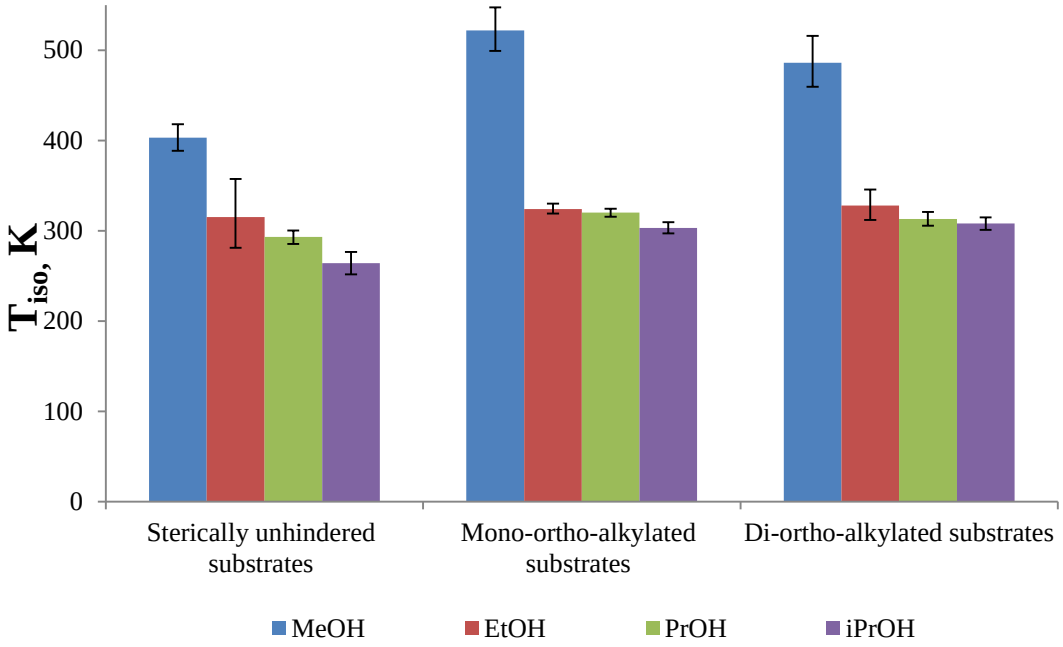


Figure 5.1 Isokinetic temperatures for different groups of substrates

In the case of solvolysis by propanol sterically unhindered sulfonyl chlorides are characterized by lower temperature of transition to enthalpic zone than hindered representatives. For the solvolysis of mono-*ortho*- and di-*ortho*-alkylated sulfonyl chlorides in *iso*-propanol is also found that T_{iso} is close to the experimental temperature range. The relative constancy of T_{iso} for all *ortho*-alkylated substrates in the series: EtOH – PrOH – *i*-PrOH points to a similar TS structure for these systems. The difference in methanol may come from to its easier approach to the reaction center due to the smaller volume of the nucleophile.

5.2 INFLUENCE OF THE SOLVENT ON THE ALCOHOLYSIS

To test the existence of a common solvolytic mechanism, the isokinetic dependences log k_{HOH} *vs.* log k_{ROH}, were built for the following substrates (Figure 5.2): X=2,4,6-Me_3-; 2,6-Me_2-4-*t*-Bu-; 2-Me-; 2-Me-5-NO_2-; 4-Me-; 4-Cl-; 4-Br-; 3-NO_2-; H-. Satisfactory correlations and negative slopes of isokinetic lines (Table 5.3) point to a single S_N2 mechanism, which has been proven by many authors in several studies as described in the state of art chapter. The slope decreases and the correlation is getting worse as the hydrocarbon "tail" of the alcohol grows. It may indicate the deviation from TS inherent for the hydrolysis caused by an increase in the steric bulkiness of the nucleophile and the decrease of the medium polarity.

Table 5.3 Parameters of log k_{HOH} *vs*. log k_{ROH}, arenesulfonyl chlorides solvolysis*, linear regression

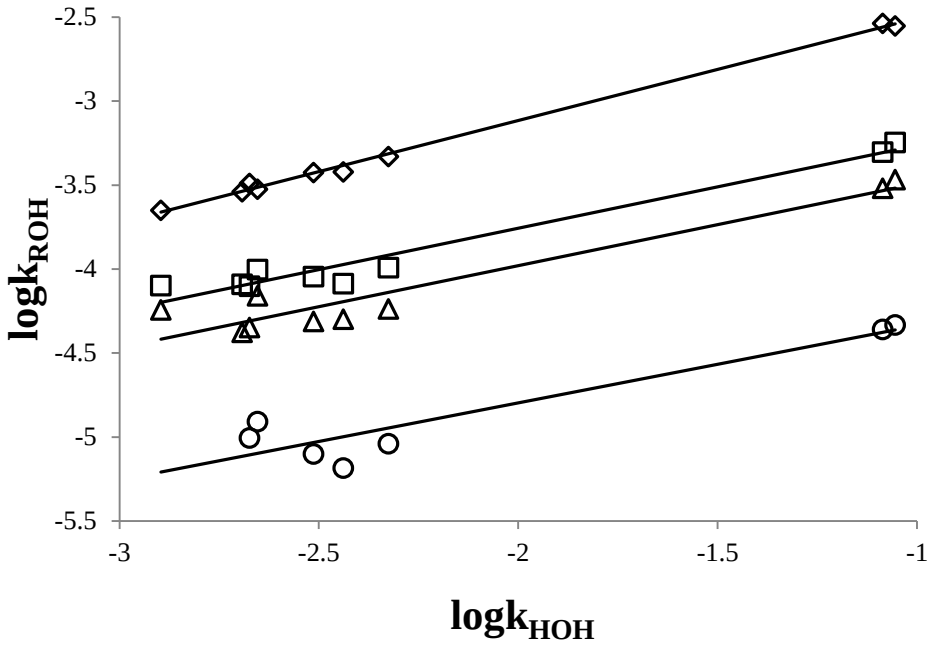
Nucleophile	Intercept a	Slope b	R^2	n**
MeOH	0.61±0.01	-1.90±0.03	0.997	9
EtOH	0.49±0.04	-2.77±0.09	0.961	9
PrOH	0.49±0.06	-3.0±0.1	0.915	9
i-PrOH	0.46±0.08	-3.9±0.2	0.874	7

* Rate constants for hydrolysis at 298 K and rate constants for alcoholysis at 313 K [2, 3] were used

**n – sample size.

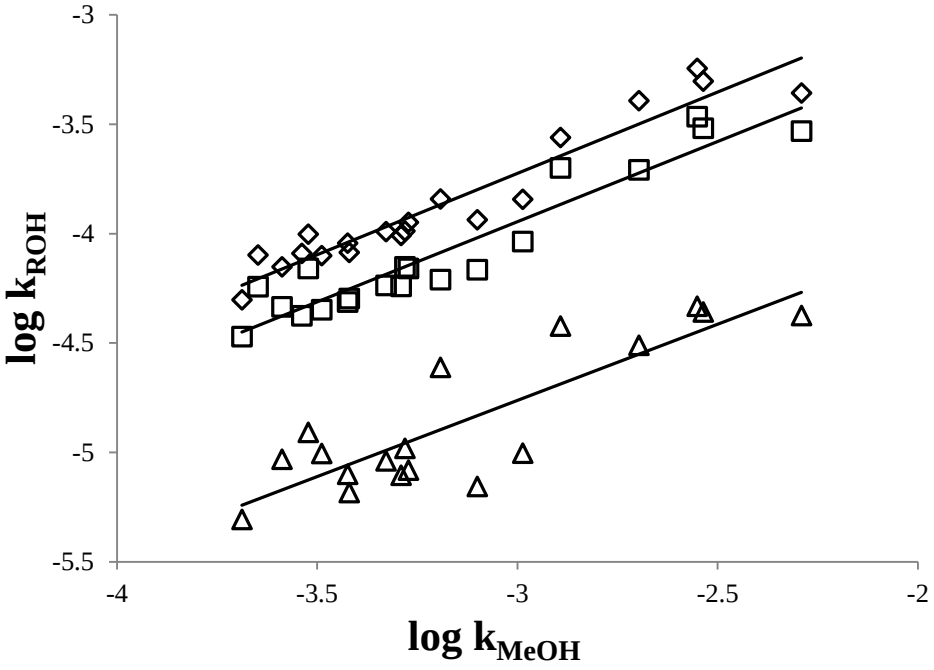
It should be noted that in EtOH, PrOH and *i*-PrOH the relative reactivity of sterically unhindered substrates practically does not differ. Sterically hindered 2,4,6-Me_3-benzenesulfonyl chloride and 2,6-Me_2-4-*t*-Bu-benzenesulfonyl chloride show enhanced reactivity relative to unsubstituted compound in all alcohols, this indicates weak variability of the *ortho*-effect, that slightly oscillates with both the polarity of the medium and the nature of the nucleophile.

The isokinetic dependences $logk_{MeOH}$-$logk_{ROH}$ (Figure 5.3) for all experimental data sets are also consistent with the idea of a common substitution mechanism in the studied alcohols.



◇ - Me, □- Et, Δ - Pr, ○ - *i*-Pr.

Figure 5.2 Isokinetic dependences log k_{HOH}-log k_{ROH} for the arenesulfonyl chlorides solvolysis



◇ - Et, □- Pr, Δ - *i*-Pr.

Figure 5.3 Isokinetic dependences log k_{MeOH}-log k_{ROH} for the arenesulfonyl chlorides solvolysis

Solvolysis by *i*-PrOH shows some deviations that may indicate a similar S_N2 mechanism in which the TS becomes crowded due to steric interactions with *i*-PrOH (nucleophile & solvent).

5.2.1 Nonspecific solvation: log k_{obs} *vs.* 1/ξ relationship

The correlation between the reactivity and the Kirkwood function (1/ξ) takes into account only nonspecific solvation, *i.e.* the ability of the solvent to promote charge transfer, as well as to polarize substrates. The polarity of the mixture (ξ_{mix}) was calculated with the Lichtenecker – Rother equation[4]:

$$\log \xi_{mix} = f_{alc} \cdot \log \xi_{alc} + f_{hex} \cdot \log \xi_{hex}, \qquad \text{(Eq. 5.1)}$$

where f_{alc}, $f_{hex}$and ξ_{alc}, ξ_{hex} are the volume fractions and the polarities of the alcohol and hexane respectively.

The following equation was used to study the corresponding correlations:

$$log\ k_{obs} = U \cdot \frac{1}{\xi} + log k_0. \qquad \text{(Eq. 5.2)}$$

The correlation was analyzed for the solvolysis of X-$ArSO_2Cl$ (X= H-; 4-Me-; 4-Br-; 2,4,6-Me_3-; 3-NO_2-; 2,6-Me_2-4-*t*-Bu-; 2,4,6-Me_3-; 2,3,5,6-Me_4-; 2,4,6-*i*-Pr_3-; 2,4-Me_2-; 2,4,6-$(OMe)_3$-;) in methanol-hexane, ethanol-hexane and *iso*-propanol-hexane mixtures (Figures. 5.4 – 5.6).

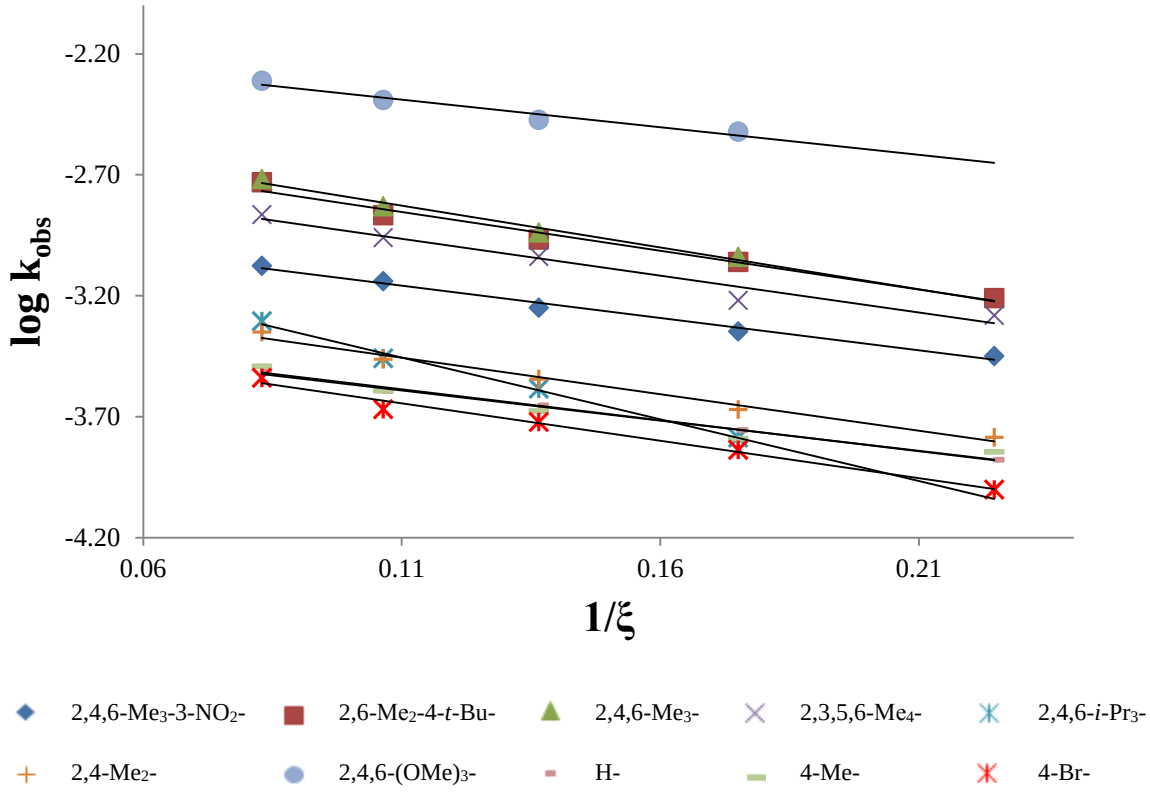


Figure 5.4 log k_{obs} *vs.* 1/ξ for the X-$ArSO_2Cl$ methanolysis in methanol-hexane mixtures at 323 K

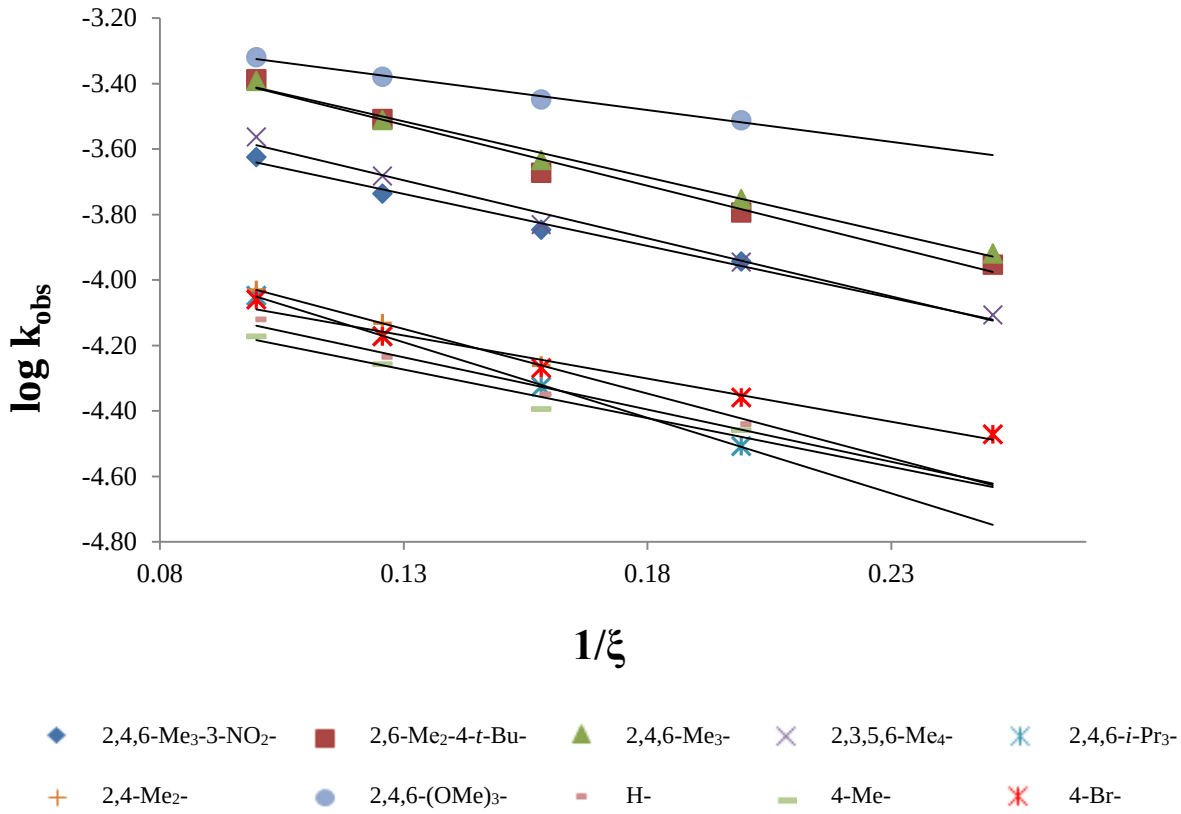


Figure 5.5 log k_{obs} *vs.* 1/ξ for the X-$ArSO_2Cl$ ethanolysis in ethanol-hexane mixtures at 323 K

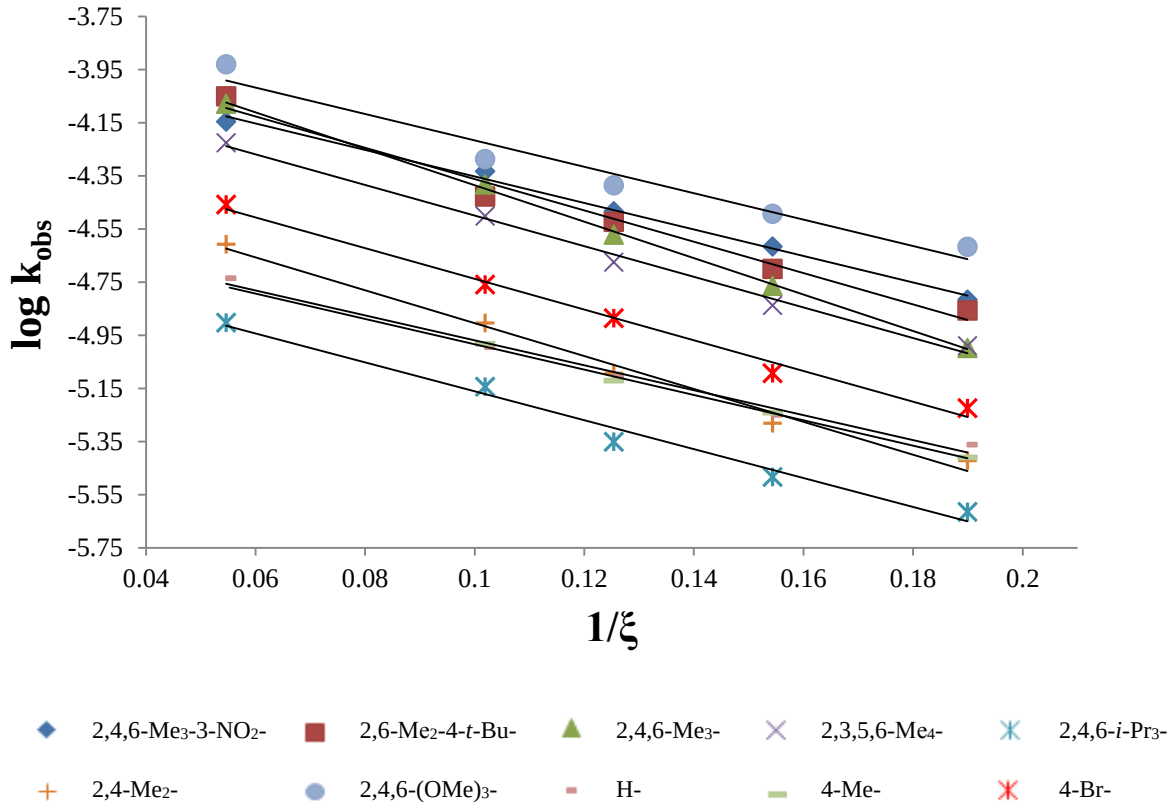


Figure 5.6 log k_{obs}*vs.* 1/ξ for the X-$ArSO_2Cl$ *iso*-propanolysis in *iso*-propanol-hexane mixtures at 323 K

The sign of sensitivity coefficient (*U*) is negative for all systems. According to Hughes–Ingold rule, [5] the higher the reactivity of substrate corresponds to a higher solvent polarity (ξ), which indicates that the activated complex is more solvated than the reactants.

For methanol-hexane and ethanol-hexane mixtures, *U* is approximately the same (Figure 5.7, Table 5.4), while for *iso*-propanol-hexane mixtures it sharply increases almost twice. Also it should be noted that the *U* variability grows inversely with the polarity of the alcohol in accordance with the principle reactivity-selectivity.

From the above it follows that the TS for the methanolysis and ethanolysis of sulfonyl chlorides is similar and much less polar than for the *iso*-propanolysis, which is confirmed by the values of ρ (Table 5.1).

Table 5.4 Correlation parameters of dependences log k_{obs} *vs.* $1/\xi$ (Eq. 5.2) for the X-$ArSO_2Cl$ solvolysis in alcohol-hexane mixtures at 323K

X	MeOH				EtOH				*i*-PrOH			
	$logk_0$	*U*	R^2	n	$logk_0$	*U*	R^2	n	$logk_0$	*U*	R^2	n
2,4,6-Me_3-3-NO_2-	-2.86±0.03	-2.7±0.2	0.99	5	-3.32±0.05	-3.2±0.3	0.98	4	-3.68±0.05	-6.1±0.4	0.99	5
2,6-Me_2-4-*t*-Bu-	-2.50±0.04	-3.2±0.3	0.98	5	-3.04±0.05	-3.7±0.3	0.98	5	-3.77±0.06	-5.9±0.5	0.98	5
2,4,6-Me_3-	-2.45±0.04	-3.5±0.3	0.98	4	-3.07±0.03	-3.4±0.2	0.99	5	-3.70±0.02	-6.9±0.1	0.99	5
2,3,5,6-Me_4-	-2.63±0.05	-3.1±0.4	0.96	5	-3.23±0.04	-3.6±0.2	0.99	5	-3.92±0.04	-5.8±0.3	0.99	5
2,4,6-*i*-Pr_3-	-2.89±0.03	-5.1±0.3	0.99	4	-3.59±0.01	-4.6±0.1	0.99	4	-4.62±0.06	-5.4±0.4	0.98	5
2,4-Me_2-	-3.12±0.03	-3.0±0.2	0.99	5	-3.64±0.01	-4.0±0.1	0.99	3	-4.29±0.05	-6.2±0.4	0.99	5
2,4,6-$(OMe)_3$-	-2.14±0.04	-2.3±0.4	0.96	4	-3.13±0.02	-1.9±0.1	0.99	4	-3.72±0.08	-5.0±0.6	0.96	5
H-	-3.31±0.02	-2.6±0.1	0.99	5	-3.82±0.05	-3.2±0.3	0.98	4	-4.50±0.04	-4.7±0.3	0.99	5
4-Me-	-3.32±0.05	-2.5±0.3	0.95	5	-3.89±0.06	-3.0±0.4	0.96	4	-4.51±0.03	-4.8±0.2	0.99	4
4-Br-	-3.48±0.02	-3.1±0.1	0.99	5	-3.83±0.04	-2.6±0.2	0.98	5	-4.16±0.04	-5.8±0.3	0.99	5

n –sample size

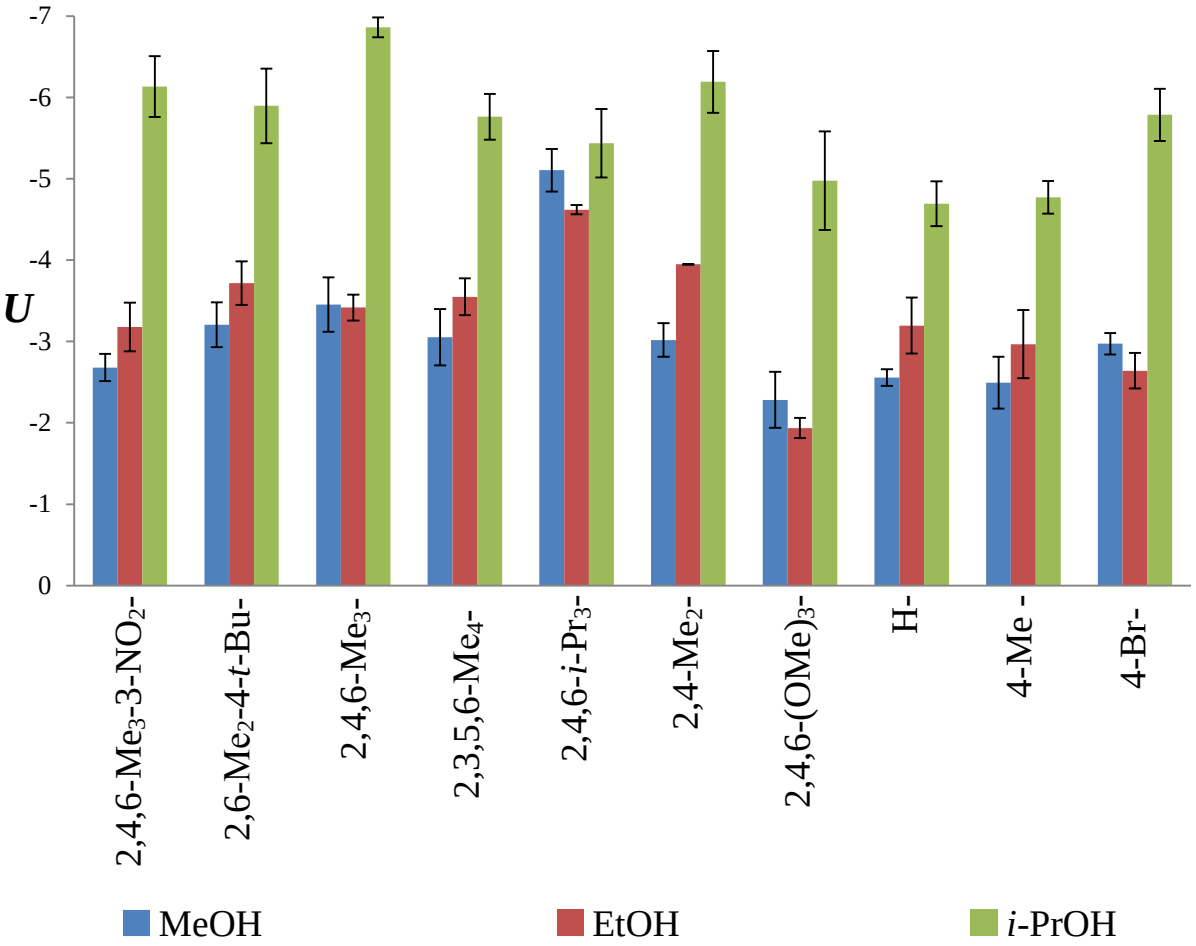


Figure 5.7 Sensitivity coefficient (*U*) (Eq. 5.2) for the X-ArSO$_2$Cl solvolysis in different alcohols

The kinetic data allow us to compare the reactivity of arenesulfonyl chlorides in different medias of equal polarity (ε≈10) that simultaneously vary by the nucleophile type (MeOH, EtOH, *i*-PrOH). The ratios of rate constants k_{MeOH}/k_{EtOH}, $k_{MeOH}/k_{i\text{-}PrOH}$ and $k_{EtOH}/k_{i\text{-}PrOH}$ correspond to sensitivity of the substrate with substituent *X* to nucleophilicity of medium. The obtained results show higher sensitivity coefficients for all steric hindered, substraites with electron donor substituents (Σσ<0, see Table 5.5) in comparison with unhindered benzenesulfonyl chloride. The observed distribution is in contrary to results of Bently [6] that may be explained by different nucleophile type (97%TFE and 40% ethanol) and the framework of polarities chosen by author.

Also it is easy to notice the relationship between the electronic nature of the *X* substituent in the benzene ring and sensitivity coefficients, see Fig. 5.8.

Table 5.5 The observed rate constants and there ratios for solvolysis of X-$ArSO_2Cl$ in MeOH-hexane, EtOH-hexane and *i*-PrOH-hexane mixtures at 323 K

X	$k_{MeOH}\cdot10^4$/ s^{-1}	$k_{EtOH}\cdot10^4$/ s^{-1}	$k_{i\text{-}PrOH}\cdot10^4$/ s^{-1}	$\frac{k_{MeOH}}{k_{EtOH}}$	$\frac{k_{MeOH}}{k_{i-PrOH}}$	$\frac{k_{EtOH}}{k_{i-PrOH}}$
	ε_{Mix} =9.4	ε_{Mix}=10.0	ε_{Mix} =9.8			
2,4,6-Me_3-3-NO_2-	7.27±0.01	2.37±0.01	0.466±0.001	3.06	15.6	5.10
2,6-Me_2-4-*t*-Bu-	13.6±0.1	4.11±0.01	0.374±0.001	3.31	36.4	11.0
2,4,6-Me_3-	14.8±0.1	4.06±0.01	0.416±0.001	3.65	35.7	9.77
2,3,5,6-Me_4-	11.0±0.1	2.74±0.01	0.315±0.001	4.02	34.9	8.68
2,4,6-*i*-Pr_3-	3.48±0.01	0.895±0.001	0.072±0.001	3.89	48.4	12.4
2,4-Me_2-	3.45±0.01	0.933±0.01	0.125±0.001	3.69	27.6	7.47
2,4,6-$(OMe)_3$-	40.8±0.01	4.79±0.01	0.517±0.001	8.51	78.9	9.27
H-	2.55±0.01	0.757±0.001	0.102±0.001	3.37	25.1	7.46
4-Me-	2.56±0.01	0.673±0.001	0.104±0.001	3.80	24.6	6.46
4-Br-	2.14±0.01	0.872±0.001	0.174±0.001	2.46	12.3	5.00

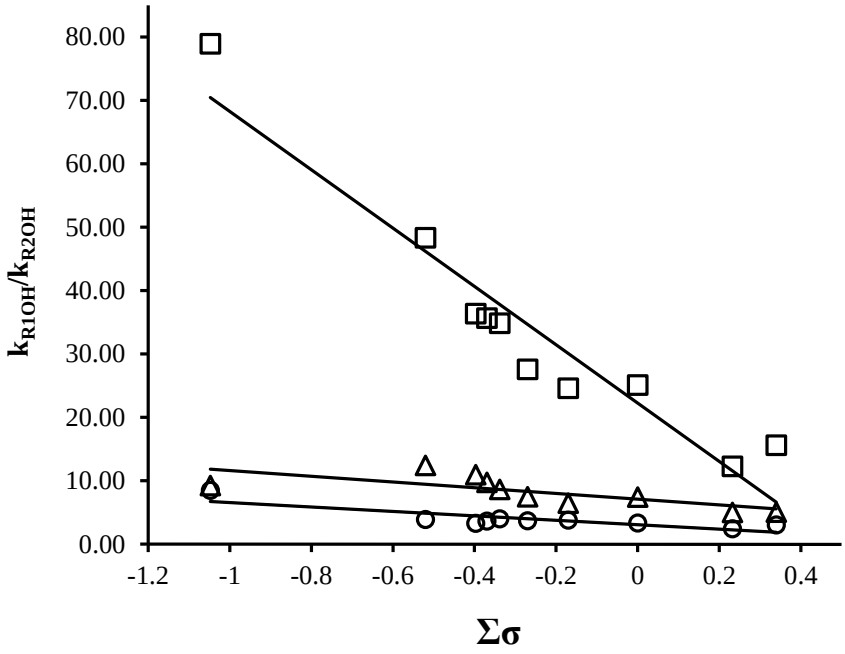


Figure 5.8 The dependence k_{R^1OH}/k_{R^2OH} *vs.* Σσ for alcoholysis of X-$ArSO_2Cl$

□ R_1=Me-, R_2=*i*-Pr-; ○ R_1=Me-, R_2=Et-; Δ R_1=Et-, R_2=*i*-Pr-.

The high sensitivity coefficients to solvent nucleophility for hindered arenesulfonyl chlorides one more time indicate a S_N2-like mechanism.

The understanding of the alcoholysis of sulfonyl chlorides cannot be confined to the effect of the macroscopic solvent polarity; thereby specific solvation should be also taken into account in evaluating the solvent influence.

5.2.2 Specific solvation: Grunwald-Winstein equation

The influence of the specific solvation on arenesulfonyl chlorides solvolysis process was studied in terms of the classical Grunwald-Winstein equation (1.3). The *Y* scale was used, it is based on the transition energy corresponding to the longest wavelength absorption band (the band charge transfer) for 1-ethyl-4-carbo-methoxy-pyridinium iodide ($E = h \cdot c \cdot \nu = 2{,}859 - 10^5/\lambda$; λ — in angstroms). The *Y* parameter is derived from the correlation data for the parameter δ,[7] also named solubility or Hildebrand parameter. It is related to the solubility of non-electrolytes, and it is a measure of the energy required for the formation of a cavity in the solvent with size corresponding to the transition state for the solute molecules.

Observed rate constants of arenesulfonyl chlorides solvolysis in methanol, ethanol and propanol were used for correlations. Points corresponding to *iso*-propanol lay down somewhat lower the correlation line, which can be explained by the additional steric interactions between *i*-PrOH and sulfonyl chlorides. As it can be seen from Table 5.6 all substrates have a positive sensitivity (*m*) to the ionizing power of solvent. The correlation between the electronic nature of the substituent *X* in the benzene ring and *m* is obvious. Electron withdrawing substituents tend to decrease *m*, whereas electron-donor ones increase it (Figure 5.9; $R^2=0.898$); such behavior is not peculiar for S_N2 reactions. 4-NO_2-derivative falls out of this dependence, which can be attributed to the direct polar conjugation with the reaction center, *i.e.* a phenomenon of different electronic nature.

Sterically hindered substrates (X=2,4,6-*i*-Pr_3-; 2,4,6-Et_3-; 2,4,6-OMe_3-) display maximum *m* values (1.65-1.40); this suggests some additional interactions between hindered substrate and solvent in the TS.

High positive values of *m* are likely associated with charge redistribution in the transition state involving molecules of alcohol. A possible explanation of the

dependence on Σσ (Figure 5.9) is a different effect of the *X* substituent on the TS solvation.[8]

Table 5.6 Parameters of the Grunwald-Winstein equation (Eq. 1.3) for the alcoholysis of X-ArSO$_2$Cl in MeOH, EtOH, PrOH at 313K

X	*m*	log k_0	R^2
Sterically unhindered substrates			
4-*t*-Bu-	1.03±0.03	-2.5±0.3	0.999
4-Me-	1.13±0.01	-2.01±0.01	0.999
H-	1.13±0.07	-2.0±0.1	0.992
4-Cl-	1.1±0.1	-2.2±0.2	0.978
4-Br-	1.09±0.05	-2.12±0.09	0.996
3-NO_2-	0.77±0.05	-2.69±0.01	0.997
4-NO_2-	1.3±0.2	-1.6±0.3	0.967
Sterically hindered substrates			
2,4,6-OMe_3-	1.7±0.1	-0.56±0.07	0.998
2,4,6-*i*-Pr_3-	1.39±0.04	-1.38±0.08	0.998
2,6-Me_2-4-*t*-Bu-	1.18±0.01	-1.08±0.01	0.999
2,4,6-Me_3-	1.28±0.03	-0.95±0.06	0.999
2,3,5,6-Me_4-	1.28±0.09	-1.1±0.2	0.990
2,4,6-Et_3-	1.38±0.09	-1.3±0.2	0.992
2,4-Me_2-	1.14±0.07	-1.9±0.1	0.993
2Me-5-*t*-Bu-	1.23±0.01	-1.76±0.01	0.999
2,5-Me_2-	1.15±0.01	-1.85±0.02	0.999
2-Me-	1.16±0.03	-1.88±0.05	0.999
2,4,6-Me_3-3-NO_2-	1.07±0.08	-1.6±0.1	0.989
2,4- Me_2-5-NO_2-	0.96±0.01	-2.39±0.01	0.997
2-Me-5-NO_2-	0.82±0.01	-2.50±0.01	0.997

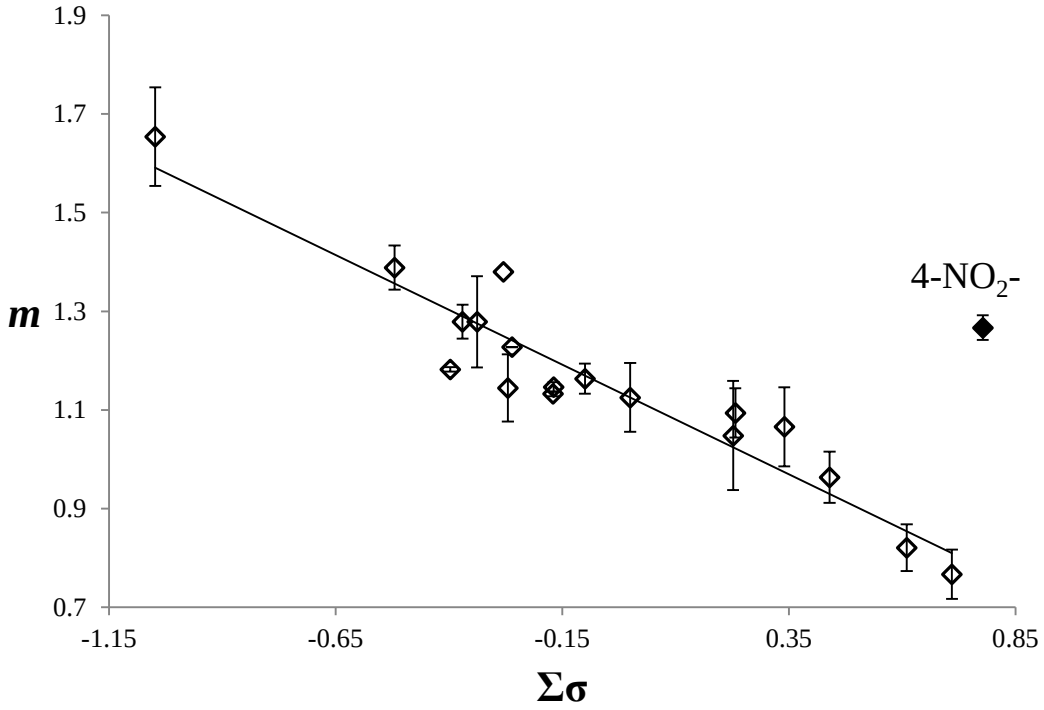


Figure 5.9 *m vs*. Σσ for the solvolysis of X-ArSO$_2$Cl at 313 K

5.2.3 Brønsted equation

Brønsted relationships were studied to analyze the influence of acid-base interactions on the transition state of the solvolysis (Figure 5.10):

$$logk_{obs} = \beta_{Nuc} \cdot pK_a + logk_0, \qquad \text{(Eq. 5.3)}$$

where β_{Nuc} is the Brønsted exponent and pK_a is the ionization constant. The β_{Nuc} value is a measure of the degree of proton transfer in the TS, when it takes place in line (180º).

The correlations show good dependences with negative slope (Table 5.7). It indicates a significant contribution of the proton transfer to the activation Gibbs free energy of the reaction.

Points for *iso*-propanolysis lie out of the correlation, which can be explained by a modified TS structure caused by the steric hindrance of the bulky *iso*-propyl group.

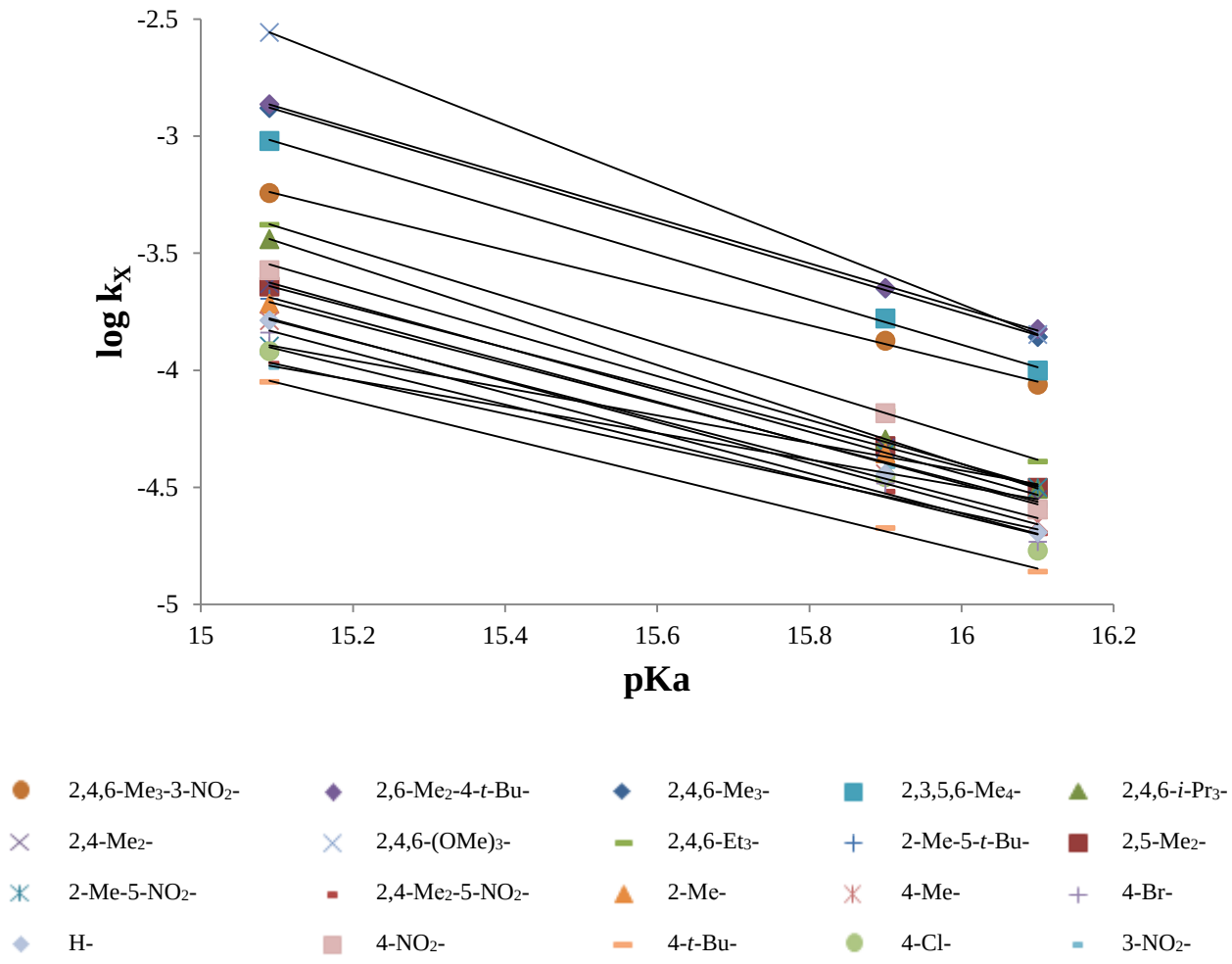


Figure 5.10 Brønsted relationship for the alcoholysis of X-ArSO$_2$Cl at 303 K

Also it is easy to notice the relationship between the electronic nature of the *X* substituent in the benzene ring and the Brønsted exponent (Figure 5.11).

Electron-donor substituents tend to increase $|\beta_{Nuc}|$, the contrary happens with electron-withdrawing ones. 4-NO$_2$-derivative lies out of this dependence that can be attributed to the specific electronic effect of the nitro group at that position.

Table 5.8 Parameters of Brønsted equation (Eq. 5.3) for the alcoholysis of X-ArSO_2Cl at 313 K

X	β_{Nuc}	$\log k_0$	R^2
Sterically unhindered substrates			
4-*t*-Bu-	-0.79±0.03	7.9±0.4	0.999
4-Me-	-0.84±0.04	8.9±0.6	0.998
H-	-0.87±0.07	9±1	0.993
4-Cl-	-0.8±0.1	8±2	0.967
4-Br-	-0.86±0.07	9±1	0.993
3-NO_2-	-0.57±0.05	4.5±0.8	0.993
4-NO_2-	-0.9±0.2	10±3	0.951
Sterically hindered substrates			
2,4,6-OMe_3-	-1.4±0.2	17.8±0.5	0.977
2,4,6-*i*-Pr_3-	-1.06±0.01	12.5±0.1	0.999
2,6-Me_2-4-*t*-Bu-	-0.96±0.01	11.6±0.2	0.999
2,4,6-Me_3-	-0.96±0.01	11.6±0.2	0.999
2,3,5,6-Me_4-	-0.96±0.03	11.5±0.5	0.999
2,4,6-Et_3-	-1.00±0.02	11.7±0.2	0.999
2,4-Me_2-	-0.90±0.04	9.9±0.6	0.998
2-Me-5-*t*-Bu-	-0.88±0.04	9.5±0.7	0.998
2,5-Me_2-	-0.85±0.01	9.2±0.1	0.999
2-Me-	-0.85±0.07	9±1	0.994
2,4,6-Me_3-3-NO_2-	-0.80±0.03	8.9±0.4	0.999
2,4-Me_2-5-NO_2-	-0.71±0.04	6.7±0.6	0.998
2-Me-5-NO_2-	-0.59±0.03	5.0±0.5	0.998

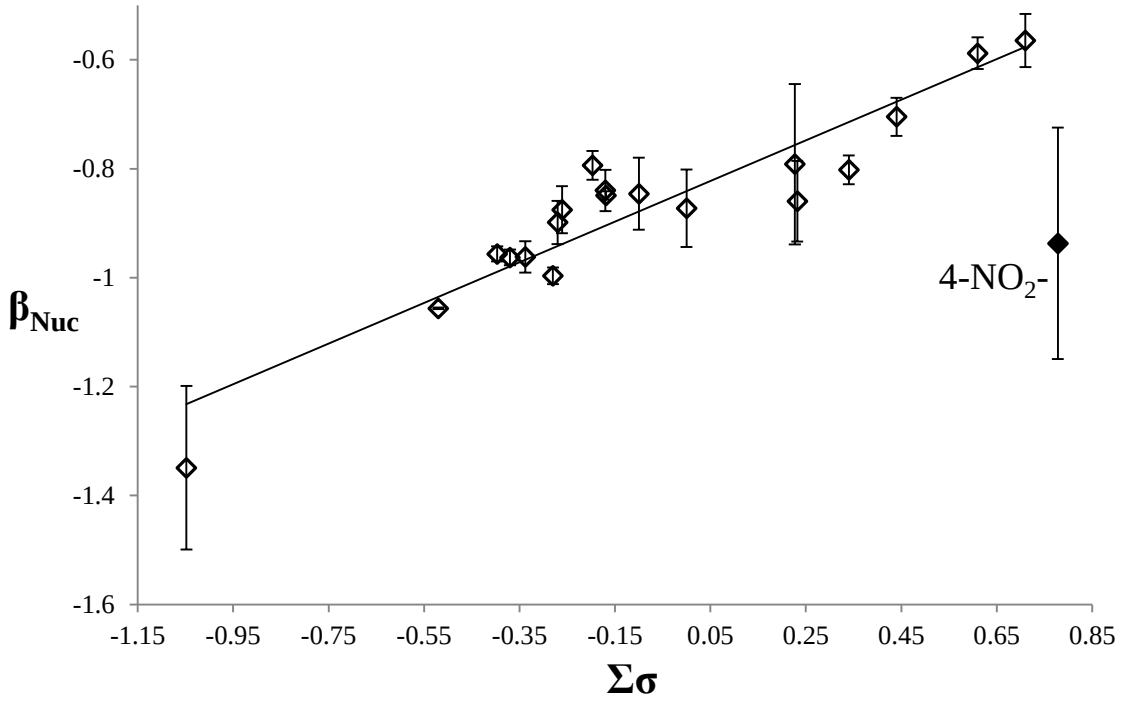


Figure 5.11 β_{Nuc} *vs* Σσ for the solvolysis of X-$ArSO_2Cl$ at 303 K

5.3 TRANSITION STATE IN ARENESULFONYL CHLORIDES ALCOHOLYSIS

5.3.1 Transition state for sterically unhindered arenesulfonyl chlorides alcoholysis

Solvolysis of arenesulfonyl chlorides in alcoholic medium is a complex process influenced by a variety of factors, often non additive and/or in opposite directions. Furthermore, there is a spectrum of TSs for each substrate-nucleophile system with unique features that ultimately determine the extent of the reactivity of the system. The following factors influence the TS: electronic, steric and solvation, which eventually are interdependent.

The values of SKIE for ethanolysis suggest a bimolecular process. The effect of the leaving group also points to the sulfur halide bond breaking does not occur in the rate determining step. These findings and conclusions are supported by

numerous researchers.[9-13] Thus it can be argued that the alcoholysis of the studied substrates can be described by a S_N2 mechanism.

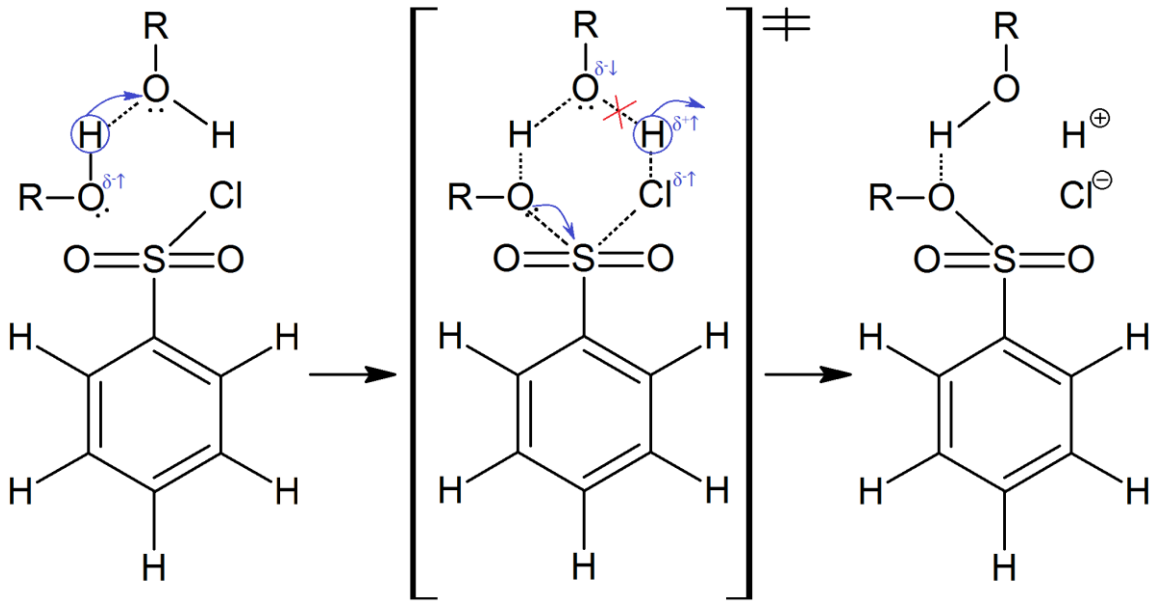
The order of the reaction on the alcohol varies between 2.0 and 3.0, and depends both on the nature of the *X* substituent and its position relative to the reaction center and on the steric volume of the nucleophile (hydrocarbon "tail" of alcohol). Such values suggest a complex TS involving more than one nucleophile molecule; the higher the steric bulk of *ortho*-substituents, the greater the reaction order on the nucleophile.

A small negative value of ρ (Table 5.1), non typical for bimolecular nucleophilic substitution reactions, points to a complex TS with charge delocalization. The relationship between the electronic nature of the *X* substituent and the sensitivity to the ionizing power of the solvent suggests that substituents able to reduce the positive charge on the sulfur atom lead to a TS more dependent on specific solvation.

All the experimental evidences we have collected point to the alcoholysis of arenesulfonyl chlorides taking place through a cyclic transition state with the participation of at least two molecules of the nucleophile (Scheme 5.1). The reaction starts with the substrate being attacked by the nucleophile (a solvent molecule) which belongs to the solvent network, all bonded together by hydrogen bonds.

Such hydrogen bond (R-OH⋯⋯OH-R) implies the interaction between one proton of the attacking molecule and the oxygen of the second molecule of alcohol thus increasing the partial negative charge of oxygen on the attacking nucleophile, *i.e.* its nucleophilicity, and as a result the rate of S⋯O bond formation. Consequently, a cyclic transition state, in which charge redistribution takes place, is formed. Then a partial positive charge on the hydrogen increases ($|\delta^+|\uparrow$) due to the partial neutralization of the charge on the oxygen of the accompanying alcohol molecule ($|\delta^-|\downarrow$) by the proton of the attacking alcohol molecule linked via hydrogen bonds, as well as the increasing interaction with chlorine ($Cl^{\delta-}$- - -$H^{\delta+}$), that causes to protons separate. This second interacting alcohol molecule

incorporates a proton of the attacking molecule and likely remains linked by hydrogen bond with the formed product after the reaction completes. At the end of the reaction the leaving group (-Cl^-) departs and protonates to yield HCl.



Scheme 5.1 Cyclic transition state involving two molecules of the nucleophile

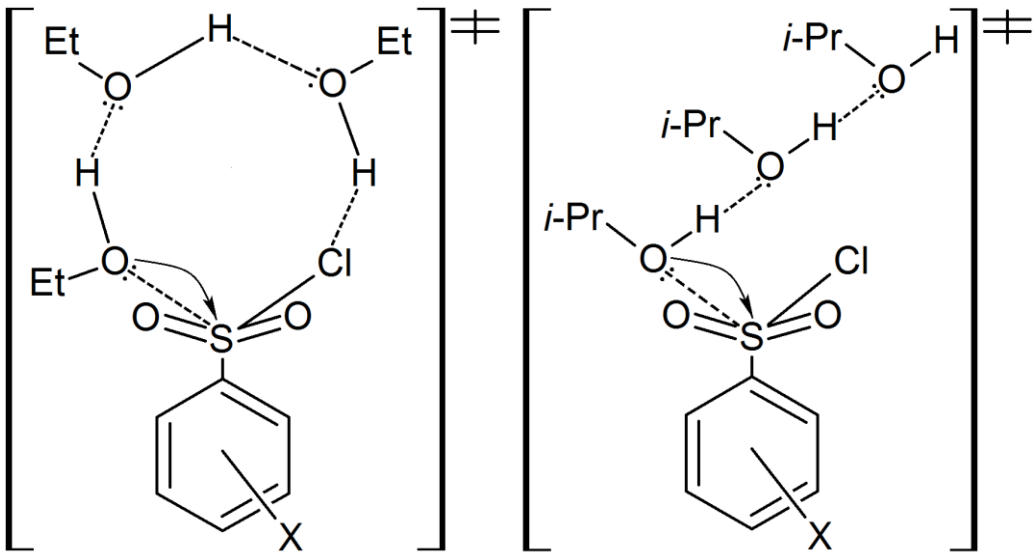
Such TS appropriately explains the low observed values of SIE, as well as the Brønsted parameters. In the cyclic TS the sum of the orders of bond-breaking and bond-forming is less than in the case of the typical nucleophile attack assisted by a second solvent molecule like in general base catalysis, *i.e.* the so-called S_N3-mecanism. [9-11,14]

The influence of the electronic nature of the substituent on the TS and its effect on reactivity is not unambiguous. Electron-withdrawing substituents contribute to the S···O bond formation, whereas electron-donating ones work in opposite direction, *i.e.* lowering the positive charge on sulfur, thereby preventing bond formation. On the other hand, electron-donating substituents increase both leaving group mobility and the negative charge at the chlorine atom ($|\delta^-| \uparrow$), which in turn promotes the hydrogen bond formation Cl- - -H and the cycle closure. Electron-withdrawing substituents reduce the negative charge on the chlorine atom ($|\delta^-| \downarrow$), which does not promote the formation of Cl- - -H bond, *i.e.*, stabilization of the corresponding TS. From this point of view, it becomes clear the practical

equality of alcoholysis reaction rates for benzenesulfonyl chloride and 4-Me-benzenesulfonyl chloride. Methyl group promotes stabilization of the cycle and eliminates its negative impact on bond-forming, and as a consequence the reactivity remains practically unchanged.

Some substrates demonstrate reaction order toward nucleophile close to 3 for ethanolysis. The most favorable packing of the molecules in the TS corresponds to 8-membered ring (Scheme 5.2 a.) due to steric hindrances caused by the ethyl groups of alcohol, as well as the steric hindrance in the vicinity of the sulfur atom in the substrate. In such structure the angles in which the hydrogens are the vertexes are almost straight, thus facilitating proton transfer and compensating the steric hindrance.

The change of ρ sign (Table 5.1) in going from unbranched alcohols to *iso*-propanol implies a significant difference in the TS involving these nucleophiles. TS for *iso*-propanolysis is more polar than for unbranched alcohols. More polar TSs occur in less polar media with a net decrease of substrate reactivity. This conclusion is corroborated by log k_{obs} *vs.* $1/\xi$ relationship (Table 5.4 & Fig. 5.7); the sensitivity (*U*) is higher for *iso*-propanol than for methanol and ethanol.



a. b.

Scheme 5.2 TS involving three alcohol molecules a. Cyclic TS; b. S_N3-like TS.

The different behavior of *iso*-propanolysis cannot be explained by the difference in the polarity of the medium because the experiment was carried out partially in the same experimental intervals of mixtures polarities (see Chapter 4.2.1). Most likely, the cause of TS change is the large steric hindrance of bulky *iso*-propyl groups of the alcohol that prevent formation of the cyclic TS. The high reaction order on the nucleophile (b ~ 3) in *iso*-propanol points to a TS involving three alcohol molecules that could be described according to a S_N3-like mechanism (Scheme 5.2b).[14]

5.3.2 Positive *ortho* steric effect of alkyl groups and transition state structure for sterically hindered sulfonyl chlorides

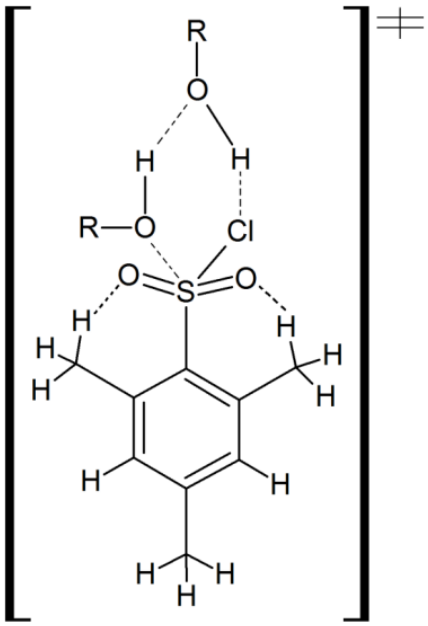
There are several hypotheses on the origin of the positive *ortho* steric effect in sulfur chemistry. According to the earliest of them [15], *ortho*-alkylated substrates change the reaction mechanism of solvolysis from S_N2 to S_N1, which explains the U-shaped dependence of the Hammett plot. However, subsequently it was proposed by many authors (see the chapter 2.1.1.1) that all arenesulfonyl chlorides undergo solvolysis under S_N2-mechanism. The results for hindered and unhindered arenesulfonyl chlorides presented in this research (isokinetic dependence, similarity of activation parameters, SKIE, and the effect of the leaving group) are in full agreement with this view.

The hypothesis of hyperconjugation was put forward to explain the above discussed discrepancies [16], but, experimental results of the secondary KIE of 2,4,6-Me_3-benzenesulfonyl chloride does not support the hypothesis of σ-π-hyperconjugation.

A change of the attack type from the backside to frontal axial or to frontal equatorial one was considered as a possible cause of the acceleration by *ortho*-alkyl groups; however, computer modeling for various sulfonyl systems does not support this theory [17].

We have hypothesized the interaction between hydrogen atoms of *ortho*-alkyl groups and oxygen atoms of the sulfo group and/or solvent molecules in the TS. However, the absence of secondary KIE —for the solvolysis of deuterated 2,4,6-Me_3-benzenesulfonyl chloride suggests that these interactions do not have a noticeable influence on the rate determining step of the reaction, which generally does not deny the fact of their presence.

In considering the influence of steric factors we should remember that sulfonyl chloride group has the possibility of free rotation around the S-C bond in sterically unhindered substrates. The introduction of two *ortho*-alkyl groups limits this rotation significantly [18, 19]. It may promote more rapid formation of the TS involving of second molecule of solvent, Scheme 5.3.



Scheme 5.3 Cyclic transition state involving two nucleophile molecules in the hindered 2,4,6-Me_3-benzenesulfonyl chloride alcoholysis; R=Me-, Et-, Pr-.

A gradual reduction of acceleration change (k_X/k_H) is observed relative to the unsubstituted benzenesulfonyl chloride on the alcohol concentration of the solution C_N (Figure 5.12). These relations might be explained by different polarities of TSs for hindered and unhindered substrates.

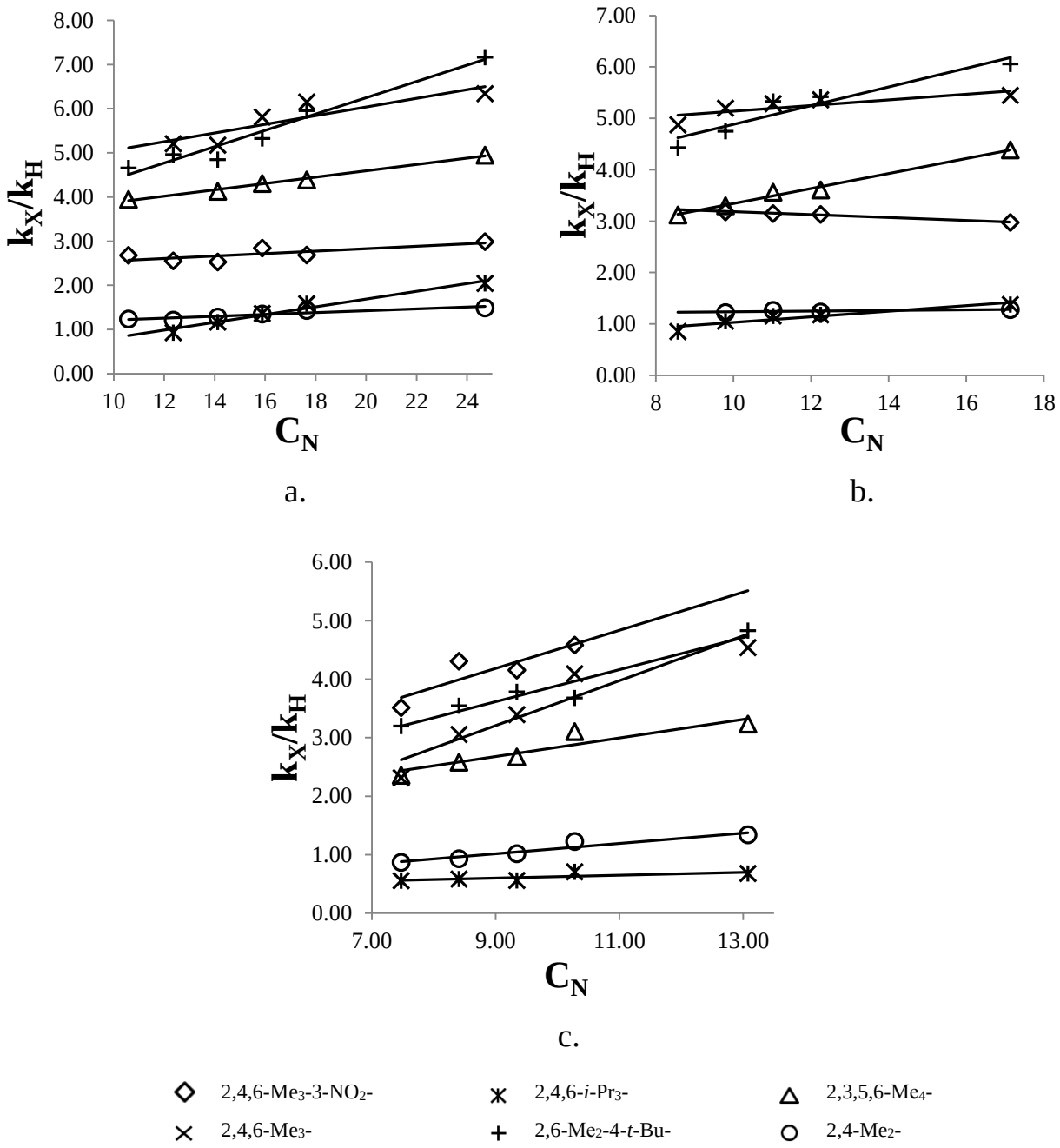


Figure 5.12 k_X/k_H *vs.* C_N for alcoholysis of arenesulfonyl chlorides at 323K
a. methanolysis; b. ethanolysis; c. *iso*-propanolysis

It should be noted that the positive *ortho*-effect tends to decrease in the series MeOH – EtOH – PrOH – *i*-PrOH, and the effect on k_X/k_H is still significant even for *iso*-propanolysis (Figure 5.12c.) where S_N3-like TS might take place. Thus we have to conclude that *o*-alkyl groups have more general mechanism of TS

stabilization that includes both of the types of TS at nucleophilic substitution (Scheme 5.2).

It is possible that *o*-alkyl groups limit the backside approach of the nucleophile whereby creating the preconditions for a frontal attack on the sulfur atom (Figure 5.13). On one hand this would facilitate a more compact arrangement of alcohol molecules in the cyclic TS, but on the other, energy is not required because oxygens of the sulfo group do not have to move as it would be in the case of backside attack (Fig. 4.22).

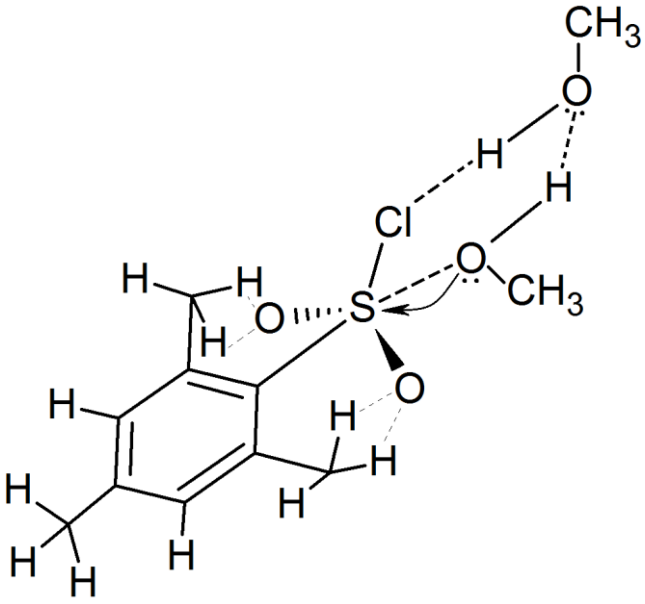


Figure 5.13 Frontal nucleophilic attack at the hindered reaction center during arenesulfonyl chloride methanolysis

2,4,6-*i*-Pr_3-benzenesulfonyl chloride along with other sterically hindered substrates exhibit large *m* =1.39, but do not show a significant acceleration relative to the extended model series. The sensitivity to solvent polarity (*U*) is comparable in all alcohols (Table 5.4) that could point to S_N3-like mechanism [14] for the solvolysis of this substrate. Likely it is related to the rather large steric bulk *iso*-propyl groups that cause tension in the benzene ring, and shield the reaction center [20]. It causes the inability of the cyclic TS formation even for small methanol molecules.

2,4,6-$(OMe)_3$-benzenesulfonyl chloride demonstrate the highest reactivity among all alcohols, but it cannot be related with S_N1-like TS due to the very low sensitivity to solvent polarity (*U*). Activation parameters just confirm this conclusion. Likely the mechanism of acceleration by (*o*-OMe-) groups is similar to the mechanism of the (*o*-Me-) ones.

As the charge redistribution in the cyclic TS plays a relevant role, the reactivity decline is quite natural; in favor of this hypothesis we can stand out the following facts:

1. The distance between the oxygens of sulfo groups and the hydrogens of *ortho*-methyl groups (2.3-3.0 Å) is comparable to the length of hydrogen bonds (2.30-2.70 Å); the larger value of the van der Waals radii sum of an oxygen and a hydrogen atoms (Σr_W = 2.72 Å) proves the C-H···O intramolecular interaction in the molecule of hindered arenesulfonyl chloride.
2. The constancy of T_{iso} for all *ortho*-alkylated substrates in the series EtOH – PrOH – *i*-PrOH points to a stable structure of the TS for these systems. The proximity of T_{iso} to experimental range of temperatures indicates the relevance of steric factors in the transition state, *i.e.*, a more rigid configuration of the molecules in the cycle.
3. The high values of sensitivity to ionizing power of the solvent *m*, higher than average for the whole series.
4. The low and negative magnitude of the Brønsted parameter (β_{Nuc}) for the solvolysis of hindered arenesulfonyl chlorides indicates that proton transfer limits the reaction rate in more extent than in case of the unhindered compounds; it points to an easier TS formation for *ortho*-alkylated substrates.
5. The positive *ortho*-effect (k_X/k_H) decreases in more aprotic media.

5.4 CONCLUSIONS

The positive *ortho*-effect is a complicated phenomenon which is based on a number of factors:

- The specific solvation of sulfonyl compounds facilitates the conditions for a cyclic or a S_N3-like transition state with the participation of few solvent molecules;
- The electronic effect of methyl groups promotes the cycle formation as well as its consequent deprotonation;
- The steric effect of *ortho*-alkyl groups is the result of the C-H···O intramolecular interaction between the oxygens of sulfo group and the hydrogens of the *ortho*-methyl groups, that creates the preconditions for a frontal attack onto the sulfur atom.

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6 CONCLUSIONS

The influence of the accelerating effect of alkyl groups in *ortho*-position to sulfonyl center on the process of nucleophilic substitution was studied and confirmed for a large set of substrates. For the first time it was studied the kinetics of sterically hindered arenesulfonyl chlorides in methanol, ethanol, propanol, *iso*-propanol, alcohols of different polarity, including their dependence on the following variables: structure of the substrate, properties of the reaction medium, nature of the leaving group, secondary kinetic isotope effects and solvent isotope effects.

The following sulfonyl compounds were synthesized: 4-*tert*-butyl benzenesulfonyl chloride; 2,4,6-trimethylbenzenesulfonyl chloride; 2,4,6-triethylbenzenesulfonyl chloride; 2-methyl-5-nitrobenzenesulfonyl chloride; 2,4-dimethylbenzenesulfonyl chloride; 2,5-dimethylbenzene sulfonyl chloride; 5-*tert*-butyl-2-methylbenzenesulfonyl chloride; 4-*tert*-butyl-2,6-dimethylbenzenesulfonyl chloride; 2,3,5,6-tetramethylbenzene sulfonyl chloride; 2,4-dimethyl-5-nitrobenzenesulfonyl chloride; 2,4,6-trimethyl-3-nitrobenzenesulfonyl chloride; 2,4,6-Trimethoxybenzene sulfonyl chloride; 4-methylbenzenesulfonyl chloride; 2,4,6-tris [($^{2}H_{3}$)methyl]($^{2}H_{2}$) benzene sulfonyl chloride. Their structure and purity were confirmed by ^{1}H & ^{13}C NMR spectroscopy and monocrystal X-ray diffraction.

Kinetic studies were carried out spectrophotometrically under pseudo-first order with respect to the nucleophile at temperatures 303-323K. The obtained kinetic data were analyzed in terms of the following linear free energy relationships: Hammett equation, Grunwald–Winstein equation, Brønsted equation and Kirkwood function. The dependence of kinetics on temperature was also studied using Arrhenius and Wynne-Jones - Eyring equations.

The following conclusions have been obtained:

- From Arrhenius and the Wynne-Jones - Eyring equations the reaction series were characterized by calculated values of T_{iso} confirming the importance of steric interactions in TS. The kinetic measurements were carried out partially in the entropic control zone for ethanol, propanol and *iso*-propanol. An isoenthalpic series was demonstrated for methanolysis.

- Solvent isotope effects (SIE) are similar to those published of analogous systems and consistent with a S_N2 mechanism.

- We have hypothesized the interaction between hydrogen atoms of *ortho*-alkyl groups and oxygen atoms of the sulfo group and/or solvent molecules in the initial state. X-Ray analysis proves the existence of the intramolecular interactions that may be the reason of the so called "positive steric effect", and explain the abnormal reactivity of those hindered compounds. On the other hand it is quite possible that *ortho*-alkyl groups limit backside approach of the nucleophile, creating the preconditions for a frontal attack of the sulfur atom.

- The absence of secondary kinetic isotope effect of the substrate (2,4,6)-tris [($^2H_3$)methyl]($^2H_2$) benzenesulfonyl chloride) let us neglect the idea of σ-π-hyperconjugation in this particular case. It follows that non-covalent intramolecular interactions between the *o*-methyl hydrogens and oxygen atoms of the sulfonyl group or/and solvent molecules are typical for hindered arenesulfonyl chlorides, and play a specific role in the formation of the S_N2-like transition state.

- Relatively low values of the leaving group effect (k_{Br}/k_{Cl} = 4 – 6) indicate the asymmetry of the TS with prevalence of bond-formation, which could be caused by the structural features of the substrates, as well as an important contribution of the specific solvation.

- Experimental determination of the reaction order with respect to the nucleophile shows that the reaction order varies between 2 and 3 for all alcohols. Large negative activation entropy values, and low, and similar, activation enthalpy values are consistent with a S_N2 mechanism with participation of, at least, a second solvent molecule in the TS. Thus, we hypothesize the existence of a polymolecular cyclic TS. Likely there is a spectrum of TS of S_N2-type whose specificity is determined by particular solvent interaction with each of the substrates.

- Electron withdrawing substituents, generally speaking, tend to decrease the sensitivity to the ionizing power of solvent *m* and the Brønsted exponent $|\beta_{Nuc}|$, whereas electron-donor substituents increase it, which points to a tangible contribution of the proton transfer to the activation Gibbs free energy of the reaction.

- All previous indirect evidences on the solvolysis mechanism of arenesulfonyl chlorides (kinetic rate laws, kinetic isotope effect, change of the nucleophile, solvent, etc.), as well as the presence of isokinetic dependencies and similar thermodynamic activation parameters for all the studied substrates point to a single bimolecular mechanism of substitution similar to S_N2 involving of at least a second molecule of the solvent in the TS through general base catalysis, likely involved in a cyclic TS.

- The change of the Hammett's ρ from negative in case of methanol, ethanol and propanol to positive for *iso*-propanol allows us to conclude that the structure and molecularity of the TS strongly depends on the structure of nucleophile, and can be cyclic in case of the unbranched alcohols (methanol, ethanol, propanol) or classical (S_N3-like mechanism) for alcohols with bulky hydrocarbon groups (*iso*-propanol).

- In case of 2,4,6-tri(propan-2-yl)benzenesulfonyl chloride a large steric volume of bulky *o*-alkyl groups promotes the formation of linear TS of S_N3-type that facilities the removal of steric hindrance to the nucleophile attack, which reflects on its reactivity.

As a summary, in this work we have obtained new data for structural parameters of aromatic sulfonic acids derivatives (sulfonyl chlorides; arenesulfonates of methanol, ethanol, propanol and *iso*-propanol), as well as reaction rate constants of alcoholysis of arenesulfonyl derivatives in various media, and kinetic correlations to describe the reactivity of substituted arenesulfonyl derivatives in these systems.

New concepts of the substitution mechanism at the sterically shielded sulfonyl center develop the theory of nucleophilic substitution processes in coordination-unsaturated centers, and are useful to introduce modifications and improvements in the knowledge of chemical processes involving arenesulfonyl compounds.

ANNEXES

A1- X-RAY ANALYSIS OF 2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE

TABLE A1.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR 2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE.

EMPIRICAL FORMULA	$C_9H_{11}CLO_5S$
FORMULA WEIGHT	266.69
TEMPERATURE	274(2) K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	TRICLINIC
SPACE GROUP	P -1
UNIT CELL DIMENSIONS	A = 7.6402(3) Å, A= 80.133(3)°.
	B = 8.1035(4) Å, B= 87.089(3)°.
	C = 9.2804(5) Å, Γ= 88.885(3)°.
VOLUME	565.31(5) $Å^3$
Z	2
DENSITY (CALCULATED)	1.567 MG/M^3
ABSORPTION COEFFICIENT	0.525 MM^{-1}
F(000)	276
CRYSTAL SIZE	0.370 × 0.350 × 0.110 MM^3
THETA RANGE FOR DATA COLLECTION	2.230 TO 27.521°.
INDEX RANGES	-9<=H<=9, -10<=K<=10, -11<=L<=11
REFLECTIONS COLLECTED	12580
INDEPENDENT REFLECTIONS	2341 [R(INT) = 0.0322]
COMPLETENESS TO THETA = 26.000°	99.1 %
ABSORPTION CORRECTION	SEMI-EMPIRICAL FROM EQUIVALENTS
MAX. AND MIN. TRANSMISSION	0.7455 AND 0.6763
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	2341 / 0 / 148
GOODNESS-OF-FIT ON F^2	1.050
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0395, WR2 = 0.0956
R INDICES (ALL DATA)	R1 = 0.0548, WR2 = 0.1050
EXTINCTION COEFFICIENT	N/A
LARGEST DIFF. PEAK AND HOLE	0.369 AND -0.437 E. $Å^{-3}$

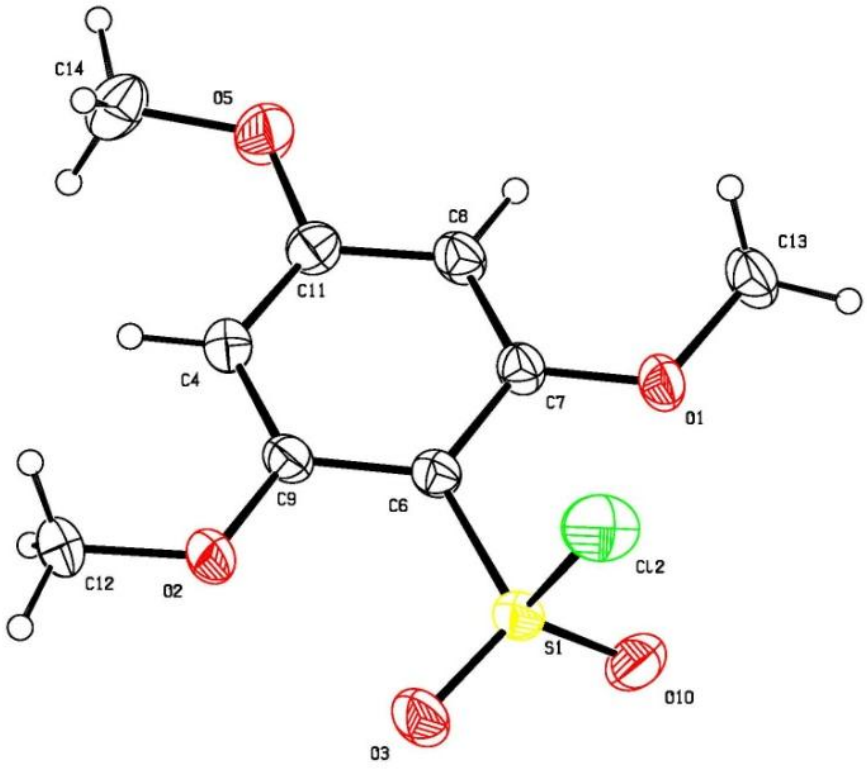


TABLE A1.2.-ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)*
S(1)	2907(1)	6728(1)	3004(1)	44(1)
CL(2)	2543(1)	5905(1)	5187(1)	76(1)
O(1)	2804(2)	9939(2)	3934(2)	49(1)
O(2)	-393(2)	6446(2)	1499(2)	55(1)
O(3)	2650(2)	5324(2)	2328(2)	64(1)
C(4)	-1495(3)	9209(3)	1597(2)	44(1)
O(5)	-2435(2)	12001(2)	1830(2)	61(1)
C(6)	1256(3)	8237(2)	2642(2)	39(1)
C(7)	1415(3)	9785(3)	3132(2)	40(1)
C(8)	170(3)	11021(3)	2820(2)	45(1)
C(9)	-243(3)	7949(3)	1896(2)	40(1)
O(10)	4577(2)	7489(2)	2812(2)	62(1)
C(11)	-1272(3)	10713(3)	2057(2)	44(1)
C(12)	-1865(3)	6133(3)	701(3)	57(1)
C(13)	3000(3)	11461(3)	4491(3)	55(1)
C(14)	-4028(3)	11774(3)	1169(3)	65(1)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A1.3 - BOND LENGTHS [Å] AND ANGLES [°] FOR 2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE

S(1)-O(3)	1.4118(16)	C(11)-C(4)-H(4)	120.3
S(1)-O(10)	1.4172(17)	C(9)-C(4)-H(4)	120.3
S(1)-C(6)	1.744(2)	C(11)-O(5)-C(14)	119.09(19)
S(1)-CL(2)	2.0281(9)	C(9)-C(6)-C(7)	119.17(18)
O(1)-C(7)	1.346(2)	C(9)-C(6)-S(1)	121.98(15)
O(1)-C(13)	1.430(2)	C(7)-C(6)-S(1)	118.85(15)
O(2)-C(9)	1.340(2)	O(1)-C(7)-C(8)	123.19(19)
O(2)-C(12)	1.427(3)	O(1)-C(7)-C(6)	116.48(17)
C(4)-C(11)	1.375(3)	C(8)-C(7)-C(6)	120.31(19)
C(4)-C(9)	1.388(3)	C(7)-C(8)-C(11)	119.12(19)
C(4)-H(4)	0.9300	C(7)-C(8)-H(8)	120.4
O(5)-C(11)	1.353(3)	C(11)-C(8)-H(8)	120.4
O(5)-C(14)	1.420(3)	O(2)-C(9)-C(4)	122.48(19)
C(6)-C(9)	1.412(3)	O(2)-C(9)-C(6)	117.82(18)
C(6)-C(7)	1.415(3)	C(4)-C(9)-C(6)	119.70(19)
C(7)-C(8)	1.372(3)	O(5)-C(11)-C(4)	123.4(2)
C(8)-C(11)	1.389(3)	O(5)-C(11)-C(8)	114.4(2)
C(8)-H(8)	0.9300	C(4)-C(11)-C(8)	122.2(2)
C(12)-H(12A)	0.9600	O(2)-C(12)-H(12A)	109.5
C(12)-H(12B)	0.9600	O(2)-C(12)-H(12B)	109.5
C(12)-H(12C)	0.9600	H(12A)-C(12)-H(12B)	109.5
C(13)-H(13A)	0.9600	O(2)-C(12)-H(12C)	109.5
C(13)-H(13B)	0.9600	H(12A)-C(12)-H(12C)	109.5
C(13)-H(13C)	0.9600	H(12B)-C(12)-H(12C)	109.5
C(14)-H(14A)	0.9600	O(1)-C(13)-H(13A)	109.5
C(14)-H(14B)	0.9600	O(1)-C(13)-H(13B)	109.5
C(14)-H(14C)	0.9600	H(13A)-C(13)-H(13B)	109.5
O(3)-S(1)-O(10)	118.05(11)	O(1)-C(13)-H(13C)	109.5
O(3)-S(1)-C(6)	112.23(10)	H(13A)-C(13)-H(13C)	109.5
O(10)-S(1)-C(6)	110.45(10)	H(13B)-C(13)-H(13C)	109.5
O(3)-S(1)-CL(2)	105.88(9)	O(5)-C(14)-H(14A)	109.5
O(10)-S(1)-CL(2)	105.74(9)	O(5)-C(14)-H(14B)	109.5
C(6)-S(1)-CL(2)	103.04(7)	H(14A)-C(14)-H(14B)	109.5
C(7)-O(1)-C(13)	118.72(16)	O(5)-C(14)-H(14C)	109.5
C(9)-O(2)-C(12)	119.20(18)	H(14A)-C(14)-H(14C)	109.5
C(11)-C(4)-C(9)	119.4(2)	H(14B)-C(14)-H(14C)	109.5

TABLE A1.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	45(1)	40(1)	48(1)	-15(1)	-7(1)	6(1)
CL(2)	95(1)	78(1)	52(1)	1(1)	-6(1)	22(1)
O(1)	49(1)	42(1)	62(1)	-21(1)	-19(1)	1(1)
O(2)	51(1)	47(1)	76(1)	-32(1)	-18(1)	3(1)
O(3)	76(1)	49(1)	78(1)	-31(1)	-28(1)	17(1)
C(4)	42(1)	46(1)	44(1)	-11(1)	-8(1)	-1(1)
O(5)	59(1)	47(1)	80(1)	-14(1)	-23(1)	15(1)
C(6)	41(1)	35(1)	42(1)	-10(1)	-4(1)	2(1)
C(7)	42(1)	36(1)	42(1)	-9(1)	-5(1)	-4(1)
C(8)	53(1)	34(1)	50(1)	-12(1)	-9(1)	1(1)
C(9)	44(1)	39(1)	41(1)	-14(1)	-1(1)	-3(1)
O(10)	40(1)	62(1)	87(1)	-21(1)	-1(1)	3(1)
C(11)	47(1)	40(1)	46(1)	-4(1)	-6(1)	5(1)
C(12)	52(1)	59(2)	69(2)	-31(1)	-13(1)	-8(1)
C(13)	65(2)	44(1)	62(2)	-21(1)	-15(1)	-6(1)
C(14)	52(2)	65(2)	75(2)	-2(1)	-16(1)	13(1)

THE ANISOTROPIC DISPLACEMENT FACTOR EXPONENT TAKES THE FORM: $-2P^2[H^2 A^2 U^{11} + ... + 2 H K A \cdot B \cdot U^{12}]$

TABLE A1.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)
H(4)	-2476	9038	1089	52
H(8)	290	12051	3116	53
H(12A)	-1917	6960	-171	85
H(12B)	-2921	6190	1298	85
H(12C)	-1748	5039	439	85
H(13A)	3101	12382	3690	82
H(13B)	4036	11388	5043	82
H(13C)	1995	11634	5113	82
H(14A)	-3778	11568	191	98
H(14B)	-4745	12765	1138	98
H(14C)	-4640	10836	1732	98

TABLE A1.6 - TORSION ANGLES [°] FOR 2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE

O(3)-S(1)-C(6)-C(9)	6.8(2)
O(10)-S(1)-C(6)-C(9)	140.76(18)
CL(2)-S(1)-C(6)-C(9)	-106.68(17)
O(3)-S(1)-C(6)-C(7)	-174.24(17)
O(10)-S(1)-C(6)-C(7)	-40.3(2)
CL(2)-S(1)-C(6)-C(7)	72.31(17)
C(13)-O(1)-C(7)-C(8)	0.0(3)
C(13)-O(1)-C(7)-C(6)	-178.3(2)
C(9)-C(6)-C(7)-O(1)	175.04(19)
S(1)-C(6)-C(7)-O(1)	-4.0(3)
C(9)-C(6)-C(7)-C(8)	-3.3(3)
S(1)-C(6)-C(7)-C(8)	177.70(17)
O(1)-C(7)-C(8)-C(11)	-176.3(2)
C(6)-C(7)-C(8)-C(11)	1.9(3)
C(12)-O(2)-C(9)-C(4)	1.9(3)
C(12)-O(2)-C(9)-C(6)	-178.0(2)
C(11)-C(4)-C(9)-O(2)	179.0(2)
C(11)-C(4)-C(9)-C(6)	-1.2(3)
C(7)-C(6)-C(9)-O(2)	-177.26(19)
S(1)-C(6)-C(9)-O(2)	1.7(3)
C(7)-C(6)-C(9)-C(4)	2.9(3)
S(1)-C(6)-C(9)-C(4)	-178.11(16)
C(14)-O(5)-C(11)-C(4)	4.2(3)
C(14)-O(5)-C(11)-C(8)	-174.8(2)
C(9)-C(4)-C(11)-O(5)	-179.1(2)
C(9)-C(4)-C(11)-C(8)	-0.2(3)
C(7)-C(8)-C(11)-O(5)	178.85(19)
C(7)-C(8)-C(11)-C(4)	-0.2(3)

SYMMETRY TRANSFORMATIONS USED TO GENERATE EQUIVALENT ATOMS.

A2- X-RAY ANALYSIS OF 2,4,6-TRIMETHYLBENZENESULFONYL CHLORIDE

TABLE A2.1. CRYSTAL DATA AND STRUCTURE REFINEMENT FOR 2,4,6-TRIMETHYLBENZENESULFONYL CHLORIDE

EMPIRICAL FORMULA	$C_9H_{11}CLO_2S$
FORMULA WEIGHT	218.69
TEMPERATURE	298(2) K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	TRICLINIC
SPACE GROUP	P -1
UNIT CELL DIMENSIONS	A = 7.8846(6) Å, A= 66.091(5)°.
	B = 7.9642(6) Å, B= 79.298(5)°.
	C = 9.2544(8) Å, Γ = 77.355(5)°.
VOLUME	515.30(7) $Å^3$
Z	2
DENSITY (CALCULATED)	1.409 MG/M^3
ABSORPTION COEFFICIENT	0.538 MM^{-1}
F(000)	228
CRYSTAL SIZE	0.500 × 0.350 × 0.220 MM^3
THETA RANGE FOR DATA COLLECTION	2.663 TO 26.371°.
INDEX RANGES	-9<=H<=9, -9<=K<=9, -11<=L<=11
REFLECTIONS COLLECTED	7989
INDEPENDENT REFLECTIONS	2105 [R(INT) = 0.0393]
COMPLETENESS TO THETA = 25.242°	99.9 %
ABSORPTION CORRECTION	MULTISCAN
MAX. AND MIN. TRANSMISSION	0.7456 AND 0.6503
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	2105 / 0 / 122
GOODNESS-OF-FIT ON F^2	1.096
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0485, WR2 = 0.1303
R INDICES (ALL DATA)	R1 = 0.0742, WR2 = 0.1482
EXTINCTION COEFFICIENT	0.057(9)
LARGEST DIFF. PEAK AND HOLE	0.334 AND -0.319 E. $Å^{-3}$

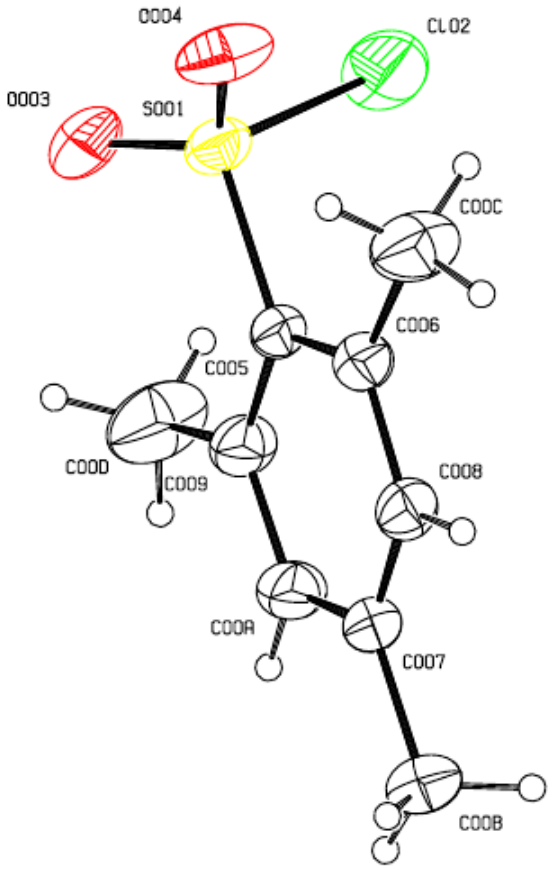


TABLE A2.2.-ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIMETHYLBENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)*
S(001)	12362(1)	3424(1)	2688(1)	58(1)
CL(02)	12552(1)	3667(2)	396(1)	116(1)
O(003)	13921(3)	3874(3)	2858(3)	83(1)
O(004)	12004(3)	1611(3)	3616(3)	90(1)
C(005)	10548(3)	5142(3)	2763(3)	46(1)
C(006)	8881(3)	4643(4)	3287(3)	51(1)
C(007)	7704(4)	7856(4)	2880(3)	57(1)
C(008)	7507(3)	6040(4)	3333(3)	55(1)
C(009)	10809(3)	6985(4)	2255(4)	60(1)
C(00A)	9357(4)	8295(4)	2338(4)	70(1)
C(00B)	6153(4)	9337(5)	2936(5)	83(1)
C(00C)	8437(4)	2724(4)	3777(5)	88(1)
C(00D)	12553(4)	7656(5)	1615(6)	112(2)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A2.3. - BOND LENGTHS [Å] AND ANGLES [°]
FOR 2,4,6-TRIMETHYLBENZENESULFONYL CHLORIDE

S(001)-O(003)	1.405(2)	C(008)-C(006)-C(005)	117.1(2)
S(001)-O(004)	1.409(2)	C(008)-C(006)-C(00C)	116.9(2)
S(001)-C(005)	1.763(2)	C(005)-C(006)-C(00C)	126.1(2)
S(001)-CL(02)	2.0301(12)	C(008)-C(007)-C(00A)	117.7(2)
C(005)-C(009)	1.398(4)	C(008)-C(007)-C(00B)	121.2(3)
C(005)-C(006)	1.399(4)	C(00A)-C(007)-C(00B)	121.1(3)
C(006)-C(008)	1.381(4)	C(007)-C(008)-C(006)	123.4(3)
C(006)-C(00C)	1.509(4)	C(007)-C(008)-H(008)	118.3
C(007)-C(008)	1.369(4)	C(006)-C(008)-H(008)	118.3
C(007)-C(00A)	1.373(4)	C(00A)-C(009)-C(005)	117.3(2)
C(007)-C(00B)	1.511(4)	C(00A)-C(009)-C(00D)	117.6(3)
C(008)-H(008)	0.9300	C(005)-C(009)-C(00D)	125.1(3)
C(009)-C(00A)	1.384(4)	C(007)-C(00A)-C(009)	122.9(3)
C(009)-C(00D)	1.513(4)	C(007)-C(00A)-H(00A)	118.5
C(00A)-H(00A)	0.9300	C(009)-C(00A)-H(00A)	118.5
C(00B)-H(00B)	0.9600	C(007)-C(00B)-H(00B)	109.5
C(00B)-H(00C)	0.9600	C(007)-C(00B)-H(00C)	109.5
C(00B)-H(00D)	0.9600	H(00B)-C(00B)-H(00C)	109.5
C(00C)-H(00E)	0.9600	C(007)-C(00B)-H(00D)	109.5
C(00C)-H(00F)	0.9600	H(00B)-C(00B)-H(00D)	109.5
C(00C)-H(00G)	0.9600	H(00C)-C(00B)-H(00D)	109.5
C(00D)-H(00H)	0.9600	C(006)-C(00C)-H(00E)	109.5
C(00D)-H(00I)	0.9600	C(006)-C(00C)-H(00F)	109.5
C(00D)-H(00J)	0.9600	H(00E)-C(00C)-H(00F)	109.5
O(003)-S(001)-O(004)	117.68(14)	C(006)-C(00C)-H(00G)	109.5
O(003)-S(001)-C(005)	112.03(13)	H(00E)-C(00C)-H(00G)	109.5
O(004)-S(001)-C(005)	112.23(13)	H(00F)-C(00C)-H(00G)	109.5
O(003)-S(001)-CL(02)	106.16(11)	C(009)-C(00D)-H(00H)	109.5
O(004)-S(001)-CL(02)	105.39(12)	C(009)-C(00D)-H(00I)	109.5
C(005)-S(001)-CL(02)	101.59(9)	H(00H)-C(00D)-H(00I)	109.5
C(009)-C(005)-C(006)	121.6(2)	C(009)-C(00D)-H(00J)	109.5
C(009)-C(005)-S(001)	118.9(2)	H(00H)-C(00D)-H(00J)	109.5
C(006)-C(005)-S(001)	119.44(19)	H(00I)-C(00D)-H(00J)	109.5

TABLE A2.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIMETHYLBENZENESULFONYL CHLORIDE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(001)	48(1)	61(1)	60(1)	-26(1)	-8(1)	10(1)
CL(02)	109(1)	159(1)	78(1)	-73(1)	-17(1)	44(1)
O(003)	44(1)	93(2)	111(2)	-44(1)	-20(1)	10(1)
O(004)	79(2)	49(1)	114(2)	-18(1)	-2(1)	12(1)
C(005)	41(1)	50(2)	48(1)	-22(1)	-9(1)	2(1)
C(006)	47(2)	52(2)	56(2)	-23(1)	-7(1)	-4(1)
C(007)	48(2)	61(2)	69(2)	-37(1)	-16(1)	8(1)
C(008)	41(2)	64(2)	61(2)	-28(1)	-4(1)	-5(1)
C(009)	44(2)	56(2)	84(2)	-29(2)	-8(1)	-7(1)
C(00A)	61(2)	52(2)	105(3)	-38(2)	-20(2)	-2(1)
C(00B)	67(2)	78(2)	112(3)	-53(2)	-24(2)	20(2)
C(00C)	64(2)	58(2)	138(3)	-31(2)	-6(2)	-14(2)
C(00D)	56(2)	75(2)	190(5)	-33(3)	-8(2)	-20(2)

TABLE A2.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)
H(008)	6391	5732	3691	66
H(00A)	9506	9526	2012	83
H(00B)	6547	10505	2625	125
H(00C)	5569	8995	3997	125
H(00D)	5357	9451	2220	125
H(00E)	7190	2784	3958	133
H(00F)	8944	1904	4736	133
H(00G)	8895	2262	2948	133
H(00H)	12374	8992	1198	167
H(00I)	13101	7224	785	167
H(00J)	13291	7179	2457	167

TABLE A2.6 - TORSION ANGLES [°] FOR2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE

O(003)-S(001)-C(005)-C(009)	28.9(3)
O(004)-S(001)-C(005)-C(009)	163.8(2)
CL(02)-S(001)-C(005)-C(009)	-84.0(2)
O(003)-S(001)-C(005)-C(006)	-152.9(2)
O(004)-S(001)-C(005)-C(006)	-17.9(3)
CL(02)-S(001)-C(005)-C(006)	94.2(2)
C(009)-C(005)-C(006)-C(008)	-2.2(4)
S(001)-C(005)-C(006)-C(008)	179.59(19)
C(009)-C(005)-C(006)-C(00C)	176.5(3)
S(001)-C(005)-C(006)-C(00C)	-1.7(4)
C(00A)-C(007)-C(008)-C(006)	0.7(4)
C(00B)-C(007)-C(008)-C(006)	179.3(3)
C(005)-C(006)-C(008)-C(007)	0.8(4)
C(00C)-C(006)-C(008)-C(007)	-178.1(3)
C(006)-C(005)-C(009)-C(00A)	2.0(4)
S(001)-C(005)-C(009)-C(00A)	-179.7(2)
C(006)-C(005)-C(009)-C(00D)	-177.6(3)
S(001)-C(005)-C(009)-C(00D)	0.6(4)
C(008)-C(007)-C(00A)-C(009)	-0.9(5)
C(00B)-C(007)-C(00A)-C(009)	-179.5(3)
C(005)-C(009)-C(00A)-C(007)	-0.5(5)
C(00D)-C(009)-C(00A)-C(007)	179.2(3)

SYMMETRY TRANSFORMATIONS USED TO GENERATE EQUIVALENT ATOMS.

A3- X-RAY ANALYSIS OF 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONYL CHLORIDE

TABLE A3.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONYL CHLORIDE

EMPIRICAL FORMULA	$C_{12}H_{17}CLO_2S$
FORMULA WEIGHT	260.76
TEMPERATURE	269(2) K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	TRICLINIC
SPACE GROUP	P -1
UNIT CELL DIMENSIONS	A = 6.5256(3) Å, A= 78.477(2)°.
	B = 9.9665(4) Å, B= 84.787(2)°.
	C = 10.5782(4) Å, Γ= 81.078(2)°.
VOLUME	664.68(5) $Å^3$
Z	2
DENSITY (CALCULATED)	1.303 MG/M^3
ABSORPTION COEFFICIENT	0.428 MM^{-1}
F(000)	276
CRYSTAL SIZE	0.500 × 0.450 × 0.420 MM^3
THETA RANGE FOR DATA COLLECTION	1.969 TO 28.315°.
INDEX RANGES	-8<=H<=8, -13<=K<=13, -13<=L<=14
REFLECTIONS COLLECTED	31013
INDEPENDENT REFLECTIONS	3278 [R(INT) = 0.0298]
COMPLETENESS TO THETA = 26.000°	100.0 %
ABSORPTION CORRECTION	SEMI-EMPIRICAL FROM EQUIVALENTS
MAX. AND MIN. TRANSMISSION	0.7457 AND 0.6560
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	3278 / 0 / 151
GOODNESS-OF-FIT ON F^2	1.079
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0540, WR2 = 0.1588
R INDICES (ALL DATA)	R1 = 0.0685, WR2 = 0.1725
EXTINCTION COEFFICIENT	0.163(13)
LARGEST DIFF. PEAK AND HOLE	0.687 AND -0.568 $E.Å^{-3}$

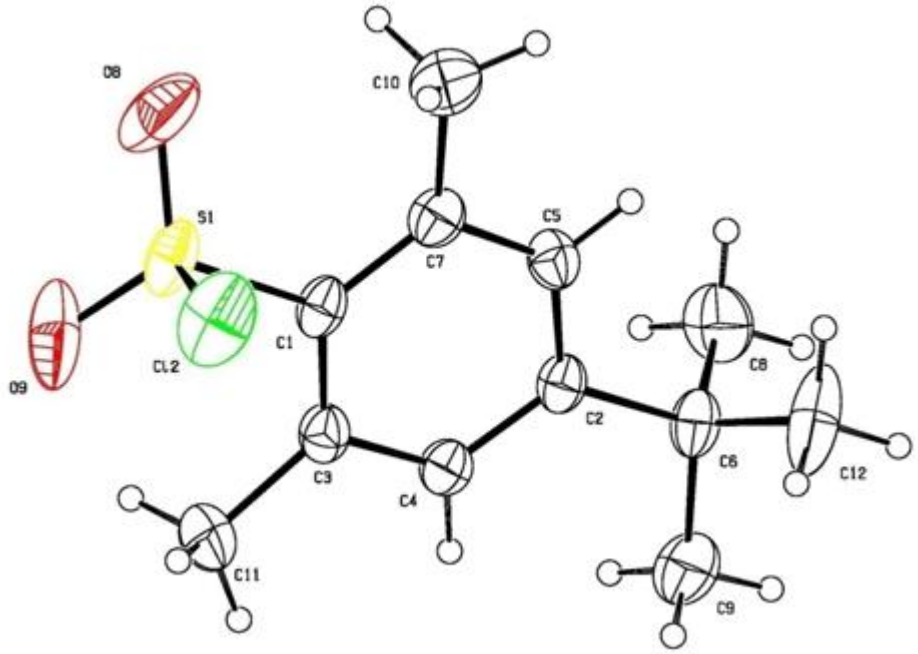


TABLE A3.2.- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)*
S(1)	2285(1)	8481(1)	7505(1)	65(1)
CL(2)	1349(2)	8079(1)	5873(1)	98(1)
C(1)	783(3)	10088(2)	7616(2)	48(1)
C(2)	-1587(3)	12639(2)	7739(2)	45(1)
C(3)	-1081(3)	10129(2)	8378(2)	49(1)
C(4)	-2212(3)	11424(2)	8415(2)	49(1)
C(5)	269(4)	12539(2)	6999(2)	51(1)
C(6)	-2864(4)	14054(2)	7780(2)	56(1)
C(7)	1490(3)	11296(2)	6904(2)	52(1)
O(8)	4408(3)	8603(3)	7234(3)	109(1)
O(9)	1730(5)	7418(2)	8505(2)	113(1)
C(10)	3426(5)	11348(4)	6009(3)	82(1)
C(11)	-1992(5)	8895(3)	9165(3)	73(1)
C(8)	-1650(6)	14877(3)	8429(4)	85(1)
C(9)	-4933(5)	13930(3)	8576(4)	83(1)
C(12)	-3313(8)	14779(4)	6418(3)	113(2)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A3.3 - BOND LENGTHS [Å] AND ANGLES [°]
FOR 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONYL CHLORIDE

S(1)-O(9)	1.405(3)	C(1)-C(3)-C(11)	126.2(2)
S(1)-O(8)	1.408(3)	C(2)-C(4)-C(3)	123.3(2)
S(1)-C(1)	1.763(2)	C(2)-C(4)-H(4)	118.3
S(1)-CL(2)	2.0147(10)	C(3)-C(4)-H(4)	118.3
C(1)-C(3)	1.396(3)	C(7)-C(5)-C(2)	123.4(2)
C(1)-C(7)	1.406(3)	C(7)-C(5)-H(5)	118.3
C(2)-C(4)	1.378(3)	C(2)-C(5)-H(5)	118.3
C(2)-C(5)	1.383(3)	C(12)-C(6)-C(8)	111.4(3)
C(2)-C(6)	1.528(3)	C(12)-C(6)-C(2)	109.0(2)
C(3)-C(4)	1.390(3)	C(8)-C(6)-C(2)	108.8(2)
C(3)-C(11)	1.512(3)	C(12)-C(6)-C(9)	108.7(3)
C(4)-H(4)	0.9300	C(8)-C(6)-C(9)	107.1(2)
C(5)-C(7)	1.382(3)	C(2)-C(6)-C(9)	111.9(2)
C(5)-H(5)	0.9300	C(5)-C(7)-C(1)	117.1(2)
C(6)-C(12)	1.510(4)	C(5)-C(7)-C(10)	117.2(2)
C(6)-C(8)	1.516(4)	C(1)-C(7)-C(10)	125.7(2)
C(6)-C(9)	1.534(4)	C(7)-C(10)-H(10A)	109.5
C(7)-C(10)	1.509(3)	C(7)-C(10)-H(10B)	109.5
C(10)-H(10A)	0.9600	H(10A)-C(10)-H(10B)	109.5
C(10)-H(10B)	0.9600	C(7)-C(10)-H(10C)	109.5
C(10)-H(10C)	0.9600	H(10A)-C(10)-H(10C)	109.5
C(11)-H(11A)	0.9600	H(10B)-C(10)-H(10C)	109.5
C(11)-H(11B)	0.9600	C(3)-C(11)-H(11A)	109.5
C(11)-H(11C)	0.9600	C(3)-C(11)-H(11B)	109.5
C(8)-H(8A)	0.9600	H(11A)-C(11)-H(11B)	109.5
C(8)-H(8B)	0.9600	C(3)-C(11)-H(11C)	109.5
C(8)-H(8C)	0.9600	H(11A)-C(11)-H(11C)	109.5
C(9)-H(9A)	0.9600	H(11B)-C(11)-H(11C)	109.5
C(9)-H(9B)	0.9600	C(6)-C(8)-H(8A)	109.5
C(9)-H(9C)	0.9600	C(6)-C(8)-H(8B)	109.5
C(12)-H(12A)	0.9600	H(8A)-C(8)-H(8B)	109.5
C(12)-H(12B)	0.9600	C(6)-C(8)-H(8C)	109.5
C(12)-H(12C)	0.9600	H(8A)-C(8)-H(8C)	109.5
O(9)-S(1)-O(8)	118.38(18)	H(8B)-C(8)-H(8C)	109.5
O(9)-S(1)-C(1)	112.06(13)	C(6)-C(9)-H(9A)	109.5
O(8)-S(1)-C(1)	111.73(13)	C(6)-C(9)-H(9B)	109.5

O(9)-S(1)-CL(2)	105.97(14)	H(9A)-C(9)-H(9B)	109.5
O(8)-S(1)-CL(2)	104.68(13)	C(6)-C(9)-H(9C)	109.5
C(1)-S(1)-CL(2)	102.22(7)	H(9A)-C(9)-H(9C)	109.5
C(3)-C(1)-C(7)	121.97(18)	H(9B)-C(9)-H(9C)	109.5
C(3)-C(1)-S(1)	119.64(16)	C(6)-C(12)-H(12A)	109.5
C(7)-C(1)-S(1)	118.38(16)	C(6)-C(12)-H(12B)	109.5
C(4)-C(2)-C(5)	117.18(18)	H(12A)-C(12)-H(12B)	109.5
C(4)-C(2)-C(6)	122.61(19)	C(6)-C(12)-H(12C)	109.5
C(5)-C(2)-C(6)	120.21(19)	H(12A)-C(12)-H(12C)	109.5
C(4)-C(3)-C(1)	117.06(19)	H(12B)-C(12)-H(12C)	109.5
C(4)-C(3)-C(11)	116.8(2)		

TABLE A3.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONYL CHLORIDE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	75(1)	50(1)	68(1)	-21(1)	-21(1)	21(1)
CL(2)	123(1)	86(1)	99(1)	-58(1)	-33(1)	16(1)
C(1)	54(1)	40(1)	50(1)	-16(1)	-12(1)	6(1)
C(2)	52(1)	38(1)	45(1)	-13(1)	-8(1)	2(1)
C(3)	55(1)	40(1)	53(1)	-10(1)	-11(1)	-4(1)
C(4)	49(1)	44(1)	53(1)	-11(1)	-2(1)	-2(1)
C(5)	60(1)	41(1)	51(1)	-8(1)	1(1)	-5(1)
C(6)	68(1)	39(1)	58(1)	-13(1)	-6(1)	9(1)
C(7)	52(1)	53(1)	51(1)	-16(1)	-2(1)	1(1)
O(8)	67(1)	92(2)	174(3)	-58(2)	-35(2)	29(1)
O(9)	172(3)	57(1)	85(2)	1(1)	0(2)	42(1)
C(10)	67(2)	84(2)	87(2)	-18(2)	20(2)	3(1)
C(11)	78(2)	46(1)	92(2)	-3(1)	-8(1)	-14(1)
C(8)	102(2)	52(1)	108(2)	-36(2)	-2(2)	-10(1)
C(9)	71(2)	63(2)	109(2)	-28(2)	5(2)	14(1)
C(12)	163(4)	79(2)	68(2)	-2(2)	-19(2)	58(2)

THE ANISOTROPIC DISPLACEMENT FACTOR EXPONENT TAKES THE FORM: $-2P^2[H^2 A^2 U^{11} + ... + 2 H K A \cdot B \cdot U^{12}]$

TABLE A3.5 - HYDROGEN COORDINATES (× 10^4) AND ISOTROPIC DISPLACEMENT PARAMETERS (Å^2·10^3) FOR 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)
H(4)	-3454	11472	8921	59
H(5)	719	13350	6542	61
H(10A)	4625	10974	6496	123
H(10B)	3526	12291	5607	123
H(10C)	3358	10814	5357	123
H(11A)	-2104	8252	8617	109
H(11B)	-3347	9197	9528	109
H(11C)	-1105	8452	9848	109
H(8A)	-1390	14391	9292	127
H(8B)	-2440	15767	8462	127
H(8C)	-352	14994	7945	127
H(9A)	-5757	13424	8185	124
H(9B)	-5669	14837	8601	124
H(9C)	-4669	13451	9440	124
H(12A)	-2028	14905	5920	169
H(12B)	-4129	15664	6437	169
H(12C)	-4067	14229	6030	169

TABLE A3.6 - TORSION ANGLES [°] FOR 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONYL CHLORIDE

O(9)-S(1)-C(1)-C(3)	-17.5(2)
O(8)-S(1)-C(1)-C(3)	-153.1(2)
CL(2)-S(1)-C(1)-C(3)	95.51(17)
O(9)-S(1)-C(1)-C(7)	163.9(2)
O(8)-S(1)-C(1)-C(7)	28.3(2)
CL(2)-S(1)-C(1)-C(7)	-83.08(18)
C(7)-C(1)-C(3)-C(4)	-0.6(3)
S(1)-C(1)-C(3)-C(4)	-179.15(15)
C(7)-C(1)-C(3)-C(11)	179.2(2)
S(1)-C(1)-C(3)-C(11)	0.6(3)
C(5)-C(2)-C(4)-C(3)	-0.3(3)
C(6)-C(2)-C(4)-C(3)	179.3(2)
C(1)-C(3)-C(4)-C(2)	0.4(3)
C(11)-C(3)-C(4)-C(2)	-179.4(2)
C(4)-C(2)-C(5)-C(7)	0.5(3)
C(6)-C(2)-C(5)-C(7)	-179.2(2)
C(4)-C(2)-C(6)-C(12)	-123.9(3)
C(5)-C(2)-C(6)-C(12)	55.7(3)
C(4)-C(2)-C(6)-C(8)	114.4(3)
C(5)-C(2)-C(6)-C(8)	-66.0(3)
C(4)-C(2)-C(6)-C(9)	-3.7(3)
C(5)-C(2)-C(6)-C(9)	175.9(2)
C(2)-C(5)-C(7)-C(1)	-0.7(3)
C(2)-C(5)-C(7)-C(10)	177.2(2)
C(3)-C(1)-C(7)-C(5)	0.7(3)
S(1)-C(1)-C(7)-C(5)	179.30(17)
C(3)-C(1)-C(7)-C(10)	-177.0(2)
S(1)-C(1)-C(7)-C(10)	1.6(3)

SYMMETRY TRANSFORMATIONS USED TO GENERATE EQUIVALENT ATOMS.

A4- X-RAY ANALYSIS OF 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONYL CHLORIDE

TABLE A4.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONYL CHLORIDE

EMPIRICAL FORMULA	$C_9D_{11}CLO_2S$
FORMULA WEIGHT	218.69
TEMPERATURE	271.95 K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	TRICLINIC
SPACE GROUP	P-1
UNIT CELL DIMENSIONS	A = 7.8768(2) Å, α= 65.7430(10)°.
	B = 7.9571(2) Å, β= 79.3400(10)°.
	C = 9.2502(2) Å, γ = 77.3870(10)°.
VOLUME	512.86(2) $Å^3$
Z	2
DENSITY (CALCULATED)	1.416 MG/M^3
ABSORPTION COEFFICIENT	0.540 MM^{-1}
F(000)	228
CRYSTAL SIZE	0.44 × 0.42 × 0.23 MM^3
THETA RANGE FOR DATA COLLECTION	2.429 TO 30.555°.
INDEX RANGES	-11<=H<=11, -11<=K<=11, -13<=L<=13
REFLECTIONS COLLECTED	21493
INDEPENDENT REFLECTIONS	3125 [R(INT) = 0.0196]
COMPLETENESS TO THETA = 25.242°	98.9 %
ABSORPTION CORRECTION	SEMI-EMPIRICAL FROM EQUIVALENTS
MAX. AND MIN. TRANSMISSION	0.7461 AND 0.7105
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	3125 / 0 / 121
GOODNESS-OF-FIT ON F^2	1.069
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0456, WR2 = 0.1308
R INDICES (ALL DATA)	R1 = 0.0518, WR2 = 0.1369
EXTINCTION COEFFICIENT	N/A
LARGEST DIFF. PEAK AND HOLE	0.536 AND -0.451 $E.Å^{-3}$

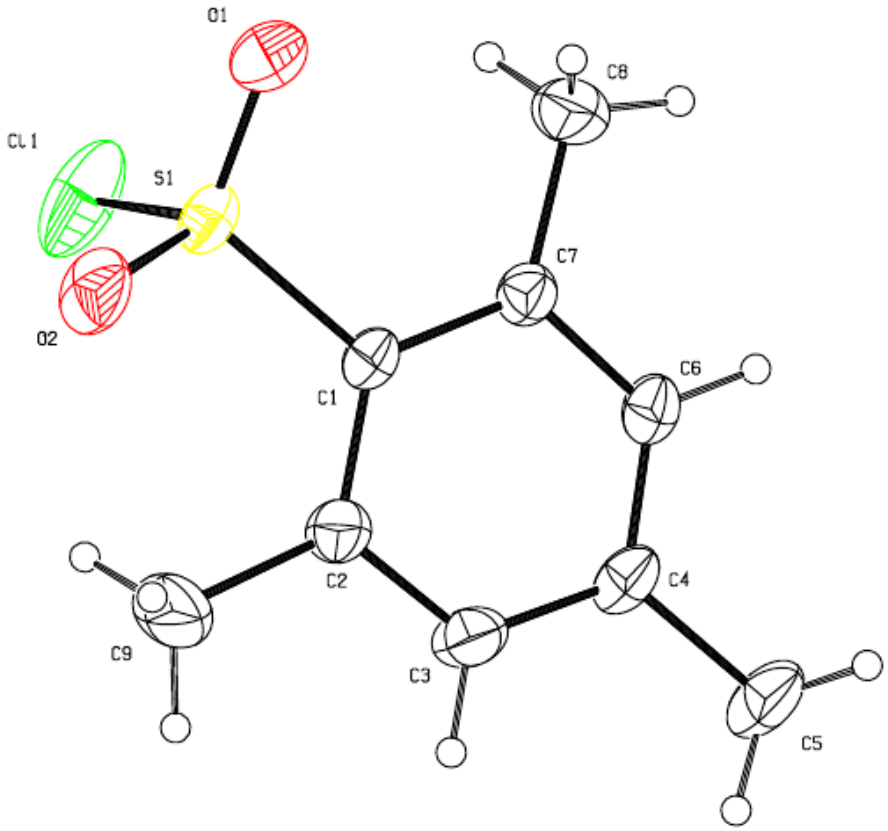


TABLE A4.2- ATOMIC COORDINATES (× 10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2·10^3) FOR 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)
CL(1)	12561(1)	-1296(1)	5383(1)	101(1)
S(1)	12367(1)	-1563(1)	7692(1)	48(1)
O(1)	12007(2)	-3387(2)	8621(2)	78(1)
O(2)	13927(2)	-1108(2)	7869(2)	71(1)
C(1)	10549(2)	162(2)	7764(2)	39(1)
C(2)	10819(2)	2011(2)	7251(2)	53(1)
C(3)	9356(2)	3327(2)	7328(3)	61(1)
C(4)	7696(2)	2881(2)	7876(2)	50(1)
C(5)	6141(3)	4354(3)	7939(3)	71(1)
C(6)	7491(2)	1054(2)	8337(2)	47(1)
C(7)	8878(2)	-348(2)	8291(2)	43(1)
C(8)	8439(3)	-2271(3)	8774(4)	77(1)
C(9)	12557(3)	2690(3)	6600(4)	97(1)

TABLE A4.3 - BOND LENGTHS [Å] AND ANGLES [°]

FOR 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONYL CHLORIDE

CL(1)-S(1)	2.0378(7)	C(1)-C(2)-C(9)	125.36(16)
S(1)-O(1)	1.4109(15)	C(3)-C(2)-C(1)	116.98(15)
S(1)-O(2)	1.4092(15)	C(3)-C(2)-C(9)	117.65(17)
S(1)-C(1)	1.7660(13)	C(2)-C(3)-H(3)	118.5
C(1)-C(2)	1.400(2)	C(4)-C(3)-C(2)	122.95(16)
C(1)-C(7)	1.403(2)	C(4)-C(3)-H(3)	118.5
C(2)-C(3)	1.391(2)	C(3)-C(4)-C(5)	121.28(17)
C(2)-C(9)	1.510(3)	C(6)-C(4)-C(3)	117.94(14)
C(3)-H(3)	0.9300	C(6)-C(4)-C(5)	120.77(17)
C(3)-C(4)	1.379(3)	C(4)-C(5)-H(5A)	109.5
C(4)-C(5)	1.510(2)	C(4)-C(5)-H(5B)	109.5
C(4)-C(6)	1.374(2)	C(4)-C(5)-H(5C)	109.5
C(5)-H(5A)	0.9600	H(5A)-C(5)-H(5B)	109.5
C(5)-H(5B)	0.9600	H(5A)-C(5)-H(5C)	109.5
C(5)-H(5C)	0.9600	H(5B)-C(5)-H(5C)	109.5
C(6)-H(6)	0.9300	C(4)-C(6)-H(6)	118.5
C(6)-C(7)	1.388(2)	C(4)-C(6)-C(7)	122.91(15)
C(7)-C(8)	1.507(2)	C(7)-C(6)-H(6)	118.5
C(8)-H(8A)	0.9600	C(1)-C(7)-C(8)	125.99(15)
C(8)-H(8B)	0.9600	C(6)-C(7)-C(1)	117.17(14)
C(8)-H(8C)	0.9600	C(6)-C(7)-C(8)	116.82(15)
C(9)-H(9A)	0.9600	C(7)-C(8)-H(8A)	109.5
C(9)-H(9B)	0.9600	C(7)-C(8)-H(8B)	109.5
C(9)-H(9C)	0.9600	C(7)-C(8)-H(8C)	109.5
O(1)-S(1)-CL(1)	105.36(9)	H(8A)-C(8)-H(8B)	109.5
O(1)-S(1)-C(1)	112.33(8)	H(8A)-C(8)-H(8C)	109.5
O(2)-S(1)-CL(1)	106.19(8)	H(8B)-C(8)-H(8C)	109.5
O(2)-S(1)-O(1)	117.84(10)	C(2)-C(9)-H(9A)	109.5
O(2)-S(1)-C(1)	111.78(8)	C(2)-C(9)-H(9B)	109.5
C(1)-S(1)-CL(1)	101.55(5)	C(2)-C(9)-H(9C)	109.5
C(2)-C(1)-S(1)	118.69(11)	H(9A)-C(9)-H(9B)	109.5
C(2)-C(1)-C(7)	122.01(13)	H(9A)-C(9)-H(9C)	109.5
C(7)-C(1)-S(1)	119.28(11)	H(9B)-C(9)-H(9C)	109.5

HERE THE SYMBOL H CORRESPONDS TO DEUTERIUM (^2H)

TABLE A4.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONYL CHLORIDE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
CL(1)	95(1)	140(1)	66(1)	-63(1)	-16(1)	38(1)
S(1)	40(1)	50(1)	50(1)	-22(1)	-6(1)	8(1)
O(1)	64(1)	47(1)	101(1)	-18(1)	-3(1)	9(1)
O(2)	39(1)	79(1)	93(1)	-36(1)	-17(1)	9(1)
C(1)	34(1)	42(1)	43(1)	-20(1)	-7(1)	2(1)
C(2)	38(1)	46(1)	76(1)	-25(1)	-9(1)	-4(1)
C(3)	48(1)	44(1)	97(1)	-34(1)	-16(1)	0(1)
C(4)	41(1)	53(1)	62(1)	-33(1)	-13(1)	8(1)
C(5)	52(1)	66(1)	101(2)	-48(1)	-19(1)	18(1)
C(6)	34(1)	55(1)	53(1)	-25(1)	-4(1)	-1(1)
C(7)	38(1)	44(1)	48(1)	-20(1)	-6(1)	-3(1)
C(8)	54(1)	51(1)	121(2)	-29(1)	-6(1)	-13(1)
C(9)	45(1)	62(1)	170(3)	-29(2)	-4(1)	-14(1)

TABLE A4.5 - HYDROGEN COORDINATES* ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)
H(3)	9504	4565	6994	73
H(5A)	5450	4635	7091	106
H(5B)	6542	5464	7820	106
H(5C)	5442	3899	8946	106
H(6)	6375	742	8696	57
H(8A)	7191	-2212	8942	116
H(8B)	8935	-3098	9743	116
H(8C)	8911	-2727	7945	116
H(9A)	12371	4030	6142	146
H(9B)	13119	2222	5796	146
H(9C)	13287	2249	7448	146

*HERE SYMBOL H CORRESPONDS TO DEUTERIUM (^2H)

TABLE A4.6 - TORSION ANGLES [°] FOR 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONYL CHLORIDE

CL(1)-S(1)-C(1)-C(2)	-83.91(13)
CL(1)-S(1)-C(1)-C(7)	94.47(12)
S(1)-C(1)-C(2)-C(3)	-179.93(14)
S(1)-C(1)-C(2)-C(9)	1.2(3)
S(1)-C(1)-C(7)-C(6)	179.55(11)
S(1)-C(1)-C(7)-C(8)	-2.1(2)
O(1)-S(1)-C(1)-C(2)	163.99(14)
O(1)-S(1)-C(1)-C(7)	-17.63(16)
O(2)-S(1)-C(1)-C(2)	28.93(16)
O(2)-S(1)-C(1)-C(7)	-152.70(13)
C(1)-C(2)-C(3)-C(4)	0.0(3)
C(2)-C(1)-C(7)-C(6)	-2.1(2)
C(2)-C(1)-C(7)-C(8)	176.23(19)
C(2)-C(3)-C(4)-C(5)	-179.97(19)
C(2)-C(3)-C(4)-C(6)	-1.2(3)
C(3)-C(4)-C(6)-C(7)	0.8(3)
C(4)-C(6)-C(7)-C(1)	0.8(2)
C(4)-C(6)-C(7)-C(8)	-177.68(19)
C(5)-C(4)-C(6)-C(7)	179.55(16)
C(7)-C(1)-C(2)-C(3)	1.7(3)
C(7)-C(1)-C(2)-C(9)	-177.1(2)
C(9)-C(2)-C(3)-C(4)	178.9(2)

A5- X-RAY ANALYSIS OF METHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

TABLE A5.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR METHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

EMPIRICAL FORMULA	$C_{13}H_{20}O_3S$
FORMULA WEIGHT	256.35
TEMPERATURE	293.75 K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	TRICLINIC
SPACE GROUP	P -1
UNIT CELL DIMENSIONS	A = 9.2885(4) Å, A= 89.957(3)°. B = 10.2632(5) Å, B= 89.926(3)°. C = 15.4268(8) Å, Γ= 67.713(2)°.
VOLUME	1360.77(12) $Å^3$
Z	4
DENSITY (CALCULATED)	1.251 MG/M^3
ABSORPTION COEFFICIENT	0.233 MM^{-1}
F(000)	552
CRYSTAL SIZE	0.5 × 0.5 × 0.5 MM^3
THETA RANGE FOR DATA COLLECTION	1.320 TO 26.423°.
INDEX RANGES	-11<=H<=11, -12<=K<=12, -19<=L<=19
REFLECTIONS COLLECTED	36307
INDEPENDENT REFLECTIONS	5597 [R(INT) = 0.0425]
COMPLETENESS TO THETA = 26.000°	100.0 %
ABSORPTION CORRECTION	SEMI-EMPIRICAL FROM EQUIVALENTS
MAX. AND MIN. TRANSMISSION	0.7454 AND 0.6773
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	5597 / 0 / 320
GOODNESS-OF-FIT ON F^2	1.027
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0495, WR2 = 0.1415
R INDICES (ALL DATA)	R1 = 0.0620, WR2 = 0.1524
EXTINCTION COEFFICIENT	0.081(5)
LARGEST DIFF. PEAK AND HOLE	0.477 AND -0.320 $E.Å^{-3}$

TABLE A5.2- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR METHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)*
S(1)	849(1)	1891(1)	3881(1)	47(1)
C(2)	-694(2)	3556(2)	3933(1)	36(1)
C(3)	-2597(2)	5439(2)	4709(1)	41(1)
C(6)	-3189(2)	6169(2)	3951(1)	37(1)
C(7)	-1358(2)	4141(2)	4726(1)	40(1)
C(10)	-1225(2)	4282(2)	3146(1)	37(1)
C(11)	-2466(2)	5564(2)	3184(1)	39(1)
O(13)	236(2)	1043(2)	3241(1)	60(1)
O(15)	1094(2)	1217(2)	4703(1)	70(1)
C(17)	-4546(2)	7595(2)	3944(1)	44(1)
C(20)	-827(3)	3496(3)	5608(1)	57(1)
C(23)	-5788(3)	7572(3)	3306(2)	73(1)
O(24)	2142(2)	2003(2)	3454(1)	79(1)
C(26)	-527(3)	3755(2)	2270(1)	53(1)
C(27)	-3947(3)	8724(2)	3664(2)	68(1)
C(29)	-5304(3)	7995(3)	4836(2)	79(1)
C(31)	-1081(4)	710(3)	3523(2)	72(1)
S(2)	5849(1)	1891(1)	1120(1)	46(1)
C(1)	4304(2)	3558(2)	1069(1)	35(1)
C(4)	2403(2)	5437(2)	292(1)	41(1)
C(5)	1809(2)	6168(2)	1048(1)	37(1)
C(8)	3641(2)	4140(2)	274(1)	38(1)
C(9)	3776(2)	4282(2)	1856(1)	37(1)
C(12)	2532(2)	5563(2)	1816(1)	39(1)
O(14)	6098(2)	1218(2)	299(1)	71(1)
O(16)	5233(2)	1043(2)	1759(1)	60(1)
C(18)	452(2)	7596(2)	1056(1)	45(1)
C(19)	4171(3)	3498(3)	-608(1)	56(1)
O(21)	7144(2)	2006(2)	1545(1)	78(1)
C(22)	-790(3)	7576(3)	1694(2)	74(1)
C(25)	4471(3)	3754(2)	2732(1)	52(1)
C(28)	1054(3)	8724(2)	1336(2)	67(1)
C(30)	-303(3)	7994(3)	162(2)	78(1)

C(32)	3915(4)	713(3)	1476(2)	71(1)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A5.3 - BOND LENGTHS [Å] AND ANGLES [°] FOR METHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

S(1)-C(2)	1.7667(18)	C(3)-C(6)-C(11)	116.92(17)
S(1)-O(13)	1.5598(18)	C(3)-C(6)-C(17)	122.63(17)
S(1)-O(15)	1.4212(17)	C(11)-C(6)-C(17)	120.44(17)
S(1)-O(24)	1.4113(19)	C(2)-C(7)-C(20)	125.53(17)
C(2)-C(7)	1.399(3)	C(3)-C(7)-C(2)	117.68(16)
C(2)-C(10)	1.412(3)	C(3)-C(7)-C(20)	116.78(17)
C(3)-C(6)	1.385(3)	C(2)-C(10)-C(26)	124.40(17)
C(3)-C(7)	1.392(3)	C(11)-C(10)-C(2)	117.64(16)
C(6)-C(11)	1.386(3)	C(11)-C(10)-C(26)	117.96(17)
C(6)-C(17)	1.527(2)	C(10)-C(11)-C(6)	123.36(17)
C(7)-C(20)	1.511(3)	C(31)-O(13)-S(1)	117.39(15)
C(10)-C(11)	1.383(3)	C(6)-C(17)-C(29)	112.27(17)
C(10)-C(26)	1.507(3)	C(23)-C(17)-C(6)	110.16(17)
O(13)-C(31)	1.455(3)	C(23)-C(17)-C(27)	109.0(2)
C(17)-C(23)	1.525(3)	C(23)-C(17)-C(29)	108.2(2)
C(17)-C(27)	1.525(3)	C(27)-C(17)-C(6)	108.91(17)
C(17)-C(29)	1.529(3)	C(27)-C(17)-C(29)	108.3(2)
S(2)-C(1)	1.7690(18)	O(14)-S(2)-C(1)	110.70(10)
S(2)-O(14)	1.4190(17)	O(14)-S(2)-O(16)	108.61(11)
S(2)-O(16)	1.5601(18)	O(16)-S(2)-C(1)	103.50(9)
S(2)-O(21)	1.4147(19)	O(21)-S(2)-C(1)	110.11(10)
C(1)-C(8)	1.400(3)	O(21)-S(2)-O(14)	117.93(12)
C(1)-C(9)	1.410(2)	O(21)-S(2)-O(16)	104.83(11)
C(4)-C(5)	1.384(3)	C(8)-C(1)-S(2)	121.06(14)
C(4)-C(8)	1.391(3)	C(8)-C(1)-C(9)	121.32(16)
C(5)-C(12)	1.387(3)	C(9)-C(1)-S(2)	117.62(14)
C(5)-C(18)	1.528(2)	C(5)-C(4)-C(8)	123.32(17)
C(8)-C(19)	1.510(3)	C(4)-C(5)-C(12)	116.89(16)
C(9)-C(12)	1.384(3)	C(4)-C(5)-C(18)	122.70(17)
C(9)-C(25)	1.508(3)	C(12)-C(5)-C(18)	120.39(17)
O(16)-C(32)	1.456(3)	C(1)-C(8)-C(19)	125.80(17)
C(18)-C(22)	1.521(3)	C(4)-C(8)-C(1)	117.53(16)
C(18)-C(28)	1.527(3)	C(4)-C(8)-C(19)	116.65(17)
C(18)-C(30)	1.531(3)	C(1)-C(9)-C(25)	124.48(17)
O(13)-S(1)-C(2)	103.57(9)	C(12)-C(9)-C(1)	117.44(16)
O(15)-S(1)-C(2)	110.61(10)	C(12)-C(9)-C(25)	118.08(17)
O(15)-S(1)-O(13)	108.56(11)	C(9)-C(12)-C(5)	123.45(17)
O(24)-S(1)-C(2)	110.21(10)	C(32)-O(16)-S(2)	117.27(15)
O(24)-S(1)-O(13)	104.65(11)	C(5)-C(18)-C(30)	112.14(17)
O(24)-S(1)-O(15)	118.06(12)	C(22)-C(18)-C(5)	110.25(17)
C(7)-C(2)-S(1)	121.25(14)	C(22)-C(18)-C(28)	108.9(2)
C(7)-C(2)-C(10)	121.09(16)	C(22)-C(18)-C(30)	108.2(2)
C(10)-C(2)-S(1)	117.65(14)	C(28)-C(18)-C(5)	108.89(17)

C(6)-C(3)-C(7)	123.25(17)	C(28)-C(18)-C(30)	108.4(2)

TABLE A5.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$)

FOR METHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	36(1)	37(1)	54(1)	2(1)	0(1)	1(1)
C(2)	31(1)	31(1)	41(1)	2(1)	1(1)	-6(1)
C(3)	40(1)	41(1)	36(1)	-2(1)	6(1)	-6(1)
C(6)	33(1)	31(1)	42(1)	-1(1)	-2(1)	-7(1)
C(7)	36(1)	40(1)	39(1)	6(1)	1(1)	-9(1)
C(10)	38(1)	34(1)	37(1)	-2(1)	2(1)	-10(1)
C(11)	41(1)	35(1)	36(1)	2(1)	-4(1)	-9(1)
O(13)	71(1)	40(1)	60(1)	-5(1)	4(1)	-9(1)
O(15)	74(1)	51(1)	60(1)	9(1)	-14(1)	5(1)
C(17)	38(1)	34(1)	51(1)	-3(1)	-3(1)	-2(1)
C(20)	53(1)	61(1)	41(1)	12(1)	3(1)	-4(1)
C(23)	46(1)	55(2)	102(2)	-17(1)	-20(1)	0(1)
O(24)	41(1)	77(1)	105(2)	-2(1)	18(1)	-6(1)
C(26)	60(1)	47(1)	38(1)	-3(1)	6(1)	-7(1)
C(27)	63(2)	35(1)	97(2)	2(1)	-7(1)	-8(1)
C(29)	68(2)	60(2)	72(2)	-8(1)	14(1)	16(1)
C(31)	85(2)	60(2)	80(2)	6(1)	-11(1)	-38(2)
S(2)	36(1)	37(1)	53(1)	-2(1)	1(1)	1(1)
C(1)	31(1)	31(1)	40(1)	-2(1)	1(1)	-7(1)
C(4)	40(1)	41(1)	34(1)	1(1)	-5(1)	-7(1)
C(5)	32(1)	32(1)	44(1)	1(1)	2(1)	-6(1)
C(8)	35(1)	38(1)	38(1)	-5(1)	-1(1)	-10(1)
C(9)	38(1)	34(1)	36(1)	1(1)	-1(1)	-10(1)
C(12)	41(1)	35(1)	35(1)	-4(1)	5(1)	-8(1)
O(14)	74(1)	50(1)	61(1)	-9(1)	16(1)	7(1)
O(16)	70(1)	40(1)	60(1)	5(1)	-3(1)	-10(1)
C(18)	38(1)	33(1)	53(1)	3(1)	4(1)	-2(1)
C(19)	52(1)	61(1)	40(1)	-12(1)	-2(1)	-5(1)
O(21)	42(1)	75(1)	104(2)	3(1)	-17(1)	-7(1)
C(22)	45(1)	56(2)	103(2)	15(1)	22(1)	0(1)
C(25)	60(1)	46(1)	38(1)	3(1)	-5(1)	-5(1)
C(28)	60(2)	36(1)	96(2)	-2(1)	9(1)	-8(1)
C(30)	67(2)	61(2)	73(2)	9(1)	-15(1)	15(1)
C(32)	84(2)	58(2)	81(2)	-6(1)	11(1)	-37(1)

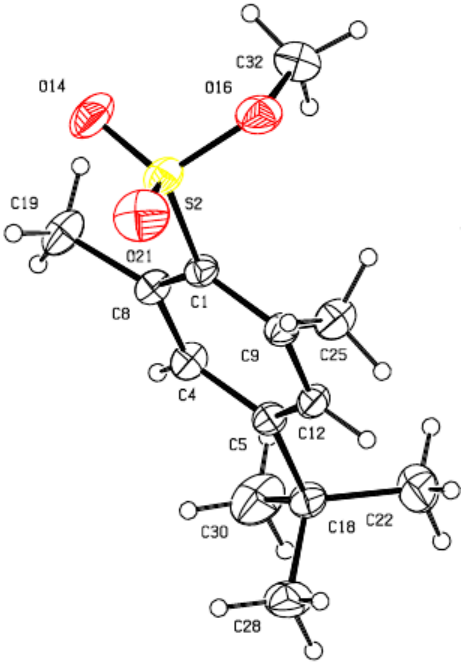
TABLE A5.5 - HYDROGEN COORDINATES (× 10^4) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR METHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
H(3)	-3050	5836	5233	50
H(11)	-2835	6044	2668	47
H(20A)	-1075	2674	5674	85
H(20B)	-1345	4168	6050	85
H(20C)	277	3235	5658	85
H(23A)	-5342	7352	2737	110
H(23B)	-6624	8479	3297	110
H(23C)	-6180	6871	3482	110
H(26A)	563	3586	2277	79
H(26B)	-1037	4449	1837	79
H(26C)	-662	2895	2137	79
H(27A)	-3181	8759	4070	102
H(27B)	-4797	9622	3646	102
H(27C)	-3486	8500	3098	102
H(29A)	-5626	7264	5041	118
H(29B)	-6193	8862	4794	118
H(29C)	-4567	8110	5235	118
H(31A)	-1335	175	3081	108
H(31B)	-1961	1567	3627	108
H(31C)	-815	167	4048	108
H(4)	1951	5833	-232	49
H(12)	2161	6043	2331	47
H(19A)	5272	3255	-664	84
H(19B)	3637	4165	-1049	84
H(19C)	3942	2666	-670	84
H(22A)	-1188	6880	1517	110
H(22B)	-1622	8486	1705	110
H(22C)	-345	7350	2262	110
H(25A)	4291	2919	2877	78
H(25B)	3995	4466	3160	78
H(25C)	5570	3542	2715	78
H(28A)	1518	8498	1900	101
H(28B)	204	9622	1356	101
H(28C)	1818	8762	928	101
H(30A)	448	8067	-243	118
H(30B)	-1165	8882	199	118
H(30C)	-665	7282	-30	118
H(32A)	4207	113	976	107
H(32B)	3061	1568	1331	107
H(32C)	3608	240	1935	107

TABLE A5.6 - TORSION ANGLES [°] FOR 2,4,6-TRIMETHOXYBENZENESULFONYL CHLORIDE

S(1)-C(2)-C(7)-C(3)	-178.24(15)
S(1)-C(2)-C(7)-C(20)	3.0(3)
S(1)-C(2)-C(10)-C(11)	177.89(14)
S(1)-C(2)-C(10)-C(26)	-2.3(3)
C(2)-S(1)-O(13)-C(31)	-66.84(18)
C(2)-C(10)-C(11)-C(6)	0.9(3)
C(3)-C(6)-C(11)-C(10)	1.0(3)
C(3)-C(6)-C(17)-C(23)	-129.2(2)
C(3)-C(6)-C(17)-C(27)	111.4(2)
C(3)-C(6)-C(17)-C(29)	-8.5(3)
C(6)-C(3)-C(7)-C(2)	-0.2(3)
C(6)-C(3)-C(7)-C(20)	178.7(2)
C(7)-C(2)-C(10)-C(11)	-2.6(3)
C(7)-C(2)-C(10)-C(26)	177.22(19)
C(7)-C(3)-C(6)-C(11)	-1.4(3)
C(7)-C(3)-C(6)-C(17)	-179.79(18)
C(10)-C(2)-C(7)-C(3)	2.3(3)
C(10)-C(2)-C(7)-C(20)	-176.53(19)
C(11)-C(6)-C(17)-C(23)	52.5(3)
C(11)-C(6)-C(17)-C(27)	-67.0(2)
C(11)-C(6)-C(17)-C(29)	173.1(2)
O(13)-S(1)-C(2)-C(7)	124.96(17)
O(13)-S(1)-C(2)-C(10)	-55.52(17)
O(15)-S(1)-C(2)-C(7)	8.8(2)
O(15)-S(1)-C(2)-C(10)	-171.67(15)
O(15)-S(1)-O(13)-C(31)	50.75(19)
C(17)-C(6)-C(11)-C(10)	179.45(18)
O(24)-S(1)-C(2)-C(7)	-123.56(18)
O(24)-S(1)-C(2)-C(10)	55.95(19)
O(24)-S(1)-O(13)-C(31)	177.67(17)
C(26)-C(10)-C(11)-C(6)	-178.90(19)
S(2)-C(1)-C(8)-C(4)	178.26(14)
S(2)-C(1)-C(8)-C(19)	-3.1(3)
S(2)-C(1)-C(9)-C(12)	-177.79(14)
S(2)-C(1)-C(9)-C(25)	2.0(3)

C(1)-S(2)-O(16)-C(32)	66.80(18)
C(1)-C(9)-C(12)-C(5)	-1.1(3)
C(4)-C(5)-C(12)-C(9)	-0.9(3)
C(4)-C(5)-C(18)-C(22)	129.2(2)
C(4)-C(5)-C(18)-C(28)	-111.4(2)
C(4)-C(5)-C(18)-C(30)	8.6(3)
C(5)-C(4)-C(8)-C(1)	0.2(3)
C(5)-C(4)-C(8)-C(19)	-178.63(19)
C(8)-C(1)-C(9)-C(12)	2.8(3)
C(8)-C(1)-C(9)-C(25)	-177.40(19)
C(8)-C(4)-C(5)-C(12)	1.4(3)
C(8)-C(4)-C(5)-C(18)	179.70(18)
C(9)-C(1)-C(8)-C(4)	-2.3(3)
C(9)-C(1)-C(8)-C(19)	176.34(19)
C(12)-C(5)-C(18)-C(22)	-52.6(3)
C(12)-C(5)-C(18)-C(28)	66.8(2)
C(12)-C(5)-C(18)-C(30)	-173.2(2)
O(14)-S(2)-C(1)-C(8)	-8.6(2)
O(14)-S(2)-C(1)-C(9)	171.94(15)
O(14)-S(2)-O(16)-C(32)	-50.87(19)
O(16)-S(2)-C(1)-C(8)	-124.82(16)
O(16)-S(2)-C(1)-C(9)	55.74(17)
C(18)-C(5)-C(12)-C(9)	-179.25(18)
O(21)-S(2)-C(1)-C(8)	123.57(18)
O(21)-S(2)-C(1)-C(9)	-55.87(18)
O(21)-S(2)-O(16)-C(32)	-177.77(17)
C(25)-C(9)-C(12)-C(5)	179.06(19)


C32
O14
O16
C19
S2
O21
C8
C1
C9
C25
C4
C5
C12
C30
C18
C22
C28

A6- X-RAY ANALYSIS OF ETHYL 4-TERT-BUTYL-2,6-DIMETHYL BENZENESULFONATE

TABLE A6.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR ETHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

EMPIRICAL FORMULA	$C_{14}H_{22}O_3S$
FORMULA WEIGHT	270.37
TEMPERATURE	297(2) K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	MONOCLINIC
SPACE GROUP	C 2/C
UNIT CELL DIMENSIONS	A = 19.6944(11) Å, α= 90°. B = 9.4733(4) Å, β= 106.923(4)°. C = 16.6261(8) Å, γ = 90°.
VOLUME	2967.6(3) $Å^3$
Z	8
DENSITY (CALCULATED)	1.210 MG/M^3
ABSORPTION COEFFICIENT	0.217 MM^{-1}
F(000)	1168
CRYSTAL SIZE	0.360 × 0.160 × 0.080 MM^3
THETA RANGE FOR DATA COLLECTION	2.162 TO 26.405°.
INDEX RANGES	-24<=H<=24, -11<=K<=11, -20<=L<=20
REFLECTIONS COLLECTED	21359
INDEPENDENT REFLECTIONS	3052 [R(INT) = 0.0556]
COMPLETENESS TO THETA = 26.000°	100.0 %
ABSORPTION CORRECTION	SEMI-EMPIRICAL FROM EQUIVALENTS
MAX. AND MIN. TRANSMISSION	0.7454 AND 0.6865
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	3052 / 0 / 170
GOODNESS-OF-FIT ON F^2	1.061
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0489, WR2 = 0.1349
R INDICES (ALL DATA)	R1 = 0.0828, WR2 = 0.1560
EXTINCTION COEFFICIENT	0.0031(7)
LARGEST DIFF. PEAK AND HOLE	0.209 AND -0.285 $E.Å^{-3}$

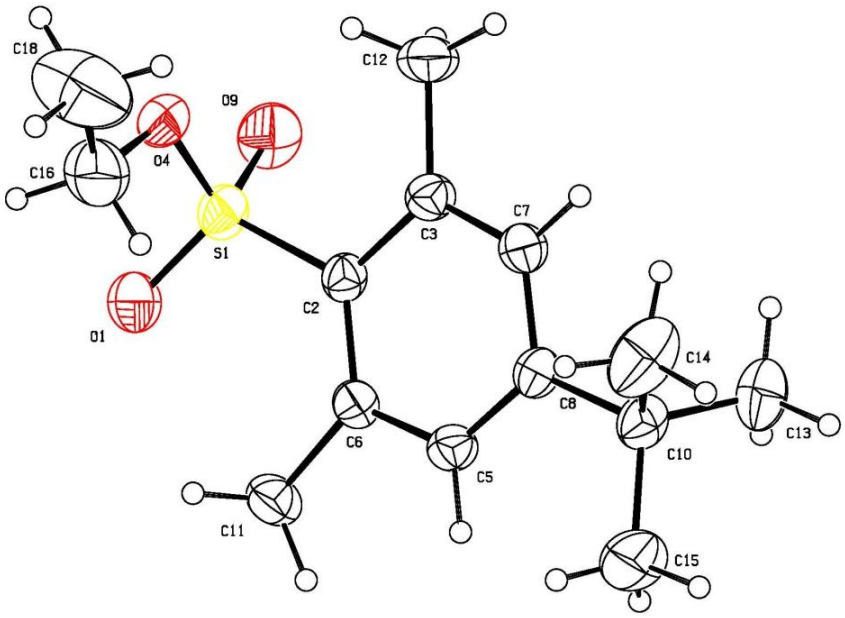


TABLE A6.2.- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR ETHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)*
S(1)	1258(1)	1959(1)	993(1)	58(1)
O(1)	740(1)	2004(2)	194(1)	76(1)
C(2)	2038(1)	1122(2)	926(1)	46(1)
C(3)	2562(1)	800(2)	1687(1)	50(1)
O(4)	980(1)	956(2)	1576(1)	66(1)
C(5)	2762(1)	88(2)	159(1)	50(1)
C(6)	2139(1)	788(2)	152(1)	47(1)
C(7)	3163(1)	103(3)	1635(1)	52(1)
C(8)	3281(1)	-283(2)	887(1)	48(1)
O(9)	1427(1)	3232(2)	1460(1)	80(1)
C(10)	3963(1)	-1040(3)	884(2)	58(1)
C(11)	1638(1)	1135(3)	-703(1)	63(1)
C(12)	2509(2)	1181(3)	2549(2)	73(1)
C(13)	4582(2)	-41(3)	1218(2)	84(1)
C(14)	4063(2)	-2326(3)	1456(2)	100(1)
C(15)	3954(2)	-1496(4)	-1(2)	101(1)
C(16)	697(2)	-397(4)	1236(2)	97(1)
C(18)	682(3)	-1363(5)	1864(3)	164(2)

TABLE A6.3 - BOND LENGTHS [Å] AND ANGLES [°]
FOR ETHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

S(1)-O(9)	1.4200(19)	C(5)-C(6)-C(11)	116.3(2)
S(1)-O(1)	1.4214(19)	C(2)-C(6)-C(11)	126.1(2)
S(1)-O(4)	1.5652(19)	C(3)-C(7)-C(8)	123.8(2)
S(1)-C(2)	1.762(2)	C(3)-C(7)-H(7)	118.1
C(2)-C(6)	1.394(3)	C(8)-C(7)-H(7)	118.1
C(2)-C(3)	1.413(3)	C(7)-C(8)-C(5)	116.5(2)
C(3)-C(7)	1.380(3)	C(7)-C(8)-C(10)	120.5(2)
C(3)-C(12)	1.511(3)	C(5)-C(8)-C(10)	123.0(2)
O(4)-C(16)	1.445(3)	C(13)-C(10)-C(14)	109.0(2)
C(5)-C(8)	1.382(3)	C(13)-C(10)-C(8)	108.7(2)
C(5)-C(6)	1.392(3)	C(14)-C(10)-C(8)	109.3(2)
C(5)-H(5)	0.9300	C(13)-C(10)-C(15)	108.1(3)
C(6)-C(11)	1.513(3)	C(14)-C(10)-C(15)	109.8(2)
C(7)-C(8)	1.380(3)	C(8)-C(10)-C(15)	111.9(2)
C(7)-H(7)	0.9300	C(6)-C(11)-H(11A)	109.5
C(8)-C(10)	1.523(3)	C(6)-C(11)-H(11B)	109.5
C(10)-C(13)	1.516(4)	H(11A)-C(11)-H(11B)	109.5
C(10)-C(14)	1.522(4)	C(6)-C(11)-H(11C)	109.5
C(10)-C(15)	1.530(4)	H(11A)-C(11)-H(11C)	109.5
C(11)-H(11A)	0.9600	H(11B)-C(11)-H(11C)	109.5
C(11)-H(11B)	0.9600	C(3)-C(12)-H(12A)	109.5
C(11)-H(11C)	0.9600	C(3)-C(12)-H(12B)	109.5
C(12)-H(12A)	0.9600	H(12A)-C(12)-H(12B)	109.5
C(12)-H(12B)	0.9600	C(3)-C(12)-H(12C)	109.5
C(12)-H(12C)	0.9600	H(12A)-C(12)-H(12C)	109.5
C(13)-H(13A)	0.9600	H(12B)-C(12)-H(12C)	109.5
C(13)-H(13B)	0.9600	C(10)-C(13)-H(13A)	109.5
C(13)-H(13C)	0.9600	C(10)-C(13)-H(13B)	109.5
C(14)-H(14A)	0.9600	H(13A)-C(13)-H(13B)	109.5
C(14)-H(14B)	0.9600	C(10)-C(13)-H(13C)	109.5
C(14)-H(14C)	0.9600	H(13A)-C(13)-H(13C)	109.5
C(15)-H(15A)	0.9600	H(13B)-C(13)-H(13C)	109.5
C(15)-H(15B)	0.9600	C(10)-C(14)-H(14A)	109.5
C(15)-H(15C)	0.9600	C(10)-C(14)-H(14B)	109.5
C(16)-C(18)	1.395(4)	H(14A)-C(14)-H(14B)	109.5
C(16)-H(16A)	0.9700	C(10)-C(14)-H(14C)	109.5

C(16)-H(16B)	0.9700	H(14A)-C(14)-H(14C)	109.5
C(18)-H(18A)	0.9600	H(14B)-C(14)-H(14C)	109.5
C(18)-H(18B)	0.9600	C(10)-C(15)-H(15A)	109.5
C(18)-H(18C)	0.9600	C(10)-C(15)-H(15B)	109.5
O(9)-S(1)-O(1)	118.45(12)	H(15A)-C(15)-H(15B)	109.5
O(9)-S(1)-O(4)	104.27(11)	C(10)-C(15)-H(15C)	109.5
O(1)-S(1)-O(4)	108.20(11)	H(15A)-C(15)-H(15C)	109.5
O(9)-S(1)-C(2)	110.25(12)	H(15B)-C(15)-H(15C)	109.5
O(1)-S(1)-C(2)	110.83(11)	C(18)-C(16)-O(4)	112.3(3)
O(4)-S(1)-C(2)	103.56(10)	C(18)-C(16)-H(16A)	109.1
C(6)-C(2)-C(3)	120.9(2)	O(4)-C(16)-H(16A)	109.1
C(6)-C(2)-S(1)	121.46(17)	C(18)-C(16)-H(16B)	109.1
C(3)-C(2)-S(1)	117.61(16)	O(4)-C(16)-H(16B)	109.1
C(7)-C(3)-C(2)	117.6(2)	H(16A)-C(16)-H(16B)	107.9
C(7)-C(3)-C(12)	118.1(2)	C(16)-C(18)-H(18A)	109.5
C(2)-C(3)-C(12)	124.3(2)	C(16)-C(18)-H(18B)	109.5
C(16)-O(4)-S(1)	117.47(18)	H(18A)-C(18)-H(18B)	109.5
C(8)-C(5)-C(6)	123.6(2)	C(16)-C(18)-H(18C)	109.5
C(8)-C(5)-H(5)	118.2	H(18A)-C(18)-H(18C)	109.5
C(6)-C(5)-H(5)	118.2	H(18B)-C(18)-H(18C)	109.5
C(5)-C(6)-C(2)	117.6(2)		

TABLE A6.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR ETHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	49(1)	60(1)	66(1)	-5(1)	18(1)	11(1)
O(1)	51(1)	100(2)	70(1)	4(1)	10(1)	24(1)
C(2)	41(1)	46(1)	51(1)	-2(1)	13(1)	4(1)
C(3)	51(1)	55(1)	47(1)	0(1)	15(1)	7(1)
O(4)	56(1)	80(1)	67(1)	-11(1)	27(1)	-3(1)
C(5)	53(1)	53(1)	48(1)	-4(1)	17(1)	4(1)
C(6)	45(1)	48(1)	47(1)	-2(1)	10(1)	0(1)
C(7)	47(1)	59(2)	49(1)	4(1)	11(1)	9(1)
C(8)	44(1)	46(1)	56(1)	1(1)	17(1)	5(1)
O(9)	82(1)	60(1)	102(2)	-22(1)	32(1)	11(1)
C(10)	51(1)	58(2)	66(2)	5(1)	20(1)	15(1)
C(11)	61(2)	72(2)	49(1)	-3(1)	6(1)	10(1)
C(12)	74(2)	98(2)	48(1)	-6(1)	21(1)	17(2)
C(13)	52(2)	93(2)	107(2)	7(2)	21(2)	8(2)
C(14)	95(3)	74(2)	146(3)	36(2)	60(2)	38(2)
C(15)	81(2)	133(3)	92(2)	-22(2)	32(2)	45(2)
C(16)	100(3)	98(3)	94(2)	-12(2)	28(2)	-37(2)
C(18)	240(6)	138(4)	104(3)	12(3)	31(4)	-88(4)

THE ANISOTROPIC DISPLACEMENT FACTOR EXPONENT TAKES THE FORM: $-2P^2[H^2 A^2 U^{11} + ... + 2 H K A \cdot B \cdot U^{12}]$

TABLE A6.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR ETHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
H(5)	2833	-143	-354	61
H(7)	3509	-119	2133	63
H(11A)	1202	624	-783	95
H(11B)	1852	872	-1131	95
H(11C)	1541	2130	-738	95
H(12A)	2474	2188	2592	109
H(12B)	2924	852	2970	109
H(12C)	2095	746	2634	109
H(13A)	4519	778	864	126
H(13B)	5015	-509	1222	126
H(13C)	4604	241	1780	126
H(14A)	4134	-2024	2026	150
H(14B)	4470	-2850	1419	150
H(14C)	3649	-2913	1284	150
H(15A)	3549	-2087	-238	151
H(15B)	4380	-2012	26	151
H(15C)	3928	-676	-348	151
H(16A)	219	-268	868	117
H(16B)	985	-775	903	117
H(18A)	477	-2233	1610	247
H(18B)	403	-988	2201	247
H(18C)	1158	-1534	2212	247

TABLE A6.6 - TORSION ANGLES [°] FOR ETHYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

O(9)-S(1)-C(2)-C(6)	-123.5(2)
O(1)-S(1)-C(2)-C(6)	9.6(2)
O(4)-S(1)-C(2)-C(6)	125.4(2)
O(9)-S(1)-C(2)-C(3)	56.3(2)
O(1)-S(1)-C(2)-C(3)	-170.57(18)
O(4)-S(1)-C(2)-C(3)	-54.8(2)
C(6)-C(2)-C(3)-C(7)	-2.2(4)
S(1)-C(2)-C(3)-C(7)	177.93(18)
C(6)-C(2)-C(3)-C(12)	177.2(2)
S(1)-C(2)-C(3)-C(12)	-2.6(3)
O(9)-S(1)-O(4)-C(16)	174.1(2)
O(1)-S(1)-O(4)-C(16)	47.2(2)
C(2)-S(1)-O(4)-C(16)	-70.5(2)
C(8)-C(5)-C(6)-C(2)	-0.3(3)
C(8)-C(5)-C(6)-C(11)	178.8(2)
C(3)-C(2)-C(6)-C(5)	2.1(3)
S(1)-C(2)-C(6)-C(5)	-178.05(16)
C(3)-C(2)-C(6)-C(11)	-176.9(2)
S(1)-C(2)-C(6)-C(11)	2.9(3)
C(2)-C(3)-C(7)-C(8)	0.6(4)
C(12)-C(3)-C(7)-C(8)	-178.9(2)
C(3)-C(7)-C(8)-C(5)	1.1(4)
C(3)-C(7)-C(8)-C(10)	179.5(2)
C(6)-C(5)-C(8)-C(7)	-1.3(4)
C(6)-C(5)-C(8)-C(10)	-179.6(2)
C(7)-C(8)-C(10)-C(13)	-66.2(3)
C(5)-C(8)-C(10)-C(13)	112.1(3)
C(7)-C(8)-C(10)-C(14)	52.7(3)
C(5)-C(8)-C(10)-C(14)	-129.1(3)
C(7)-C(8)-C(10)-C(15)	174.5(2)
C(5)-C(8)-C(10)-C(15)	-7.3(4)
S(1)-O(4)-C(16)-C(18)	160.4(3)

A7- X-RAY ANALYSIS OF PROPYL 4-TERT-BUTYL-2,6-DIMETHYL BENZENESULFONATE

TABLE A7.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR PROPYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

EMPIRICAL FORMULA	$C_{15}H_{27}O_3S$
FORMULA WEIGHT	287.42
TEMPERATURE	277.55 K
WAVELENGTH	0.71073 E
CRYSTAL SYSTEM	ORTHORHOMBIC
SPACE GROUP	P B C A
UNIT CELL DIMENSIONS	A = 9.5728(4) Å, α= 90°.
	B = 17.0595(9) Å, β= 90°.
	C = 19.4606(9) Å, γ = 90°.
VOLUME	3178.1(3) $Å^3$
Z	8
DENSITY (CALCULATED)	1.201 MG/M^3
ABSORPTION COEFFICIENT	0.206 MM-1
F(000)	1256
CRYSTAL SIZE	0.5 × 0.23 × 0.1 MM^3
THETA RANGE FOR DATA COLLECTION	3.824 TO 26.426°.
INDEX RANGES	-11<=H<=11, -21<=K<=21, -24<=L<=24
REFLECTIONS COLLECTED	40959
INDEPENDENT REFLECTIONS	3254 [R(INT) = 0.1123]
COMPLETENESS TO THETA = 26.000°	99.7 %
ABSORPTION CORRECTION	NONE
MAX. AND MIN. TRANSMISSION	0.7454 AND 0.6648
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	3254 / 0 / 178
GOODNESS-OF-FIT ON F^2	1.055
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0678, WR2 = 0.1874
R INDICES (ALL DATA)	R1 = 0.1219, WR2 = 0.2309
EXTINCTION COEFFICIENT	0.006(2)
LARGEST DIFF. PEAK AND HOLE	0.357 AND -0.281 $E.Å^{-3}$

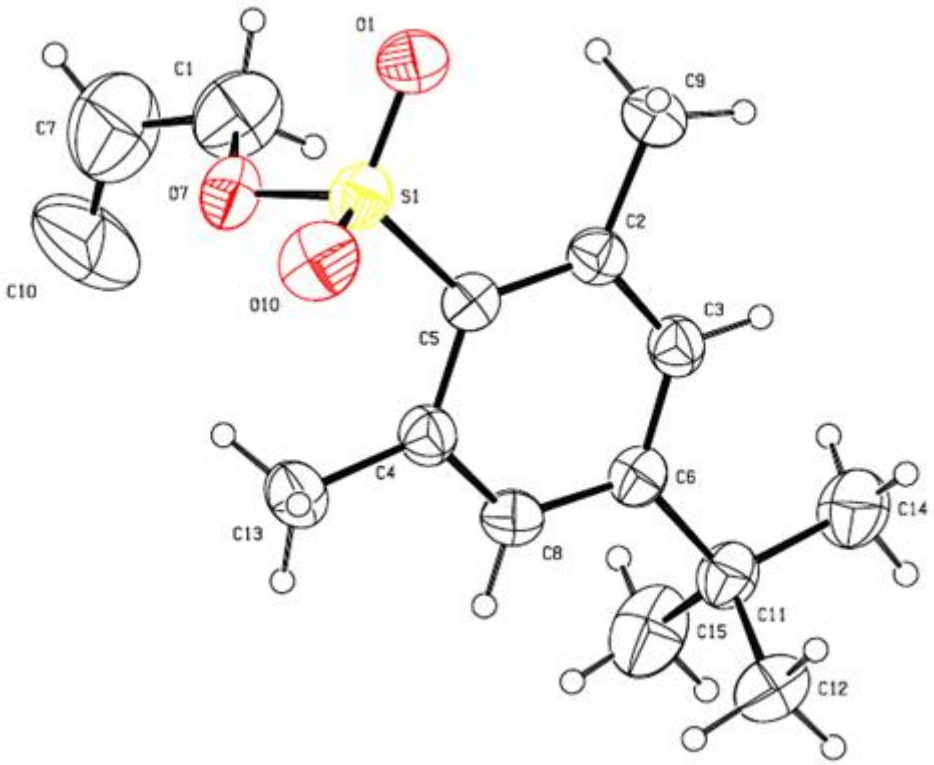


TABLE A7.2.- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
S(1)	5338(1)	1350(1)	6191(1)	68(1)
O(1)	5127(3)	716(2)	6657(1)	88(1)
C(2)	6652(3)	258(2)	5365(2)	57(1)
C(3)	7423(4)	74(2)	4784(2)	61(1)
C(4)	6688(3)	1625(2)	4985(2)	62(1)
C(5)	6294(3)	1045(2)	5466(2)	57(1)
C(6)	7854(3)	618(2)	4307(2)	60(1)
O(7)	6332(3)	1959(2)	6544(1)	80(1)
C(8)	7457(4)	1392(2)	4425(2)	64(1)
C(9)	6269(4)	-410(2)	5837(2)	72(1)
O(10)	4173(3)	1797(2)	5983(2)	94(1)
C(11)	8683(4)	403(2)	3661(2)	69(1)
C(12)	7762(5)	539(3)	3033(2)	88(1)
C(13)	6310(5)	2477(2)	5040(2)	85(1)
C(14)	9126(6)	-446(2)	3656(3)	104(2)
C(15)	10003(5)	902(3)	3630(3)	110(2)
C(1)	7574(6)	1646(4)	6897(3)	124(2)
C(7)	8469(8)	2272(5)	7161(5)	178(3)
C(10)	9194(12)	2704(5)	6734(5)	215(5)

TABLE A7.3 - BOND LENGTHS [Å] AND ANGLES [°]
FOR PROPYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

S(1)-O(1)	1.427(3)	O(10)-S(1)-O(7)	104.31(17)
S(1)-C(5)	1.760(3)	C(3)-C(2)-C(5)	117.6(3)
S(1)-O(7)	1.568(3)	C(3)-C(2)-C(9)	117.0(3)
S(1)-O(10)	1.410(3)	C(5)-C(2)-C(9)	125.4(3)
C(2)-C(3)	1.386(5)	C(6)-C(3)-C(2)	123.8(3)
C(2)-C(5)	1.400(5)	C(5)-C(4)-C(13)	124.5(3)
C(2)-C(9)	1.509(4)	C(8)-C(4)-C(5)	117.7(3)
C(3)-C(6)	1.376(5)	C(8)-C(4)-C(13)	117.8(3)
C(4)-C(5)	1.413(5)	C(2)-C(5)-S(1)	121.6(3)
C(4)-C(8)	1.375(5)	C(2)-C(5)-C(4)	120.9(3)
C(4)-C(13)	1.500(5)	C(4)-C(5)-S(1)	117.5(3)
C(6)-C(8)	1.393(5)	C(3)-C(6)-C(8)	116.5(3)
C(6)-C(11)	1.530(5)	C(3)-C(6)-C(11)	123.2(3)
O(7)-C(1)	1.473(6)	C(8)-C(6)-C(11)	120.2(3)
C(11)-C(12)	1.525(5)	C(1)-O(7)-S(1)	117.0(3)
C(11)-C(14)	1.510(5)	C(4)-C(8)-C(6)	123.5(3)
C(11)-C(15)	1.525(5)	C(12)-C(11)-C(6)	108.8(3)
C(1)-C(7)	1.464(8)	C(14)-C(11)-C(6)	112.4(3)
C(7)-C(10)	1.309(11)	C(14)-C(11)-C(12)	107.6(4)
O(1)-S(1)-C(5)	111.01(16)	C(14)-C(11)-C(15)	107.6(4)
O(1)-S(1)-O(7)	108.01(17)	C(15)-C(11)-C(6)	109.2(3)
O(7)-S(1)-C(5)	103.44(15)	C(15)-C(11)-C(12)	111.2(4)
O(10)-S(1)-O(1)	118.77(18)	C(7)-C(1)-O()	111.8(5)
O(10)-S(1)-C(5)	109.95(17)	C(10)-C(7)-C(1)	119.8(8)

TABLE A7.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	62(1)	74(1)	67(1)	-6(1)	8(1)	2(1)
O(1)	104(2)	86(2)	73(2)	5(1)	24(2)	-7(2)
C(2)	54(2)	59(2)	58(2)	3(2)	-4(2)	0(2)
C(3)	64(2)	54(2)	64(2)	-3(2)	-5(2)	5(2)
C(4)	64(2)	57(2)	64(2)	-1(2)	-1(2)	3(2)
C(5)	55(2)	61(2)	55(2)	-1(2)	0(2)	0(2)
C(6)	55(2)	65(2)	58(2)	-5(2)	1(2)	-1(2)
O(7)	83(2)	80(2)	76(2)	-20(1)	5(1)	-1(1)
C(8)	69(2)	64(2)	59(2)	6(2)	8(2)	-5(2)
C(9)	82(3)	62(2)	72(2)	10(2)	-3(2)	5(2)
O(10)	67(2)	115(2)	99(2)	-4(2)	6(2)	26(2)
C(11)	63(2)	76(2)	67(2)	-9(2)	6(2)	-1(2)
C(12)	90(3)	110(3)	65(2)	-2(2)	4(2)	-1(2)
C(13)	110(3)	59(2)	86(3)	2(2)	14(3)	7(2)
C(14)	118(4)	97(3)	95(3)	-14(3)	25(3)	33(3)
C(15)	71(3)	145(4)	115(4)	-36(4)	28(3)	-23(3)
C(1)	99(3)	157(5)	114(4)	-7(4)	-26(3)	-5(4)
C(7)	180(7)	182(7)	171(7)	-33(6)	-65(6)	-43(6)
C(10)	277(11)	131(6)	237(11)	54(6)	56(9)	-72(7)

TABLE A7.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
H(3)	7662	-448	4712	73
H(8)	7727	1770	4108	77
H(9A)	6601	-894	5646	108
H(9B)	5271	-432	5886	108
H(9C)	6688	-327	6279	108
H(12A)	6912	245	3080	133
H(12B)	8248	370	2628	133
H(12C)	7546	1087	2995	133
H(13A)	5323	2538	4971	127
H(13B)	6807	2769	4697	127
H(13C)	6559	2668	5488	127
H(14A)	9696	-551	4052	155
H(14B)	9651	-552	3246	155
H(14C)	8313	-775	3667	155
H(15A)	9751	1445	3590	165
H(15B)	10550	750	3238	165
H(15C)	10539	825	4041	165
H(1A)	7279	1314	7274	148

H(1B)	8104	1325	6578	148
H(7)	8523	2364	7631	213

TABLE A7.6 - TORSION ANGLES [°]
FOR PROPYL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

S(1)-O(7)-C(1)-C(7)	175.8(5)
O(1)-S(1)-C(5)-C(2)	5.4(3)
O(1)-S(1)-C(5)-C(4)	-174.7(3)
O(1)-S(1)-O(7)-C(1)	45.2(3)
C(2)-C(3)-C(6)-C(8)	-1.0(5)
C(2)-C(3)-C(6)-C(11)	-179.0(3)
C(3)-C(2)-C(5)-S(1)	-179.2(2)
C(3)-C(2)-C(5)-C(4)	0.9(5)
C(3)-C(6)-C(8)-C(4)	0.6(5)
C(3)-C(6)-C(11)-C(12)	111.8(4)
C(3)-C(6)-C(11)-C(14)	-7.3(5)
C(3)-C(6)-C(11)-C(15)	-126.6(4)
C(5)-S(1)-O(7)-C(1)	-72.6(3)
C(5)-C(2)-C(3)-C(6)	0.2(5)
C(5)-C(4)-C(8)-C(6)	0.5(5)
O(7)-S(1)-C(5)-C(2)	121.0(3)
O(7)-S(1)-C(5)-C(4)	-59.1(3)
O(7)-C(1)-C(7)-C(10)	-71.4(10)
C(8)-C(4)-C(5)-S(1)	178.8(2)
C(8)-C(4)-C(5)-C(2)	-1.3(5)
C(8)-C(6)-C(11)-C(12)	-66.1(4)
C(8)-C(6)-C(11)-C(14)	174.8(4)
C(8)-C(6)-C(11)-C(15)	55.5(5)
C(9)-C(2)-C(3)-C(6)	-179.8(3)
C(9)-C(2)-C(5)-S(1)	0.9(5)
C(9)-C(2)-C(5)-C(4)	-179.0(3)
O(10)-S(1)-C(5)-C(2)	-128.1(3)
O(10)-S(1)-C(5)-C(4)	51.8(3)
O(10)-S(1)-O(7)-C(1)	172.4(3)
C(11)-C(6)-C(8)-C(4)	178.7(3)
C(13)-C(4)-C(5)-S(1)	-2.0(5)
C(13)-C(4)-C(5)-C(2)	178.0(3)
C(13)-C(4)-C(8)-C(6)	-178.8(4)

A8- X-RAY ANALYSIS OF PROPAN-2-YL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

TABLE A8.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR PROPAN-2-YL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

EMPIRICAL FORMULA	$C_{15}H_{24}O_3S$
FORMULA WEIGHT	284.40
TEMPERATURE	298(2) K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	ORTHORHOMBIC
SPACE GROUP	P B C A
UNIT CELL DIMENSIONS	A = 9.8137(4) Å, α= 90°.
	B = 16.9744(7) Å, β= 90°.
	C = 19.3251(8) Å, γ = 90°.
VOLUME	3219.2(2) $Å^3$
Z	8
DENSITY (CALCULATED)	1.174 MG/M^3
ABSORPTION COEFFICIENT	0.203 MM^{-1}
F(000)	1232
CRYSTAL SIZE	0.500 × 0.260 × 0.100 MM^3
THETA RANGE FOR DATA COLLECTION	2.619 TO 26.460°.
INDEX RANGES	-12<=H<=12, -21<=K<=21, -24<=L<=24
REFLECTIONS COLLECTED	67908
INDEPENDENT REFLECTIONS	3326 [R(INT) = 0.1061]
COMPLETENESS TO THETA = 25.242°	99.9 %
ABSORPTION CORRECTION	SEMI-EMPIRICAL FROM EQUIVALENTS
MAX. AND MIN. TRANSMISSION	0.7454 AND 0.5910
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	3326 / 0 / 180
GOODNESS-OF-FIT ON F^2	1.015
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0531, WR2 = 0.1349
R INDICES (ALL DATA)	R1 = 0.0949, WR2 = 0.1649
EXTINCTION COEFFICIENT	0.0096(13)
LARGEST DIFF. PEAK AND HOLE	0.286 AND -0.203 $E.Å^{-3}$

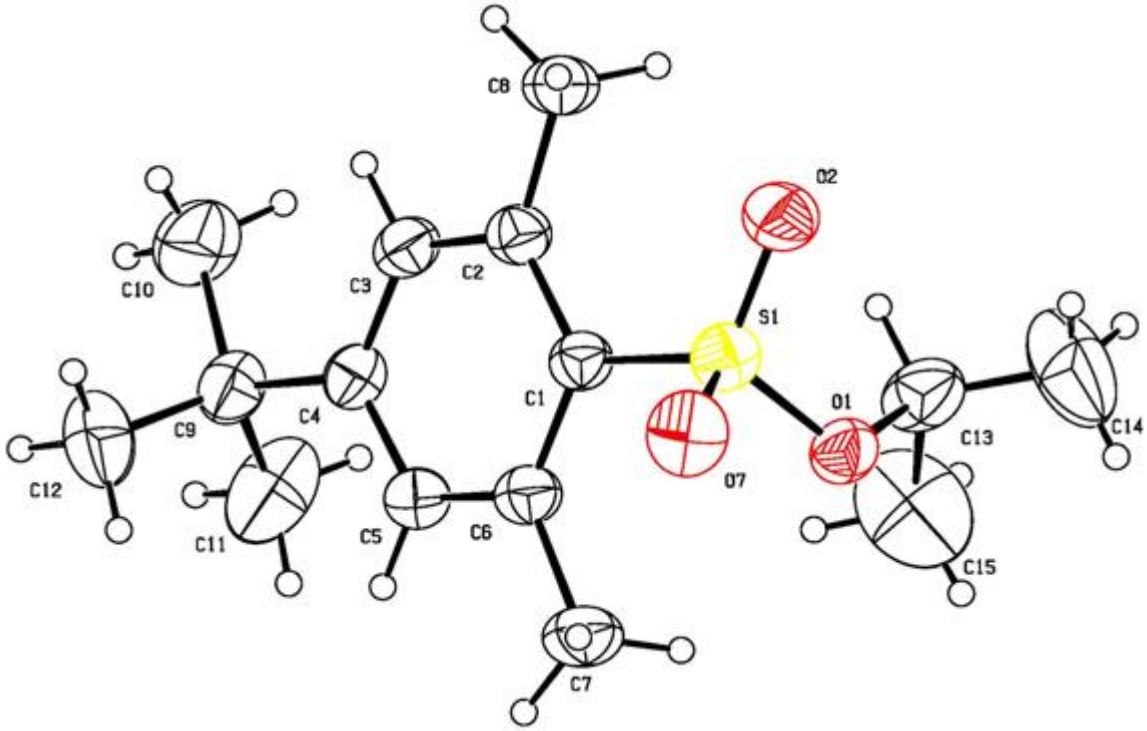


TABLE A8.2.- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPAN-2-YL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)*
S(1)	273(1)	1398(1)	3864(1)	68(1)
O(1)	1122(2)	2096(1)	3558(1)	71(1)
O(2)	164(2)	802(1)	3352(1)	86(1)
C(2)	1654(3)	281(1)	4635(1)	60(1)
C(4)	2878(2)	610(1)	5696(1)	63(1)
C(6)	1631(3)	1631(1)	5076(1)	63(1)
C(1)	1260(2)	1073(1)	4570(1)	57(1)
O(7)	-934(2)	1757(1)	4110(1)	90(1)
C(5)	2437(3)	1382(1)	5620(1)	66(1)
C(3)	2451(3)	78(1)	5202(1)	64(1)
C(9)	3744(3)	371(2)	6313(2)	76(1)
C(8)	1270(3)	-377(2)	4149(2)	77(1)
C(13)	2382(4)	1927(2)	3171(2)	96(1)
C(7)	1200(3)	2487(2)	5070(2)	86(1)
C(12)	2861(4)	390(2)	6951(2)	114(1)
C(11)	4943(4)	935(2)	6388(2)	135(2)
C(10)	4328(5)	-465(2)	6232(2)	121(1)
C(15)	3463(4)	2443(4)	3485(3)	174(2)
C(14)	2119(5)	2114(3)	2446(2)	168(2)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A8.3 - BOND LENGTHS [Å] AND ANGLES [°]
FOR PROPAN-2-YL 4-TERT-BUTYL-2,6-
DIMETHYLBENZENESULFONATE

S(1)-O(7)	1.414(2)	C(6)-C(1)-S(1)	117.98(18)
S(1)-O(2)	1.418(2)	C(6)-C(5)-C(4)	123.2(2)
S(1)-O(1)	1.5640(18)	C(6)-C(5)-H(5)	118.4
S(1)-C(1)	1.763(2)	C(4)-C(5)-H(5)	118.4
O(1)-C(13)	1.473(3)	C(4)-C(3)-C(2)	123.6(2)
C(2)-C(3)	1.391(3)	C(4)-C(3)-H(3)	118.2
C(2)-C(1)	1.405(3)	C(2)-C(3)-H(3)	118.2
C(2)-C(8)	1.507(3)	C(12)-C(9)-C(4)	108.3(2)
C(4)-C(3)	1.380(4)	C(12)-C(9)-C(11)	110.6(3)
C(4)-C(5)	1.386(3)	C(4)-C(9)-C(11)	109.8(2)
C(4)-C(9)	1.519(4)	C(12)-C(9)-C(10)	108.5(3)
C(6)-C(5)	1.383(3)	C(4)-C(9)-C(10)	112.1(2)
C(6)-C(1)	1.408(3)	C(11)-C(9)-C(10)	107.5(3)
C(6)-C(7)	1.514(3)	C(2)-C(8)-H(8A)	109.5
C(5)-H(5)	0.9300	C(2)-C(8)-H(8B)	109.5
C(3)-H(3)	0.9300	H(8A)-C(8)-H(8B)	109.5
C(9)-C(12)	1.508(4)	C(2)-C(8)-H(8C)	109.5
C(9)-C(11)	1.524(4)	H(8A)-C(8)-H(8C)	109.5
C(9)-C(10)	1.538(4)	H(8B)-C(8)-H(8C)	109.5
C(8)-H(8A)	0.9600	C(14)-C(13)-O(1)	107.2(3)
C(8)-H(8B)	0.9600	C(14)-C(13)-C(15)	112.6(4)
C(8)-H(8C)	0.9600	O(1)-C(13)-C(15)	106.0(3)
C(13)-C(14)	1.459(6)	C(14)-C(13)-H(13)	110.3
C(13)-C(15)	1.503(5)	O(1)-C(13)-H(13)	110.3
C(13)-H(13)	0.9800	C(15)-C(13)-H(13)	110.3
C(7)-H(7A)	0.9600	C(6)-C(7)-H(7A)	109.5
C(7)-H(7B)	0.9600	C(6)-C(7)-H(7B)	109.5
C(7)-H(7C)	0.9600	H(7A)-C(7)-H(7B)	109.5
C(12)-H(12A)	0.9600	C(6)-C(7)-H(7C)	109.5
C(12)-H(12B)	0.9600	H(7A)-C(7)-H(7C)	109.5
C(12)-H(12C)	0.9600	H(7B)-C(7)-H(7C)	109.5
C(11)-H(11A)	0.9600	C(9)-C(12)-H(12A)	109.5
C(11)-H(11B)	0.9600	C(9)-C(12)-H(12B)	109.5
C(11)-H(11C)	0.9600	H(12A)-C(12)-H(12B)	109.5

C(10)-H(10A)	0.9600	C(9)-C(12)-H(12C)	109.5
C(10)-H(10B)	0.9600	H(12A)-C(12)-H(12C)	109.5
C(10)-H(10C)	0.9600	H(12B)-C(12)-H(12C)	109.5
C(15)-H(15A)	0.9600	C(9)-C(11)-H(11A)	109.5
C(15)-H(15B)	0.9600	C(9)-C(11)-H(11B)	109.5
C(15)-H(15C)	0.9600	H(11A)-C(11)-H(11B)	109.5
C(14)-H(14A)	0.9600	C(9)-C(11)-H(11C)	109.5
C(14)-H(14B)	0.9600	H(11A)-C(11)-H(11C)	109.5
C(14)-H(14C)	0.9600	H(11B)-C(11)-H(11C)	109.5
O(7)-S(1)-O(2)	118.55(13)	C(9)-C(10)-H(10A)	109.5
O(7)-S(1)-O(1)	104.30(12)	C(9)-C(10)-H(10B)	109.5
O(2)-S(1)-O(1)	108.45(12)	H(10A)-C(10)-H(10B)	109.5
O(7)-S(1)-C(1)	109.56(12)	C(9)-C(10)-H(10C)	109.5
O(2)-S(1)-C(1)	111.01(12)	H(10A)-C(10)-H(10C)	109.5
O(1)-S(1)-C(1)	103.73(11)	H(10B)-C(10)-H(10C)	109.5
C(13)-O(1)-S(1)	119.44(16)	C(13)-C(15)-H(15A)	109.5
C(3)-C(2)-C(1)	117.5(2)	C(13)-C(15)-H(15B)	109.5
C(3)-C(2)-C(8)	116.6(2)	H(15A)-C(15)-H(15B)	109.5
C(1)-C(2)-C(8)	125.8(2)	C(13)-C(15)-H(15C)	109.5
C(3)-C(4)-C(5)	116.8(2)	H(15A)-C(15)-H(15C)	109.5
C(3)-C(4)-C(9)	122.5(2)	H(15B)-C(15)-H(15C)	109.5
C(5)-C(4)-C(9)	120.7(2)	C(13)-C(14)-H(14A)	109.5
C(5)-C(6)-C(1)	118.1(2)	C(13)-C(14)-H(14B)	109.5
C(5)-C(6)-C(7)	117.3(2)	H(14A)-C(14)-H(14B)	109.5
C(1)-C(6)-C(7)	124.6(2)	C(13)-C(14)-H(14C)	109.5
C(2)-C(1)-C(6)	120.7(2)	H(14A)-C(14)-H(14C)	109.5
C(2)-C(1)-S(1)	121.29(18)	H(14B)-C(14)-H(14C)	109.5

TABLE A8.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPAN-2-YL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	64(1)	68(1)	73(1)	2(1)	-5(1)	4(1)
O(1)	77(1)	59(1)	76(1)	5(1)	9(1)	12(1)
O(2)	104(2)	77(1)	78(1)	-7(1)	-20(1)	-8(1)
C(2)	59(1)	56(1)	65(1)	-4(1)	9(1)	-2(1)
C(4)	63(2)	60(1)	66(2)	6(1)	2(1)	-5(1)
C(6)	66(2)	54(1)	69(2)	-4(1)	3(1)	2(1)
C(1)	57(1)	52(1)	62(1)	-1(1)	4(1)	1(1)
O(7)	59(1)	107(2)	104(2)	8(1)	3(1)	17(1)
C(5)	74(2)	58(1)	64(2)	-2(1)	-1(1)	-6(1)
C(3)	69(2)	51(1)	72(2)	4(1)	4(1)	2(1)
C(9)	79(2)	73(2)	76(2)	13(1)	-10(2)	-9(1)
C(8)	89(2)	58(2)	82(2)	-12(1)	-2(2)	2(1)
C(13)	95(2)	72(2)	121(3)	4(2)	34(2)	6(2)
C(7)	106(2)	58(2)	92(2)	-11(1)	-7(2)	16(2)
C(12)	125(3)	146(3)	72(2)	14(2)	-8(2)	-4(2)
C(11)	109(3)	133(3)	164(4)	53(3)	-62(3)	-43(2)
C(10)	149(3)	95(2)	119(3)	19(2)	-39(3)	31(2)
C(15)	91(3)	252(6)	181(5)	-35(5)	6(3)	-46(4)
C(14)	159(4)	249(6)	96(3)	-18(3)	40(3)	-32(4)

THE ANISOTROPIC DISPLACEMENT FACTOR EXPONENT TAKES THE FORM: $-2P^2[H^2 A^2 U^{11} + ... + 2 H K A \cdot B \cdot U^{12}]$

TABLE A8.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPAN-2-YL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
H(5)	2697	1750	5952	79
H(3)	2711	-446	5252	77
H(8A)	298	-388	4093	115
H(8B)	1574	-870	4336	115
H(8C)	1693	-291	3707	115
H(13)	2630	1371	3221	115
H(7A)	1604	2748	4680	128
H(7B)	1497	2737	5489	128
H(7C)	225	2519	5037	128
H(12A)	2496	910	7011	171
H(12B)	3398	252	7348	171
H(12C)	2127	21	6901	171
H(11A)	5475	929	5972	203
H(11B)	5500	772	6771	203
H(11C)	4609	1458	6470	203
H(10A)	3598	-841	6243	181
H(10B)	4950	-570	6604	181
H(10C)	4801	-504	5799	181
H(15A)	3225	2986	3416	262
H(15B)	4322	2337	3266	262
H(15C)	3531	2336	3971	262
H(14A)	1344	1819	2288	252
H(14B)	2901	1977	2174	252
H(14C)	1938	2667	2401	252

TABLE A8.6 - TORSION ANGLES [°] FOR PROPAN-2-YL 4-TERT-BUTYL-2,6-DIMETHYLBENZENESULFONATE

O(7)-S(1)-O(1)-C(13)	-172.2(2)
O(2)-S(1)-O(1)-C(13)	-45.0(2)
C(1)-S(1)-O(1)-C(13)	73.1(2)
C(3)-C(2)-C(1)-C(6)	-1.8(4)
C(8)-C(2)-C(1)-C(6)	177.1(2)
C(3)-C(2)-C(1)-S(1)	178.96(18)
C(8)-C(2)-C(1)-S(1)	-2.2(4)
C(5)-C(6)-C(1)-C(2)	2.5(4)
C(7)-C(6)-C(1)-C(2)	-177.0(2)
C(5)-C(6)-C(1)-S(1)	-178.21(19)
C(7)-C(6)-C(1)-S(1)	2.3(4)
O(7)-S(1)-C(1)-C(2)	123.1(2)
O(2)-S(1)-C(1)-C(2)	-9.8(2)
O(1)-S(1)-C(1)-C(2)	-126.0(2)
O(7)-S(1)-C(1)-C(6)	-56.2(2)
O(2)-S(1)-C(1)-C(6)	170.96(19)
O(1)-S(1)-C(1)-C(6)	54.7(2)
C(1)-C(6)-C(5)-C(4)	-1.0(4)
C(7)-C(6)-C(5)-C(4)	178.5(3)
C(3)-C(4)-C(5)-C(6)	-1.2(4)
C(9)-C(4)-C(5)-C(6)	-179.0(2)
C(5)-C(4)-C(3)-C(2)	2.0(4)
C(9)-C(4)-C(3)-C(2)	179.7(2)
C(1)-C(2)-C(3)-C(4)	-0.5(4)
C(8)-C(2)-C(3)-C(4)	-179.5(2)
C(3)-C(4)-C(9)-C(12)	-107.2(3)
C(5)-C(4)-C(9)-C(12)	70.4(3)
C(3)-C(4)-C(9)-C(11)	131.9(3)
C(5)-C(4)-C(9)-C(11)	-50.4(4)
C(3)-C(4)-C(9)-C(10)	12.5(4)
C(5)-C(4)-C(9)-C(10)	-169.9(3)
S(1)-O(1)-C(13)-C(14)	110.2(3)
S(1)-O(1)-C(13)-C(15)	-129.2(3)

A9- X-RAY ANALYSIS OF METHYL 2,4,6-TRIMETHYL BENZENESULFONATE

TABLE A9.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR METHYL 2,4,6-TRIMETHYLBENZENESULFONATE

EMPIRICAL FORMULA	$C_{10}\ H_{14}\ O_3\ S$
FORMULA WEIGHT	214.27
TEMPERATURE	99.65 K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	MONOCLINIC
SPACE GROUP	P 1 21/N 1
UNIT CELL DIMENSIONS	A = 5.9389(2) Å, α= 90°.
	B = 15.7078(5) Å, β= 92.7938(15)°.
	C = 11.1715(4) Å, γ = 90°.
VOLUME	1040.92(6) $Å^3$
Z	4
DENSITY (CALCULATED)	1.367 MG/M^3
ABSORPTION COEFFICIENT	0.289 MM^{-1}
F(000)	456
CRYSTAL SIZE	0.486 × 0.327 × 0.253 MM^3
THETA RANGE FOR DATA COLLECTION	2.239 TO 30.512°.
INDEX RANGES	-8<=H<=8, -22<=K<=22, -15<=L<=15
REFLECTIONS COLLECTED	18246
INDEPENDENT REFLECTIONS	3123 [R(INT) = 0.0247]
COMPLETENESS TO THETA = 26.000°	99.6 %
ABSORPTION CORRECTION	NONE
MAX. AND MIN. TRANSMISSION	0.7461 AND 0.7104
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	3123 / 0 / 183
GOODNESS-OF-FIT ON F^2	1.066
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0285, WR2 = 0.0808
R INDICES (ALL DATA)	R1 = 0.0309, WR2 = 0.0829
EXTINCTION COEFFICIENT	N/A
LARGEST DIFF. PEAK AND HOLE	0.411 AND -0.316 $E.Å^{-3}$

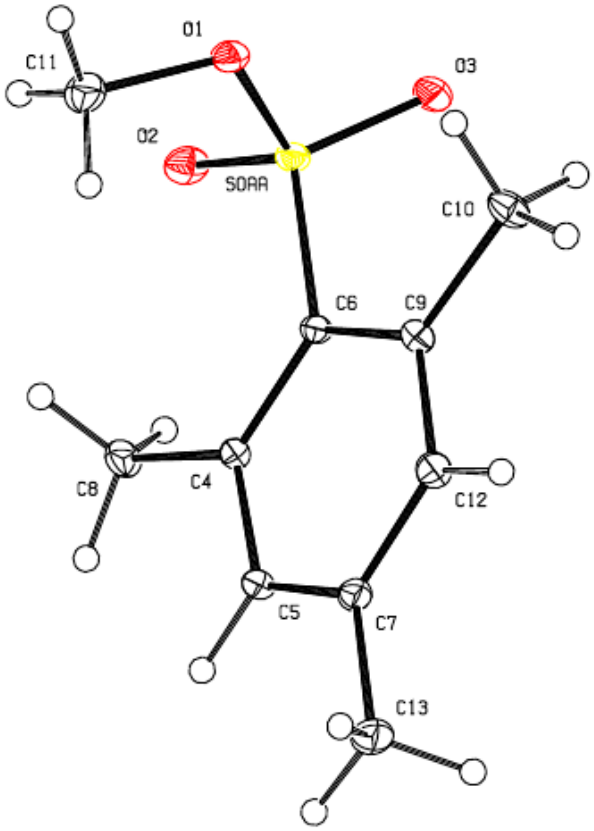


TABLE A9.2.- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR METHYL 2,4,6-TRIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
S(0AA)	2089(1)	8474(1)	1970(1)	16(1)
O(1)	3801(1)	8012(1)	1150(1)	20(1)
O(2)	232(1)	8780(1)	1233(1)	23(1)
O(3)	1655(1)	7856(1)	2871(1)	23(1)
C(4)	3105(2)	10180(1)	2368(1)	15(1)
C(5)	4490(2)	10811(1)	2889(1)	17(1)
C(6)	3687(1)	9324(1)	2608(1)	14(1)
C(7)	6398(2)	10623(1)	3607(1)	18(1)
C(8)	1122(2)	10482(1)	1579(1)	21(1)
C(9)	5604(2)	9109(1)	3354(1)	16(1)
C(10)	6338(2)	8212(1)	3659(1)	22(1)
C(11)	4546(2)	8487(1)	125(1)	26(1)
C(12)	6911(2)	9772(1)	3832(1)	19(1)
C(13)	7893(2)	11324(1)	4113(1)	25(1)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A9.3 - BOND LENGTHS [Å] AND ANGLES [°]
FOR METHYL 2,4,6-TRIMETHYLBENZENESULFONATE

S(0AA)-O(1)	1.5786(7)	C(7)-C(5)-C(4)	122.53(9)
S(0AA)-O(2)	1.4279(8)	C(7)-C(5)-H(5)	119.7(9)
S(0AA)-O(3)	1.4298(8)	C(4)-C(6)-S(0AA)	121.41(7)
S(0AA)-C(6)	1.7678(9)	C(4)-C(6)-C(9)	121.38(8)
O(1)-C(11)	1.4532(13)	C(9)-C(6)-S(0AA)	117.20(7)
C(4)-C(5)	1.3970(13)	C(5)-C(7)-C(12)	118.32(9)
C(4)-C(6)	1.4117(12)	C(5)-C(7)-C(13)	120.75(9)
C(4)-C(8)	1.5122(13)	C(12)-C(7)-C(13)	120.92(9)
C(5)-C(7)	1.3871(13)	C(4)-C(8)-H(8A)	111.2(9)
C(5)-H(5)	0.971(15)	C(4)-C(8)-H(8B)	112.2(9)
C(6)-C(9)	1.4174(12)	C(4)-C(8)-H(8C)	109.9(8)
C(7)-C(12)	1.3915(14)	H(8A)-C(8)-H(8B)	108.9(12)
C(7)-C(13)	1.5067(14)	H(8A)-C(8)-H(8C)	107.6(12)
C(8)-H(8A)	0.961(15)	H(8B)-C(8)-H(8C)	106.9(12)
C(8)-H(8B)	0.960(15)	C(6)-C(9)-C(10)	124.72(9)
C(8)-H(8C)	0.977(16)	C(12)-C(9)-C(6)	117.71(9)
C(9)-C(10)	1.5098(13)	C(12)-C(9)-C(10)	117.56(9)
C(9)-C(12)	1.3899(13)	C(9)-C(10)-H(10A)	114.9(9)
C(10)-H(10A)	0.954(16)	C(9)-C(10)-H(10B)	111.6(11)
C(10)-H(10B)	0.960(18)	C(9)-C(10)-H(10C)	111.2(10)
C(10)-H(10C)	0.971(18)	H(10A)-C(10)-H(10B)	104.1(14)
C(11)-H(11A)	0.914(17)	H(10A)-C(10)-H(10C)	106.6(13)
C(11)-H(11B)	0.934(18)	H(10B)-C(10)-H(10C)	108.0(14)
C(11)-H(11C)	0.958(19)	O(1)-C(11)-H(11A)	106.2(10)
C(12)-H(12)	0.962(15)	O(1)-C(11)-H(11B)	108.5(11)
C(13)-H(13A)	0.972(15)	O(1)-C(11)-H(11C)	109.6(11)
C(13)-H(13B)	0.948(18)	H(11A)-C(11)-H(11B)	109.3(14)
C(13)-H(13C)	0.974(17)	H(11A)-C(11)-H(11C)	110.4(15)
O(1)-S(0AA)-C(6)	103.48(4)	H(11B)-C(11)-H(11C)	112.6(15)
O(2)-S(0AA)-O(1)	108.74(4)	C(7)-C(12)-H(12)	121.1(9)
O(2)-S(0AA)-O(3)	118.30(5)	C(9)-C(12)-C(7)	122.48(9)
O(2)-S(0AA)-C(6)	111.23(4)	C(9)-C(12)-H(12)	116.4(8)
O(3)-S(0AA)-O(1)	103.89(4)	C(7)-C(13)-H(13A)	111.7(9)
O(3)-S(0AA)-C(6)	109.90(4)	C(7)-C(13)-H(13B)	111.1(11)
C(11)-O(1)-S(0AA)	116.81(7)	C(7)-C(13)-H(13C)	111.3(10)
C(5)-C(4)-C(6)	117.57(8)	H(13A)-C(13)-H(13B)	106.2(14)
C(5)-C(4)-C(8)	116.49(8)	H(13A)-C(13)-H(13C)	109.8(14)
C(6)-C(4)-C(8)	125.93(8)	H(13B)-C(13)-H(13C)	106.6(14)
C(4)-C(5)-H(5)	117.7(9)		

TABLE A9.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR METHYL 2,4,6-TRIMETHYLBENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(0AA)	17(1)	13(1)	17(1)	-1(1)	1(1)	-3(1)
O(1)	26(1)	15(1)	20(1)	-3(1)	5(1)	1(1)
O(2)	19(1)	23(1)	28(1)	-3(1)	-5(1)	-2(1)
O(3)	31(1)	17(1)	23(1)	1(1)	5(1)	-9(1)
C(4)	18(1)	13(1)	14(1)	1(1)	1(1)	0(1)
C(5)	23(1)	12(1)	17(1)	0(1)	2(1)	-1(1)
C(6)	15(1)	11(1)	15(1)	-1(1)	1(1)	-1(1)
C(7)	21(1)	17(1)	16(1)	-1(1)	2(1)	-5(1)
C(8)	22(1)	18(1)	22(1)	4(1)	-4(1)	2(1)
C(9)	16(1)	14(1)	18(1)	2(1)	1(1)	1(1)
C(10)	20(1)	16(1)	31(1)	4(1)	-2(1)	4(1)
C(11)	32(1)	26(1)	22(1)	-3(1)	10(1)	-3(1)
C(12)	17(1)	19(1)	20(1)	1(1)	-2(1)	-2(1)
C(13)	29(1)	22(1)	24(1)	-4(1)	-1(1)	-10(1)
C(14)	52(2)	65(2)	75(2)	-2(1)	-16(1)	13(1)

THE ANISOTROPIC DISPLACEMENT FACTOR EXPONENT TAKES THE FORM: $-2P^2[H^2 A^2 U^{11} + ... + 2 H K A \cdot B \cdot U^{12}]$

TABLE A9.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR METHYL 2,4,6-TRIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
H(8A)	1270(20)	10309(9)	762(14)	28(4)
H(5)	4100(30)	11401(9)	2720(13)	27(4)
H(12)	8230(20)	9613(9)	4317(13)	26(3)
H(8B)	-290(20)	10277(9)	1850(13)	26(3)
H(10A)	6550(30)	7853(10)	2985(14)	32(4)
H(8C)	1050(20)	11104(10)	1591(13)	28(4)
H(13A)	8020(30)	11307(9)	4984(14)	28(4)
H(10B)	5230(30)	7918(12)	4102(15)	47(5)
H(11A)	5380(30)	8116(11)	-304(14)	36(4)
H(11B)	3280(30)	8656(11)	-342(15)	40(4)
H(13B)	7300(30)	11867(12)	3904(15)	43(4)
H(13C)	9390(30)	11296(11)	3795(15)	40(4)
H(11C)	5460(30)	8958(12)	398(16)	51(5)
H(10C)	7750(30)	8208(11)	4137(15)	44(4)

TABLE A9.6 - TORSION ANGLES [°]FOR METHYL 2,4,6-TRIMETHYLBENZENESULFONATE

S(0AA)-C(6)-C(9)-C(10)	-1.42(13)
S(0AA)-C(6)-C(9)-C(12)	178.15(7)
O(1)-S(0AA)-C(6)-C(4)	116.06(8)
O(1)-S(0AA)-C(6)-C(9)	-62.76(8)
O(2)-S(0AA)-O(1)-C(11)	52.38(8)
O(2)-S(0AA)-C(6)-C(4)	-0.53(9)
O(2)-S(0AA)-C(6)-C(9)	-179.35(7)
O(3)-S(0AA)-O(1)-C(11)	179.22(7)
O(3)-S(0AA)-C(6)-C(4)	-133.49(8)
O(3)-S(0AA)-C(6)-C(9)	47.68(8)
C(4)-C(5)-C(7)-C(12)	-1.39(14)
C(4)-C(5)-C(7)-C(13)	177.65(9)
C(4)-C(6)-C(9)-C(10)	179.76(9)
C(4)-C(6)-C(9)-C(12)	-0.68(13)
C(5)-C(4)-C(6)-S(0AA)	-178.64(7)
C(5)-C(4)-C(6)-C(9)	0.14(13)
C(5)-C(7)-C(12)-C(9)	0.80(15)
C(6)-S(0AA)-O(1)-C(11)	-65.95(8)
C(6)-C(4)-C(5)-C(7)	0.93(14)
C(6)-C(9)-C(12)-C(7)	0.20(14)
C(8)-C(4)-C(5)-C(7)	-178.32(9)
C(8)-C(4)-C(6)-S(0AA)	0.52(13)
C(8)-C(4)-C(6)-C(9)	179.30(9)
C(10)-C(9)-C(12)-C(7)	179.80(9)
C(13)-C(7)-C(12)-C(9)	-178.23(9)

A10- X-RAY ANALYSIS OF PROPAN-2-YL 2,4,6-TRIMETHYLBENZENE SULFONATE

TABLE A10.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR PROPAN-2-YL 2,4,6-TRIMETHYLBENZENESULFONATE

EMPIRICAL FORMULA	$C_{12}\ H_{18}\ O_3\ S$
FORMULA WEIGHT	242.32
TEMPERATURE	297.25 K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	TRICLINIC
SPACE GROUP	P -1
UNIT CELL DIMENSIONS	A = 7.6288(2) Å, α= 108.8314(10)°. B = 8.1300(2) Å, β= 103.3969(10)°. C = 11.8423(2) Å, γ = 98.7032(10)°.
VOLUME	655.54(3) $Å^3$
Z	2
DENSITY (CALCULATED)	1.228 MG/M^3
ABSORPTION COEFFICIENT	0.238 MM^{-1}
F(000)	260
CRYSTAL SIZE	0.4 × 0.3 × 0.2 MM^3
THETA RANGE FOR DATA COLLECTION	2.900 TO 28.320°.
INDEX RANGES	-10<=H<=10, -10<=K<=10, -15<=L<=15
REFLECTIONS COLLECTED	19453
INDEPENDENT REFLECTIONS	3231 [R(INT) = 0.0179]
COMPLETENESS TO THETA = 26.000°	98.8 %
ABSORPTION CORRECTION	NONE
MAX. AND MIN. TRANSMISSION	0.7457 AND 0.6835
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	3231 / 0 / 150
GOODNESS-OF-FIT ON F^2	1.052
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0406, WR2 = 0.1162
R INDICES (ALL DATA)	R1 = 0.0444, WR2 = 0.1200
EXTINCTION COEFFICIENT	N/A
LARGEST DIFF. PEAK AND HOLE	0.285 AND -0.262 $E.Å^{-3}$

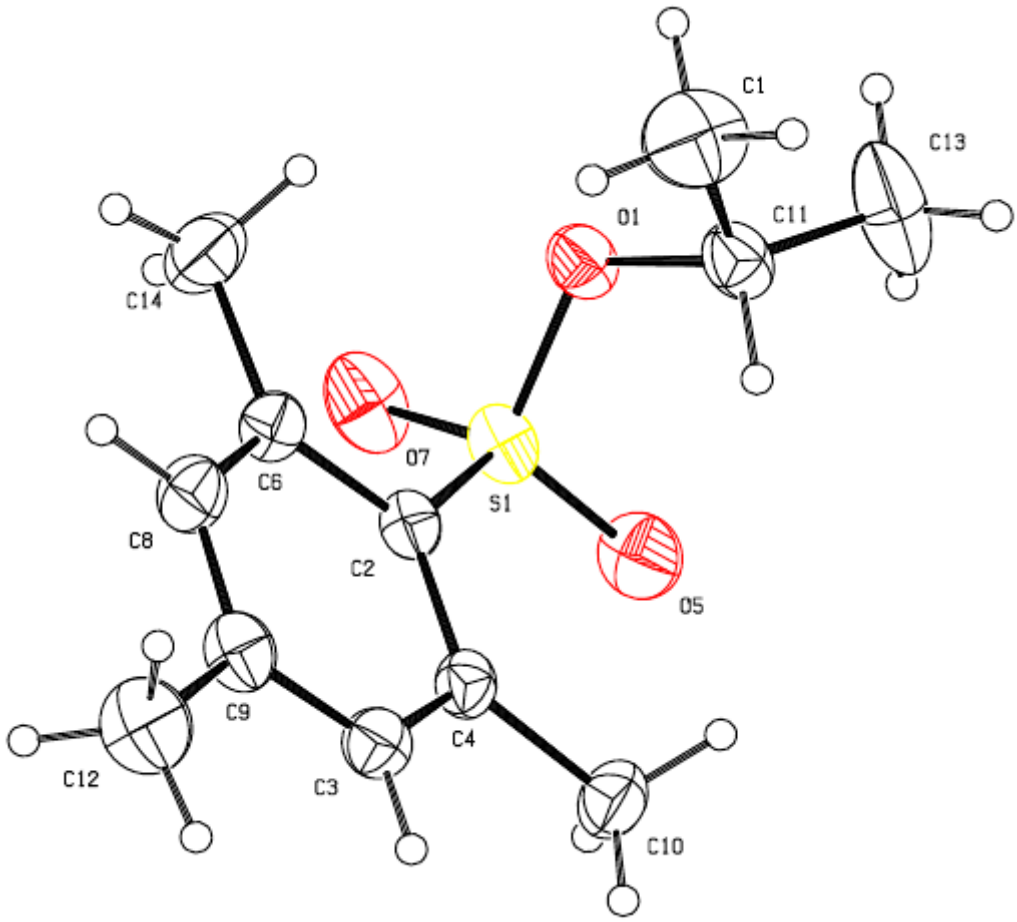


TABLE A10.2.- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPAN-2-YL 2,4,6-TRIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)*
S(1)	5092(1)	8180(1)	2227(1)	52(1)
O(1)	6081(1)	8192(2)	1208(1)	54(1)
C(2)	6211(2)	10270(2)	3470(1)	43(1)
C(3)	7870(2)	12060(2)	5606(1)	50(1)
C(4)	7147(2)	10362(2)	4667(1)	44(1)
O(5)	5398(2)	6743(1)	2617(1)	71(1)
C(6)	6044(2)	11837(2)	3224(1)	50(1)
O(7)	3226(2)	8180(2)	1674(1)	75(1)
C(8)	6817(2)	13474(2)	4209(2)	56(1)
C(9)	7710(2)	13618(2)	5402(1)	54(1)
C(10)	7453(2)	8803(2)	5046(2)	60(1)
C(11)	8033(2)	8062(2)	1466(1)	57(1)
C(12)	8480(3)	15415(3)	6470(2)	82(1)
C(13)	8058(4)	6242(4)	651(3)	116(1)
C(14)	5074(3)	11861(3)	1964(2)	74(1)
C(1)	9073(3)	9573(4)	1238(3)	97(1)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A10.3 - BOND LENGTHS [Å] AND ANGLES [°] FOR PROPAN-2-YL 2,4,6-TRIMETHYLBENZENESULFONATE

S(1)-O(1)	1.5666(11)	C(3)-C(4)-C(2)	117.24(12)
S(1)-C(2)	1.7737(13)	C(3)-C(4)-C(10)	116.19(13)
S(1)-O(5)	1.4194(13)	C(2)-C(6)-C(14)	124.75(14)
S(1)-O(7)	1.4225(12)	C(8)-C(6)-C(2)	117.81(13)
O(1)-C(11)	1.4766(17)	C(8)-C(6)-C(14)	117.44(14)
C(2)-C(4)	1.4038(19)	C(6)-C(8)-H(8)	118.7
C(2)-C(6)	1.4124(18)	C(9)-C(8)-C(6)	122.62(13)
C(3)-H(3)	0.9300	C(9)-C(8)-H(8)	118.7
C(3)-C(4)	1.393(2)	C(3)-C(9)-C(12)	120.34(15)
C(3)-C(9)	1.381(2)	C(8)-C(9)-C(3)	118.05(13)
C(4)-C(10)	1.5074(18)	C(8)-C(9)-C(12)	121.61(15)
C(6)-C(8)	1.386(2)	C(4)-C(10)-H(10A)	109.5
C(6)-C(14)	1.512(2)	C(4)-C(10)-H(10B)	109.5
C(8)-H(8)	0.9300	C(4)-C(10)-H(10C)	109.5
C(8)-C(9)	1.378(2)	H(10A)-C(10)-H(10B)	109.5
C(9)-C(12)	1.511(2)	H(10A)-C(10)-H(10C)	109.5
C(10)-H(10A)	0.9600	H(10B)-C(10)-H(10C)	109.5
C(10)-H(10B)	0.9600	O(1)-C(11)-H(11)	109.3
C(10)-H(10C)	0.9600	O(1)-C(11)-C(13)	107.68(14)
C(11)-H(11)	0.9800	O(1)-C(11)-C(1)	106.11(15)
C(11)-C(13)	1.489(3)	C(13)-C(11)-H(11)	109.3
C(11)-C(1)	1.493(3)	C(13)-C(11)-C(1)	114.9(2)
C(12)-H(12A)	0.9600	C(1)-C(11)-H(11)	109.3
C(12)-H(12B)	0.9600	C(9)-C(12)-H(12A)	109.5
C(12)-H(12C)	0.9600	C(9)-C(12)-H(12B)	109.5
C(13)-H(13A)	0.9600	C(9)-C(12)-H(12C)	109.5
C(13)-H(13B)	0.9600	H(12A)-C(12)-H(12B)	109.5
C(13)-H(13C)	0.9600	H(12A)-C(12)-H(12C)	109.5

C(14)-H(14A)	0.9600	H(12B)-C(12)-H(12C)	109.5
C(14)-H(14B)	0.9600	C(11)-C(13)-H(13A)	109.5
C(14)-H(14C)	0.9600	C(11)-C(13)-H(13B)	109.5
C(1)-H(1A)	0.9600	C(11)-C(13)-H(13C)	109.5
C(1)-H(1B)	0.9600	H(13A)-C(13)-H(13B)	109.5
C(1)-H(1C)	0.9600	H(13A)-C(13)-H(13C)	109.5
O(1)-S(1)-C(2)	104.00(6)	H(13B)-C(13)-H(13C)	109.5
O(5)-S(1)-O(1)	109.21(7)	C(6)-C(14)-H(14A)	109.5
O(5)-S(1)-C(2)	110.56(7)	C(6)-C(14)-H(14B)	109.5
O(5)-S(1)-O(7)	117.94(8)	C(6)-C(14)-H(14C)	109.5
O(7)-S(1)-O(1)	104.65(7)	H(14A)-C(14)-H(14B)	109.5
O(7)-S(1)-C(2)	109.43(7)	H(14A)-C(14)-H(14C)	109.5
C(11)-O(1)-S(1)	117.95(9)	H(14B)-C(14)-H(14C)	109.5
C(4)-C(2)-S(1)	121.29(10)	C(11)-C(1)-H(1A)	109.5
C(4)-C(2)-C(6)	121.28(12)	C(11)-C(1)-H(1B)	109.5
C(6)-C(2)-S(1)	117.35(10)	C(11)-C(1)-H(1C)	109.5
C(4)-C(3)-H(3)	118.5	H(1A)-C(1)-H(1B)	109.5
C(9)-C(3)-H(3)	118.5	H(1A)-C(1)-H(1C)	109.5
C(9)-C(3)-C(4)	122.98(13)	H(1B)-C(1)-H(1C)	109.5
C(2)-C(4)-C(10)	126.58(13)		

TABLE A10.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPAN-2-YL 2,4,6-TRIMETHYLBENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	45(1)	45(1)	57(1)	9(1)	17(1)	6(1)
O(1)	45(1)	64(1)	47(1)	12(1)	11(1)	15(1)
C(2)	40(1)	40(1)	49(1)	14(1)	17(1)	11(1)
C(3)	45(1)	55(1)	49(1)	17(1)	13(1)	12(1)
C(4)	39(1)	45(1)	54(1)	21(1)	18(1)	14(1)
O(5)	91(1)	41(1)	76(1)	16(1)	31(1)	9(1)
C(6)	52(1)	49(1)	54(1)	22(1)	17(1)	17(1)
O(7)	41(1)	80(1)	80(1)	4(1)	13(1)	6(1)
C(8)	66(1)	41(1)	66(1)	22(1)	22(1)	15(1)
C(9)	53(1)	43(1)	60(1)	11(1)	18(1)	7(1)
C(10)	63(1)	56(1)	70(1)	33(1)	20(1)	22(1)
C(11)	44(1)	70(1)	50(1)	12(1)	12(1)	17(1)
C(12)	95(1)	51(1)	75(1)	3(1)	15(1)	5(1)
C(13)	85(2)	100(2)	127(2)	-12(2)	31(1)	42(1)
C(14)	92(1)	71(1)	64(1)	33(1)	12(1)	30(1)
C(1)	56(1)	128(2)	113(2)	58(2)	25(1)	8(1)

TABLE A10.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPAN-2-YL 2,4,6-TRIMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
H(3)	8488	12148	6407	60
H(8)	6729	14517	4058	68
H(10A)	6273	8030	4901	90
H(10B)	8136	9241	5918	90
H(10C)	8144	8145	4561	90
H(11)	8525	8216	2345	69
H(12A)	9024	15243	7227	123
H(12B)	7494	16003	6570	123
H(12C)	9411	16143	6292	123
H(13A)	7240	5353	785	174
H(13B)	9299	6083	851	174
H(13C)	7652	6117	-210	174
H(14A)	5631	11249	1355	112
H(14B)	5195	13079	2019	112
H(14C)	3782	11269	1718	112
H(1A)	8571	9443	383	146
H(1B)	10362	9556	1402	146

H(1C)	8956	10690	1782	146

TABLE A10.6 - TORSION ANGLES [°] FOR PROPAN-2-YL 2,4,6-TRIMETHYLBENZENESULFONATE

S(1)-O(1)-C(11)-C(13)	107.88(18)
S(1)-O(1)-C(11)-C(1)	-128.65(15)
S(1)-C(2)-C(4)-C(3)	-175.53(9)
S(1)-C(2)-C(4)-C(10)	4.40(19)
S(1)-C(2)-C(6)-C(8)	176.15(11)
S(1)-C(2)-C(6)-C(14)	-3.5(2)
O(1)-S(1)-C(2)-C(4)	-120.59(11)
O(1)-S(1)-C(2)-C(6)	62.47(11)
C(2)-S(1)-O(1)-C(11)	69.56(11)
C(2)-C(6)-C(8)-C(9)	-0.7(2)
C(4)-C(2)-C(6)-C(8)	-0.8(2)
C(4)-C(2)-C(6)-C(14)	179.55(15)
C(4)-C(3)-C(9)-C(8)	-1.0(2)
C(4)-C(3)-C(9)-C(12)	178.30(15)
O(5)-S(1)-O(1)-C(11)	-48.49(12)
O(5)-S(1)-C(2)-C(4)	-3.48(13)
O(5)-S(1)-C(2)-C(6)	179.58(10)
C(6)-C(2)-C(4)-C(3)	1.29(19)
C(6)-C(2)-C(4)-C(10)	-178.78(13)
C(6)-C(8)-C(9)-C(3)	1.5(2)
C(6)-C(8)-C(9)-C(12)	-177.75(16)
O(7)-S(1)-O(1)-C(11)	-175.64(10)
O(7)-S(1)-C(2)-C(4)	128.04(12)
O(7)-S(1)-C(2)-C(6)	-48.90(12)
C(9)-C(3)-C(4)-C(2)	-0.4(2)
C(9)-C(3)-C(4)-C(10)	179.68(13)
C(14)-C(6)-C(8)-C(9)	179.02(16)

SYMMETRY TRANSFORMATIONS USED TO GENERATE EQUIVALENT ATOMS.

A11- X-RAY ANALYSIS OF PROPYL 2,3,5,6-TETRAMETHYLBENZENE SULFONATE

TABLE A11.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR PROPYL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

EMPIRICAL FORMULA	$C_{13}H_{20}O_3S$
FORMULA WEIGHT	256.35
TEMPERATURE	99.65 K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	MONOCLINIC
SPACE GROUP	P 1 21/C 1
UNIT CELL DIMENSIONS	A = 13.8462(8) Å, A= 90°. B = 9.0698(5) Å, B= 98.794(3)°. C = 10.7029(6) Å, Γ= 90°.
VOLUME	1328.29(13) $Å^3$
Z	4
DENSITY (CALCULATED)	1.282 MG/M^3
ABSORPTION COEFFICIENT	0.238 MM^{-1}
F(000)	552
CRYSTAL SIZE	0.48 × 0.36 × 0.35 MM^3
THETA RANGE FOR DATA COLLECTION	2.694 TO 28.370°.
INDEX RANGES	-18<=H<=18, -12<=K<=12, -14<=L<=14
REFLECTIONS COLLECTED	52533
INDEPENDENT REFLECTIONS	3309 [R(INT) = 0.0170]
COMPLETENESS TO THETA = 26.000°	99.6 %
ABSORPTION CORRECTION	NONE
MAX. AND MIN. TRANSMISSION	0.7457 AND 0.7065
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	3309 / 0 / 234
GOODNESS-OF-FIT ON F^2	1.050
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0298, WR2 = 0.0809
R INDICES (ALL DATA)	R1 = 0.0310, WR2 = 0.0818
EXTINCTION COEFFICIENT	N/A
LARGEST DIFF. PEAK AND HOLE	0.403 AND -0.355 $E.Å^{-3}$

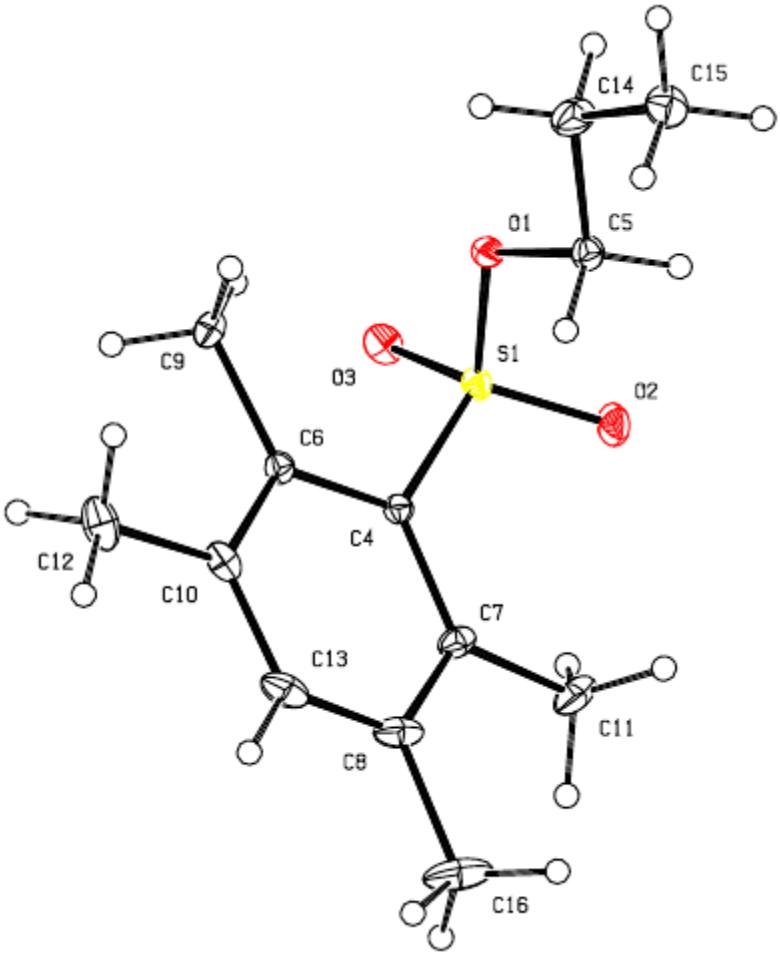


TABLE A11.2- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPYL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)*
S(1)	2185(1)	244(1)	744(1)	16(1)
O(1)	1827(1)	1302(1)	-396(1)	18(1)
O(2)	1342(1)	-319(1)	1206(1)	26(1)
O(3)	2870(1)	1105(1)	1575(1)	23(1)
C(4)	2803(1)	-1186(1)	47(1)	15(1)
C(5)	1031(1)	802(1)	-1368(1)	19(1)
C(6)	3487(1)	-754(1)	-739(1)	16(1)
C(7)	2588(1)	-2677(1)	271(1)	20(1)
C(8)	3030(1)	-3753(1)	-394(1)	26(1)
C(9)	3780(1)	823(1)	-936(1)	21(1)
C(10)	3921(1)	-1864(1)	-1376(1)	22(1)
C(11)	1940(1)	-3189(1)	1208(1)	28(1)
C(12)	4626(1)	-1493(2)	-2273(1)	32(1)
C(13)	3675(1)	-3325(1)	-1201(1)	27(1)
C(14)	864(1)	2012(1)	-2333(1)	30(1)
C(15)	85(1)	1610(1)	-3440(1)	28(1)
C(16)	2806(2)	-5374(1)	-269(1)	42(1)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A11.3 - BOND LENGTHS [Å] AND ANGLES [°]
FOR PROPYL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

S(1)-O(1)	1.5718(7)	H(5A)-C(5)-H(5B)	109.1(12)
S(1)-O(2)	1.4297(8)	C(4)-C(6)-C(9)	124.39(9)
S(1)-O(3)	1.4304(8)	C(10)-C(6)-C(4)	117.73(9)
S(1)-C(4)	1.7799(10)	C(10)-C(6)-C(9)	117.89(9)
O(1)-C(5)	1.4672(11)	C(4)-C(7)-C(11)	124.52(10)
C(4)-C(6)	1.4146(13)	C(8)-C(7)-C(4)	117.37(9)
C(4)-C(7)	1.4131(13)	C(8)-C(7)-C(11)	118.08(10)
C(5)-C(14)	1.5005(15)	C(7)-C(8)-C(16)	121.35(12)
C(5)-H(5A)	0.974(15)	C(13)-C(8)-C(7)	119.55(10)
C(5)-H(5B)	0.970(14)	C(13)-C(8)-C(16)	119.10(12)
C(6)-C(9)	1.5102(14)	C(6)-C(9)-H(9A)	113.1(9)
C(6)-C(10)	1.4022(14)	C(6)-C(9)-H(9B)	108.3(10)
C(7)-C(8)	1.4020(15)	C(6)-C(9)-H(9C)	112.3(10)
C(7)-C(11)	1.5168(15)	H(9A)-C(9)-H(9B)	108.5(13)
C(8)-C(13)	1.3893(17)	H(9A)-C(9)-H(9C)	106.7(13)
C(8)-C(16)	1.5133(16)	H(9B)-C(9)-H(9C)	107.7(13)
C(9)-H(9A)	0.947(15)	C(6)-C(10)-C(12)	121.11(10)
C(9)-H(9B)	0.966(16)	C(13)-C(10)-C(6)	119.19(10)
C(9)-H(9C)	0.954(16)	C(13)-C(10)-C(12)	119.68(10)
C(10)-C(12)	1.5081(15)	C(7)-C(11)-H(11A)	112.4(9)
C(10)-C(13)	1.3874(16)	C(7)-C(11)-H(11B)	107.7(11)
C(11)-H(11A)	0.973(16)	C(7)-C(11)-H(11C)	111.0(9)
C(11)-H(11B)	0.973(19)	H(11A)-C(11)-H(11B)	104.0(14)
C(11)-H(11C)	0.982(16)	H(11A)-C(11)-H(11C)	110.7(13)
C(12)-H(12A)	0.991(18)	H(11B)-C(11)-H(11C)	110.7(14)
C(12)-H(12B)	0.973(17)	C(10)-C(12)-H(12A)	113.0(10)
C(12)-H(12C)	0.990(19)	C(10)-C(12)-H(12B)	112.1(9)
C(13)-H(13)	0.966(17)	C(10)-C(12)-H(12C)	110.7(11)
C(14)-C(15)	1.5194(16)	H(12A)-C(12)-H(12B)	106.2(13)
C(14)-H(14A)	0.95(2)	H(12A)-C(12)-H(12C)	105.9(14)
C(14)-H(14B)	0.931(19)	H(12B)-C(12)-H(12C)	108.6(14)
C(15)-H(15A)	0.957(17)	C(8)-C(13)-H(13)	117.9(10)
C(15)-H(15B)	0.973(19)	C(10)-C(13)-C(8)	123.05(10)
C(15)-H(15C)	0.974(17)	C(10)-C(13)-H(13)	119.1(10)
C(16)-H(16A)	0.92(2)	C(5)-C(14)-C(15)	112.16(10)
C(16)-H(16B)	0.983(18)	C(5)-C(14)-H(14A)	108.4(12)
C(16)-H(16C)	0.99(2)	C(5)-C(14)-H(14B)	108.5(11)
O(1)-S(1)-C(4)	103.58(4)	C(15)-C(14)-H(14A)	110.1(11)
O(2)-S(1)-O(1)	108.05(4)	C(15)-C(14)-H(14B)	110.7(11)
O(2)-S(1)-O(3)	118.62(5)	H(14A)-C(14)-H(14B)	106.8(15)
O(2)-S(1)-C(4)	110.84(5)	C(14)-C(15)-H(15A)	111.4(10)
O(3)-S(1)-O(1)	104.44(4)	C(14)-C(15)-H(15B)	110.1(10)
O(3)-S(1)-C(4)	110.03(4)	C(14)-C(15)-H(15C)	111.0(10)
C(5)-O(1)-S(1)	118.34(6)	H(15A)-C(15)-H(15B)	108.0(14)
C(6)-C(4)-S(1)	117.10(7)	H(15A)-C(15)-H(15C)	107.6(14)

C(7)-C(4)-S(1)	119.91(7)	H(15B)-C(15)-H(15C)	108.6(14)
C(7)-C(4)-C(6)	122.97(9)	C(8)-C(16)-H(16A)	108.3(12)
O(1)-C(5)-C(14)	106.37(8)	C(8)-C(16)-H(16B)	112.2(11)
O(1)-C(5)-H(5A)	107.9(8)	C(8)-C(16)-H(16C)	112.2(13)
O(1)-C(5)-H(5B)	109.0(8)	H(16A)-C(16)-H(16B)	105.4(15)
C(14)-C(5)-H(5A)	111.7(9)	H(16A)-C(16)-H(16C)	108.2(17)
C(14)-C(5)-H(5B)	112.6(9)	H(16B)-C(16)-H(16C)	110.1(16)

TABLE A11.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPYL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	15(1)	19(1)	17(1)	0(1)	4(1)	1(1)
O(1)	16(1)	16(1)	21(1)	1(1)	0(1)	1(1)
O(2)	19(1)	34(1)	27(1)	6(1)	10(1)	1(1)
O(3)	23(1)	25(1)	20(1)	-6(1)	1(1)	2(1)
C(4)	14(1)	14(1)	17(1)	0(1)	1(1)	0(1)
C(5)	16(1)	20(1)	20(1)	0(1)	1(1)	-1(1)
C(6)	14(1)	18(1)	17(1)	0(1)	1(1)	0(1)
C(7)	23(1)	16(1)	18(1)	3(1)	-4(1)	-4(1)
C(8)	38(1)	14(1)	21(1)	-1(1)	-6(1)	1(1)
C(9)	19(1)	21(1)	22(1)	2(1)	6(1)	-4(1)
C(10)	17(1)	27(1)	20(1)	-4(1)	1(1)	5(1)
C(11)	32(1)	24(1)	25(1)	7(1)	1(1)	-12(1)
C(12)	23(1)	48(1)	28(1)	-8(1)	10(1)	5(1)
C(13)	32(1)	22(1)	24(1)	-6(1)	-3(1)	10(1)
C(14)	30(1)	26(1)	31(1)	10(1)	-7(1)	-6(1)
C(15)	27(1)	34(1)	22(1)	4(1)	-1(1)	1(1)
C(16)	78(1)	14(1)	30(1)	-1(1)	-4(1)	-2(1)

THE ANISOTROPIC DISPLACEMENT FACTOR EXPONENT TAKES THE FORM: $-2P^2[H^2 A^2 U^{11} + ... + 2 H K A \cdot B \cdot U^{12}]$

TABLE A11.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPYL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
H(5A)	1240(10)	-107(16)	-1729(14)	26(3)
H(9A)	3618(10)	1473(16)	-308(14)	28(4)
H(9B)	4479(12)	852(18)	-922(15)	35(4)
H(11A)	2038(11)	-2612(17)	1984(15)	32(4)
H(5B)	458(10)	604(16)	-975(14)	28(3)
H(9C)	3479(11)	1206(18)	-1731(15)	35(4)
H(16A)	3102(13)	-5890(20)	-853(18)	49(5)
H(11B)	2148(13)	-4180(20)	1482(17)	48(5)

H(13)	3945(12)	-4083(19)	-1678(15)	38(4)
H(14A)	679(13)	2880(20)	-1932(18)	54(5)
H(14B)	1455(14)	2220(20)	-2611(17)	50(5)
H(11C)	1250(12)	-3185(18)	824(15)	37(4)
H(12A)	4361(12)	-760(20)	-2924(16)	44(4)
H(15A)	-29(12)	2401(19)	-4036(16)	42(4)
H(12B)	5233(12)	-1079(18)	-1836(15)	36(4)
H(16B)	3090(12)	-5770(20)	560(17)	45(4)
H(12C)	4781(13)	-2380(20)	-2743(18)	54(5)
H(15B)	289(12)	750(20)	-3878(16)	46(5)
H(15C)	-533(12)	1386(18)	-3153(16)	42(4)
H(16C)	2098(17)	-5580(20)	-440(20)	69(6)

TABLE A11.6 - TORSION ANGLES [°] FOR PROPYL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

S(1)-O(1)-C(5)-C(14)	-178.89(7)
S(1)-C(4)-C(6)-C(9)	5.09(13)
S(1)-C(4)-C(6)-C(10)	-174.90(7)
S(1)-C(4)-C(7)-C(8)	174.22(7)
S(1)-C(4)-C(7)-C(11)	-7.79(14)
O(1)-S(1)-C(4)-C(6)	48.12(8)
O(1)-S(1)-C(4)-C(7)	-130.74(8)
O(1)-C(5)-C(14)-C(15)	177.19(10)
O(2)-S(1)-O(1)-C(5)	-46.45(8)
O(2)-S(1)-C(4)-C(6)	163.78(7)
O(2)-S(1)-C(4)-C(7)	-15.08(9)
O(3)-S(1)-O(1)-C(5)	-173.62(7)
O(3)-S(1)-C(4)-C(6)	-63.05(8)
O(3)-S(1)-C(4)-C(7)	118.10(8)
C(4)-S(1)-O(1)-C(5)	71.17(7)
C(4)-C(6)-C(10)-C(12)	177.45(9)
C(4)-C(6)-C(10)-C(13)	-0.78(14)
C(4)-C(7)-C(8)-C(13)	2.09(15)
C(4)-C(7)-C(8)-C(16)	-176.88(10)
C(6)-C(4)-C(7)-C(8)	-4.57(14)
C(6)-C(4)-C(7)-C(11)	173.42(9)
C(6)-C(10)-C(13)-C(8)	-1.57(16)
C(7)-C(4)-C(6)-C(9)	-176.09(9)
C(7)-C(4)-C(6)-C(10)	3.92(14)

C(7)-C(8)-C(13)-C(10)	0.89(16)
C(9)-C(6)-C(10)-C(12)	-2.55(14)
C(9)-C(6)-C(10)-C(13)	179.23(9)
C(11)-C(7)-C(8)-C(13)	-176.03(10)
C(11)-C(7)-C(8)-C(16)	5.00(16)
C(12)-C(10)-C(13)-C(8)	-179.82(10)
C(16)-C(8)-C(13)-C(10)	179.89(11)

SYMMETRY TRANSFORMATIONS USED TO GENERATE EQUIVALENT ATOMS.

A12- X-RAY ANALYSIS OF PROPAN-2-YL 2,3,5,6-TETRAMETHYL BENZENESULFONATE

TABLE A12.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR PROPAN-2-YL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

EMPIRICAL FORMULA	$C_{13}H_{20}O_3S$
FORMULA WEIGHT	256.35
TEMPERATURE	99.65 K
WAVELENGTH	0.71073 E
CRYSTAL SYSTEM	MONOCLINIC
SPACE GROUP	P 1 21/N 1
UNIT CELL DIMENSIONS	A = 17.8761(17) Å, A= 90°. B = 7.5391(7) Å, B= 107.975(5)°. C = 20.6840(19) Å, Γ= 90°.
VOLUME	2651.5(4) $Å^3$
Z	8
DENSITY (CALCULATED)	1.284 MG/M^3
ABSORPTION COEFFICIENT	0.239 MM^{-1}
F(000)	1104
CRYSTAL SIZE	0.435 × 0.305 × 0.155 MM^3
THETA RANGE FOR DATA COLLECTION	2.893 TO 25.430°.
INDEX RANGES	-21<=H<=15, -7<=K<=8, -23<=L<=24
REFLECTIONS COLLECTED	17503
INDEPENDENT REFLECTIONS	4747 [R(INT) = 0.0741]
COMPLETENESS TO THETA = 26.000°	91.0 %
ABSORPTION CORRECTION	NONE
MAX. AND MIN. TRANSMISSION	0.7452 AND 0.3242
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	4747 / 0 / 319
GOODNESS-OF-FIT ON F^2	1.018
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0584, WR2 = 0.1409
R INDICES (ALL DATA)	R1 = 0.0795, WR2 = 0.1517
EXTINCTION COEFFICIENT	N/A
LARGEST DIFF. PEAK AND HOLE	0.326 AND -0.548 $E.Å^{-3}$

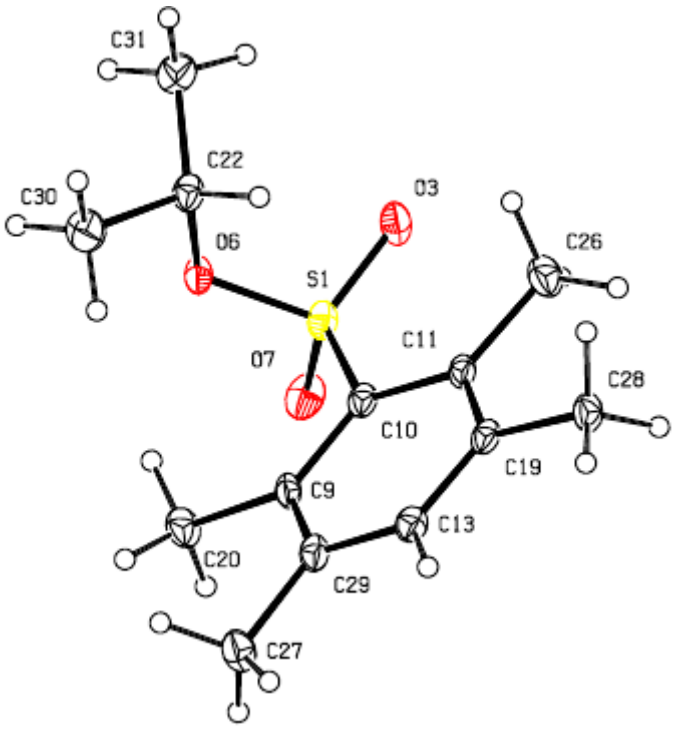


TABLE A12.2.- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPAN-2-YL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)*
S(1)	1853(1)	2714(1)	1052(1)	28(1)
S(2)	5935(1)	4695(1)	2420(1)	26(1)
O(1)	6425(1)	5190(2)	2018(1)	32(1)
O(2)	5597(1)	2964(2)	2326(1)	34(1)
O(3)	1042(1)	3178(2)	805(1)	35(1)
O(4)	5216(1)	6001(2)	2251(1)	26(1)
C(5)	5952(2)	5292(3)	3731(1)	23(1)
O(6)	2273(1)	4002(2)	1652(1)	27(1)
O(7)	2055(1)	977(2)	1324(1)	38(1)
C(8)	7247(2)	5302(3)	3531(1)	24(1)
C(9)	3163(2)	2934(3)	650(1)	25(1)
C(10)	2342(2)	3172(3)	434(1)	25(1)
C(11)	1915(2)	3762(3)	-225(1)	25(1)
C(12)	8466(2)	6236(4)	4476(2)	35(1)
C(13)	3154(2)	3926(3)	-453(1)	27(1)
C(14)	6423(2)	5110(3)	3302(1)	24(1)
C(15)	7785(2)	4820(4)	3117(1)	34(1)
C(16)	4928(2)	8903(3)	2593(1)	31(1)
C(17)	7592(2)	5880(3)	4200(1)	25(1)
C(18)	7125(2)	6177(3)	4611(1)	27(1)
C(19)	2347(2)	4137(3)	-672(1)	26(1)
C(20)	3635(2)	2227(4)	1345(1)	33(1)
C(21)	5369(2)	7925(3)	2191(1)	27(1)
C(22)	2171(2)	5933(3)	1521(1)	28(1)

C(23)	6320(2)	5860(3)	4402(1)	25(1)
C(24)	5085(2)	4837(4)	3527(1)	29(1)
C(25)	5861(2)	6124(3)	4889(1)	31(1)
C(26)	1036(2)	4018(4)	-486(1)	36(1)
C(27)	4453(2)	3139(4)	382(2)	36(1)
C(28)	1959(2)	4802(4)	-1382(1)	31(1)
C(29)	3569(2)	3334(3)	191(1)	27(1)
C(30)	2967(2)	6749(4)	1831(2)	39(1)
C(31)	1558(2)	6603(4)	1824(2)	38(1)
C(32)	5104(2)	8371(4)	1444(1)	34(1)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A12.3 - BOND LENGTHS [Å] AND ANGLES [°] FOR PROPAN-2-YL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

S(1)-O(3)	1.423(2)	H(12A)-C(12)-H(12C)	109.5
S(1)-O(6)	1.5724(18)	H(12B)-C(12)-H(12C)	109.5
S(1)-O(7)	1.4272(18)	C(17)-C(12)-H(12A)	109.5
S(1)-C(10)	1.790(3)	C(17)-C(12)-H(12B)	109.5
S(2)-O(1)	1.4304(19)	C(17)-C(12)-H(12C)	109.5
S(2)-O(2)	1.4257(18)	C(19)-C(13)-H(13)	118.4
S(2)-O(4)	1.5707(18)	C(19)-C(13)-C(29)	123.3(3)
S(2)-C(14)	1.791(3)	C(29)-C(13)-H(13)	118.4
O(4)-C(21)	1.489(3)	C(5)-C(14)-S(2)	117.5(2)
C(5)-C(14)	1.405(4)	C(5)-C(14)-C(8)	123.1(2)
C(5)-C(23)	1.406(4)	C(8)-C(14)-S(2)	119.3(2)
C(5)-C(24)	1.515(4)	C(8)-C(15)-H(15A)	109.5
O(6)-C(22)	1.482(3)	C(8)-C(15)-H(15B)	109.5
C(8)-C(14)	1.410(4)	C(8)-C(15)-H(15C)	109.5
C(8)-C(15)	1.515(4)	H(15A)-C(15)-H(15B)	109.5
C(8)-C(17)	1.399(4)	H(15A)-C(15)-H(15C)	109.5
C(9)-C(10)	1.407(4)	H(15B)-C(15)-H(15C)	109.5
C(9)-C(20)	1.522(4)	H(16A)-C(16)-H(16B)	109.5
C(9)-C(29)	1.394(4)	H(16A)-C(16)-H(16C)	109.5
C(10)-C(11)	1.413(4)	H(16B)-C(16)-H(16C)	109.5
C(11)-C(19)	1.405(4)	C(21)-C(16)-H(16A)	109.5
C(11)-C(26)	1.508(4)	C(21)-C(16)-H(16B)	109.5
C(12)-H(12A)	0.9800	C(21)-C(16)-H(16C)	109.5
C(12)-H(12B)	0.9800	C(8)-C(17)-C(12)	121.2(3)
C(12)-H(12C)	0.9800	C(18)-C(17)-C(8)	119.5(2)
C(12)-C(17)	1.513(4)	C(18)-C(17)-C(12)	119.3(2)
C(13)-H(13)	0.9500	C(17)-C(18)-H(18)	118.5
C(13)-C(19)	1.382(4)	C(17)-C(18)-C(23)	123.1(3)
C(13)-C(29)	1.384(4)	C(23)-C(18)-H(18)	118.5
C(15)-H(15A)	0.9800	C(11)-C(19)-C(28)	121.9(2)
C(15)-H(15B)	0.9800	C(13)-C(19)-C(11)	119.4(2)
C(15)-H(15C)	0.9800	C(13)-C(19)-C(28)	118.7(2)
C(16)-H(16A)	0.9800	C(9)-C(20)-H(20A)	109.5

C(16)-H(16B)	0.9800	C(9)-C(20)-H(20B)	109.5
C(16)-H(16C)	0.9800	C(9)-C(20)-H(20C)	109.5
C(16)-C(21)	1.505(4)	H(20A)-C(20)-H(20B)	109.5
C(17)-C(18)	1.381(4)	H(20A)-C(20)-H(20C)	109.5
C(18)-H(18)	0.9500	H(20B)-C(20)-H(20C)	109.5
C(18)-C(23)	1.389(4)	O(4)-C(21)-C(16)	106.9(2)
C(19)-C(28)	1.504(3)	O(4)-C(21)-H(21)	109.6
C(20)-H(20A)	0.9800	O(4)-C(21)-C(32)	107.2(2)
C(20)-H(20B)	0.9800	C(16)-C(21)-H(21)	109.6
C(20)-H(20C)	0.9800	C(16)-C(21)-C(32)	113.9(2)
C(21)-H(21)	1.0000	C(32)-C(21)-H(21)	109.6
C(21)-C(32)	1.507(4)	O(6)-C(22)-H(22)	109.5
C(22)-H(22)	1.0000	O(6)-C(22)-C(30)	106.1(2)
C(22)-C(30)	1.500(4)	O(6)-C(22)-C(31)	108.5(2)
C(22)-C(31)	1.507(4)	C(30)-C(22)-H(22)	109.5
C(23)-C(25)	1.496(4)	C(30)-C(22)-C(31)	113.6(2)
C(24)-H(24A)	0.9800	C(31)-C(22)-H(22)	109.5
C(24)-H(24B)	0.9800	C(5)-C(23)-C(25)	121.2(2)
C(24)-H(24C)	0.9800	C(18)-C(23)-C(5)	118.9(3)
C(25)-H(25A)	0.9800	C(18)-C(23)-C(25)	119.9(2)
C(25)-H(25B)	0.9800	C(5)-C(24)-H(24A)	109.5
C(25)-H(25C)	0.9800	C(5)-C(24)-H(24B)	109.5
C(26)-H(26A)	0.9800	C(5)-C(24)-H(24C)	109.5
C(26)-H(26B)	0.9800	H(24A)-C(24)-H(24B)	109.5
C(26)-H(26C)	0.9800	H(24A)-C(24)-H(24C)	109.5
C(27)-H(27A)	0.9800	H(24B)-C(24)-H(24C)	109.5
C(27)-H(27B)	0.9800	C(23)-C(25)-H(25A)	109.5
C(27)-H(27C)	0.9800	C(23)-C(25)-H(25B)	109.5
C(27)-C(29)	1.512(4)	C(23)-C(25)-H(25C)	109.5
C(28)-H(28A)	0.9800	H(25A)-C(25)-H(25B)	109.5
C(28)-H(28B)	0.9800	H(25A)-C(25)-H(25C)	109.5
C(28)-H(28C)	0.9800	H(25B)-C(25)-H(25C)	109.5
C(30)-H(30A)	0.9800	C(11)-C(26)-H(26A)	109.5
C(30)-H(30B)	0.9800	C(11)-C(26)-H(26B)	109.5
C(30)-H(30C)	0.9800	C(11)-C(26)-H(26C)	109.5
C(31)-H(31A)	0.9800	H(26A)-C(26)-H(26B)	109.5
C(31)-H(31B)	0.9800	H(26A)-C(26)-H(26C)	109.5
C(31)-H(31C)	0.9800	H(26B)-C(26)-H(26C)	109.5
C(32)-H(32A)	0.9800	H(27A)-C(27)-H(27B)	109.5
C(32)-H(32B)	0.9800	H(27A)-C(27)-H(27C)	109.5
C(32)-H(32C)	0.9800	H(27B)-C(27)-H(27C)	109.5
O(3)-S(1)-O(6)	108.42(11)	C(29)-C(27)-H(27A)	109.5
O(3)-S(1)-O(7)	118.20(12)	C(29)-C(27)-H(27B)	109.5
O(3)-S(1)-C(10)	111.36(12)	C(29)-C(27)-H(27C)	109.5
O(6)-S(1)-C(10)	103.00(11)	C(19)-C(28)-H(28A)	109.5
O(7)-S(1)-O(6)	104.75(11)	C(19)-C(28)-H(28B)	109.5
O(7)-S(1)-C(10)	109.80(12)	C(19)-C(28)-H(28C)	109.5
O(1)-S(2)-O(4)	108.28(10)	H(28A)-C(28)-H(28B)	109.5

O(1)-S(2)-C(14)	110.71(12)	H(28A)-C(28)-H(28C)	109.5
O(2)-S(2)-O(1)	118.02(12)	H(28B)-C(28)-H(28C)	109.5
O(2)-S(2)-O(4)	105.08(10)	C(9)-C(29)-C(27)	121.6(2)
O(2)-S(2)-C(14)	110.52(12)	C(13)-C(29)-C(9)	119.2(3)
O(4)-S(2)-C(14)	102.97(11)	C(13)-C(29)-C(27)	119.2(2)
C(21)-O(4)-S(2)	118.05(16)	C(22)-C(30)-H(30A)	109.5
C(14)-C(5)-C(23)	117.6(2)	C(22)-C(30)-H(30B)	109.5
C(14)-C(5)-C(24)	124.3(2)	C(22)-C(30)-H(30C)	109.5
C(23)-C(5)-C(24)	118.1(2)	H(30A)-C(30)-H(30B)	109.5
C(22)-O(6)-S(1)	117.43(16)	H(30A)-C(30)-H(30C)	109.5
C(14)-C(8)-C(15)	124.4(2)	H(30B)-C(30)-H(30C)	109.5
C(17)-C(8)-C(14)	117.4(2)	C(22)-C(31)-H(31A)	109.5
C(17)-C(8)-C(15)	118.1(2)	C(22)-C(31)-H(31B)	109.5
C(10)-C(9)-C(20)	124.3(2)	C(22)-C(31)-H(31C)	109.5
C(29)-C(9)-C(10)	117.9(2)	H(31A)-C(31)-H(31B)	109.5
C(29)-C(9)-C(20)	117.7(2)	H(31A)-C(31)-H(31C)	109.5
C(9)-C(10)-S(1)	116.1(2)	H(31B)-C(31)-H(31C)	109.5
C(9)-C(10)-C(11)	123.1(3)	C(21)-C(32)-H(32A)	109.5
C(11)-C(10)-S(1)	120.8(2)	C(21)-C(32)-H(32B)	109.5
C(10)-C(11)-C(26)	125.4(3)	C(21)-C(32)-H(32C)	109.5
C(19)-C(11)-C(10)	117.1(3)	H(32A)-C(32)-H(32B)	109.5
C(19)-C(11)-C(26)	117.5(2)	H(32A)-C(32)-H(32C)	109.5
H(12A)-C(12)-H(12B)	109.5	H(32B)-C(32)-H(32C)	109.5

TABLE A12.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPAN-2-YL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	32(1)	24(1)	24(1)	-1(1)	3(1)	-6(1)
S(2)	26(1)	24(1)	22(1)	1(1)	-2(1)	2(1)
O(1)	29(1)	41(1)	22(1)	2(1)	3(1)	4(1)
O(2)	37(1)	22(1)	31(1)	-2(1)	-6(1)	0(1)
O(3)	28(1)	46(1)	27(1)	-2(1)	2(1)	-7(1)
O(4)	24(1)	22(1)	25(1)	2(1)	-2(1)	-1(1)
C(5)	25(2)	16(1)	24(2)	4(1)	-2(1)	0(1)
O(6)	31(1)	23(1)	20(1)	0(1)	-1(1)	-2(1)
O(7)	56(2)	22(1)	34(1)	2(1)	11(1)	-6(1)
C(8)	23(2)	21(2)	26(2)	3(1)	1(1)	1(1)
C(9)	27(2)	21(1)	19(2)	-1(1)	-4(1)	1(1)
C(10)	31(2)	17(1)	22(2)	-2(1)	2(1)	-1(1)
C(11)	29(2)	18(2)	22(2)	-4(1)	-1(1)	1(1)
C(12)	28(2)	36(2)	34(2)	0(1)	-2(2)	-2(1)
C(13)	32(2)	24(2)	24(2)	-1(1)	7(1)	-1(1)
C(14)	25(2)	17(1)	23(2)	2(1)	0(1)	1(1)
C(15)	25(2)	40(2)	29(2)	-1(1)	-1(1)	2(1)
C(16)	29(2)	22(2)	33(2)	1(1)	-2(2)	-3(1)
C(17)	22(2)	22(2)	25(2)	2(1)	-2(1)	1(1)
C(18)	31(2)	23(2)	19(2)	2(1)	-4(1)	-2(1)
C(19)	36(2)	17(1)	20(2)	-3(1)	2(1)	1(1)
C(20)	34(2)	32(2)	27(2)	7(1)	1(2)	4(1)
C(21)	23(2)	23(2)	27(2)	2(1)	-3(1)	-2(1)
C(22)	35(2)	23(2)	22(2)	2(1)	3(1)	-1(1)
C(23)	27(2)	19(1)	25(2)	6(1)	1(1)	2(1)
C(24)	26(2)	30(2)	28(2)	5(1)	4(1)	-1(1)
C(25)	34(2)	29(2)	28(2)	2(1)	6(1)	0(1)
C(26)	34(2)	37(2)	31(2)	5(1)	0(2)	3(1)
C(27)	32(2)	44(2)	28(2)	2(1)	2(2)	0(1)
C(28)	35(2)	32(2)	19(2)	2(1)	0(1)	2(1)
C(29)	30(2)	22(2)	23(2)	-2(1)	1(1)	-3(1)
C(30)	35(2)	30(2)	49(2)	-5(1)	8(2)	-8(1)
C(31)	42(2)	35(2)	38(2)	-6(1)	11(2)	-1(1)
C(32)	34(2)	36(2)	29(2)	10(1)	5(2)	5(1)

TABLE A12.5 - HYDROGEN COORDINATES (× 10^4) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR PROPAN-2-YL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
H(12A)	8754	5115	4518	53
H(12B)	8587	6800	4924	53
H(12C)	8624	7026	4165	53
H(13)	3439	4201	-759	33
H(15A)	7532	3911	2782	50
H(15B)	8283	4361	3420	50
H(15C)	7886	5878	2882	50
H(16A)	4366	8628	2411	46
H(16B)	5006	10183	2560	46
H(16C)	5124	8537	3071	46
H(18)	7365	6618	5057	32
H(20A)	3373	2557	1680	49
H(20B)	4165	2737	1478	49
H(20C)	3670	932	1325	49
H(21)	5945	8166	2388	32
H(22)	1991	6153	1020	33
H(24A)	4774	5931	3435	44
H(24B)	4973	4186	3897	44
H(24C)	4946	4098	3117	44
H(25A)	5404	6879	4678	47
H(25B)	6195	6694	5303	47
H(25C)	5682	4972	5004	47
H(26A)	775	3014	-345	55
H(26B)	866	4086	-984	55
H(26C)	895	5119	-301	55
H(27A)	4703	3867	783	54
H(27B)	4631	3530	2	54
H(27C)	4597	1892	484	54
H(28A)	1605	3888	-1646	46
H(28B)	2362	5075	-1599	46
H(28C)	1657	5876	-1365	46
H(30A)	3138	6550	2324	59
H(30B)	2938	8026	1739	59
H(30C)	3344	6203	1634	59
H(31A)	1058	5999	1608	58
H(31B)	1490	7884	1748	58
H(31C)	1728	6361	2313	58
H(32A)	5410	7677	1214	51
H(32B)	5185	9638	1385	51
H(32C)	4544	8086	1249	51

TABLE A12.6 - TORSION ANGLES [°]
FOR PROPAN-2-YL 2,3,5,6-TETRAMETHYLBENZENESULFONATE

S(1)-O(6)-C(22)-C(30)	-136.83(19)
S(1)-O(6)-C(22)-C(31)	100.8(2)
S(1)-C(10)-C(11)-C(19)	178.32(17)
S(1)-C(10)-C(11)-C(26)	-1.8(4)
S(2)-O(4)-C(21)-C(16)	-133.46(19)
S(2)-O(4)-C(21)-C(32)	104.1(2)
O(1)-S(2)-O(4)-C(21)	-43.11(19)
O(1)-S(2)-C(14)-C(5)	158.36(18)
O(1)-S(2)-C(14)-C(8)	-19.4(2)
O(2)-S(2)-O(4)-C(21)	-170.08(17)
O(2)-S(2)-C(14)-C(5)	-69.0(2)
O(2)-S(2)-C(14)-C(8)	113.3(2)
O(3)-S(1)-O(6)-C(22)	-53.0(2)
O(3)-S(1)-C(10)-C(9)	173.69(18)
O(3)-S(1)-C(10)-C(11)	-5.4(2)
O(4)-S(2)-C(14)-C(5)	42.8(2)
O(4)-S(2)-C(14)-C(8)	-134.92(19)
O(6)-S(1)-C(10)-C(9)	57.7(2)
O(6)-S(1)-C(10)-C(11)	-121.4(2)
O(7)-S(1)-O(6)-C(22)	179.96(18)
O(7)-S(1)-C(10)-C(9)	-53.5(2)
O(7)-S(1)-C(10)-C(11)	127.5(2)
C(8)-C(17)-C(18)-C(23)	2.7(4)
C(9)-C(10)-C(11)-C(19)	-0.7(4)
C(9)-C(10)-C(11)-C(26)	179.2(2)
C(10)-S(1)-O(6)-C(22)	65.1(2)
C(10)-C(9)-C(29)-C(13)	-0.6(4)
C(10)-C(9)-C(29)-C(27)	179.3(2)
C(10)-C(11)-C(19)-C(13)	-0.3(4)
C(10)-C(11)-C(19)-C(28)	-179.0(2)
C(12)-C(17)-C(18)-C(23)	-179.0(2)
C(14)-S(2)-O(4)-C(21)	74.16(19)
C(14)-C(5)-C(23)-C(18)	-1.2(4)
C(14)-C(5)-C(23)-C(25)	178.8(2)
C(14)-C(8)-C(17)-C(12)	-176.0(2)
C(14)-C(8)-C(17)-C(18)	2.2(4)
C(15)-C(8)-C(14)-S(2)	-13.0(3)
C(15)-C(8)-C(14)-C(5)	169.4(2)
C(15)-C(8)-C(17)-C(12)	7.5(4)
C(15)-C(8)-C(17)-C(18)	-174.2(2)
C(17)-C(8)-C(14)-S(2)	170.84(19)
C(17)-C(8)-C(14)-C(5)	-6.8(4)
C(17)-C(18)-C(23)-C(5)	-3.2(4)
C(17)-C(18)-C(23)-C(25)	176.8(2)
C(19)-C(13)-C(29)-C(9)	-0.4(4)
C(19)-C(13)-C(29)-C(27)	179.7(2)
C(20)-C(9)-C(10)-S(1)	3.6(3)

C(20)-C(9)-C(10)-C(11)	-177.3(2)
C(20)-C(9)-C(29)-C(13)	178.0(2)
C(20)-C(9)-C(29)-C(27)	-2.1(4)
C(23)-C(5)-C(14)-S(2)	-171.36(18)
C(23)-C(5)-C(14)-C(8)	6.3(4)
C(24)-C(5)-C(14)-S(2)	11.6(3)
C(24)-C(5)-C(14)-C(8)	-170.7(2)
C(24)-C(5)-C(23)-C(18)	176.0(2)
C(24)-C(5)-C(23)-C(25)	-4.0(4)
C(26)-C(11)-C(19)-C(13)	179.8(2)
C(26)-C(11)-C(19)-C(28)	1.1(4)
C(29)-C(9)-C(10)-S(1)	-177.89(18)
C(29)-C(9)-C(10)-C(11)	1.2(4)
C(29)-C(13)-C(19)-C(11)	0.9(4)
C(29)-C(13)-C(19)-C(28)	179.6(2)

A13- X-RAY ANALYSIS OF METHYL 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$) BENZENESULFONATE

TABLE A13.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR METHYL 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONATE

EMPIRICAL FORMULA	$C_{10}D_{11}H_3O_3S$
FORMULA WEIGHT	214.27
TEMPERATURE	272.65 K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	MONOCLINIC
SPACE GROUP	P 1 21/N 1
UNIT CELL DIMENSIONS	A = 6.10820(10) Å, α= 90°. B = 15.8142(3) Å, β= 93.3150(10)°. C = 11.2274(2) Å, γ = 90°.
VOLUME	1082.71(3) $Å^3$
Z	4
DENSITY (CALCULATED)	1.315 MG/M^3
ABSORPTION COEFFICIENT	0.278 MM^{-1}
F(000)	456
CRYSTAL SIZE	0.49 × 0.38 × 0.21 MM^3
THETA RANGE FOR DATA COLLECTION	2.576 TO 28.601°.
INDEX RANGES	-8<=H<=8, -21<=K<=21, -15<=L<=15
REFLECTIONS COLLECTED	33081
INDEPENDENT REFLECTIONS	2753 [R(INT) = 0.0210]
COMPLETENESS TO THETA = 26.000°	99.4 %
ABSORPTION CORRECTION	NONE
MAX. AND MIN. TRANSMISSION	0.7457 AND 0.7219
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	2753 / 0 / 131
GOODNESS-OF-FIT ON F^2	1.072
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0383, WR2 = 0.1171
R INDICES (ALL DATA)	R1 = 0.0433, WR2 = 0.1216
EXTINCTION COEFFICIENT	N/A
LARGEST DIFF. PEAK AND HOLE	0.277 AND -0.204 $E.Å^{-3}$

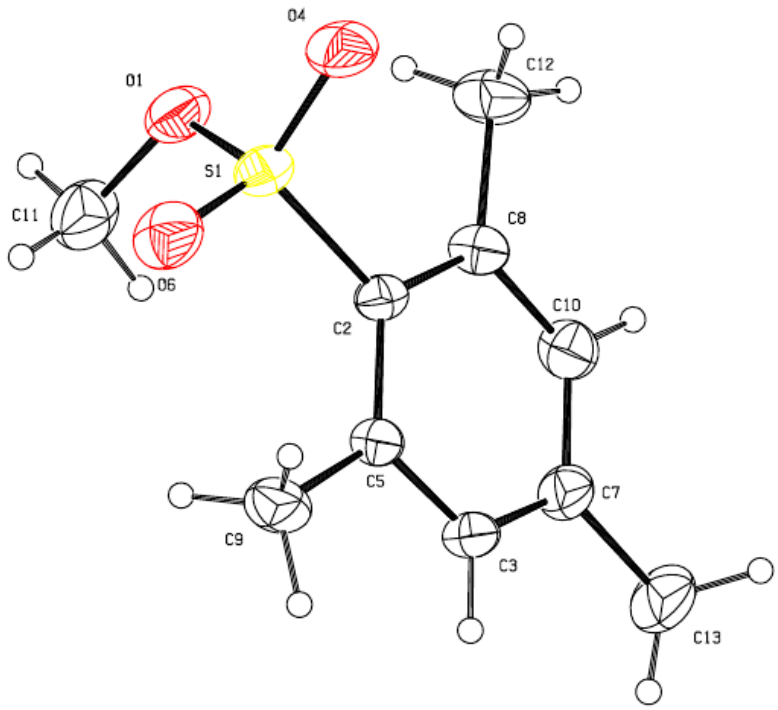


TABLE A13.2.- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR METHYL 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONATE

	X	Y	Z	U(EQ)
S(1)	2219(1)	1531(1)	6925(1)	49(1)
O(1)	3908(2)	1987(1)	6139(1)	63(1)
C(2)	3744(2)	686(1)	7583(1)	40(1)
C(3)	4435(3)	-787(1)	7910(1)	51(1)
O(4)	1767(2)	2143(1)	7811(1)	70(1)
C(5)	3112(2)	-162(1)	7379(1)	44(1)
O(6)	433(2)	1230(1)	6176(1)	72(1)
C(7)	6309(3)	-612(1)	8607(1)	54(1)
C(8)	5633(2)	889(1)	8311(1)	47(1)
C(9)	1131(3)	-454(1)	6619(2)	64(1)
C(10)	6860(3)	227(1)	8801(2)	56(1)
C(11)	4669(4)	1522(1)	5133(2)	78(1)
C(12)	6421(3)	1777(1)	8586(2)	67(1)
C(13)	7737(4)	-1317(1)	9135(2)	79(1)

TABLE A13.3 - BOND LENGTHS [Å] AND ANGLES [°]
FOR METHYL 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONATE

S(1)-O(1)	1.5708(12)	C(7)-C(3)-H(3)	118.5
S(1)-C(2)	1.7663(13)	C(7)-C(3)-C(5)	123.08(14)
S(1)-O(4)	1.4264(12)	C(2)-C(5)-C(9)	125.74(13)
S(1)-O(6)	1.4202(14)	C(3)-C(5)-C(2)	117.31(13)
O(1)-C(11)	1.447(2)	C(3)-C(5)-C(9)	116.94(13)
C(2)-C(5)	1.4119(18)	C(3)-C(7)-C(10)	117.96(14)
C(2)-C(8)	1.4117(19)	C(3)-C(7)-C(13)	121.03(16)
C(3)-H(3)	0.9300	C(10)-C(7)-C(13)	121.00(17)
C(3)-C(5)	1.389(2)	C(2)-C(8)-C(12)	124.70(14)
C(3)-C(7)	1.377(2)	C(10)-C(8)-C(2)	117.71(13)
C(5)-C(9)	1.511(2)	C(10)-C(8)-C(12)	117.59(14)
C(7)-C(10)	1.383(2)	C(5)-C(9)-H(9A)	109.5
C(7)-C(13)	1.515(2)	C(5)-C(9)-H(9B)	109.5
C(8)-C(10)	1.382(2)	C(5)-C(9)-H(9C)	109.5
C(8)-C(12)	1.511(2)	H(9A)-C(9)-H(9B)	109.5
C(9)-H(9A)	0.9600	H(9A)-C(9)-H(9C)	109.5
C(9)-H(9B)	0.9600	H(9B)-C(9)-H(9C)	109.5
C(9)-H(9C)	0.9600	C(7)-C(10)-H(10)	118.6
C(10)-H(10)	0.9300	C(8)-C(10)-C(7)	122.82(15)
C(11)-H(11A) *	0.9600	C(8)-C(10)-H(10)	118.6
C(11)-H(11B) *	0.9600	O(1)-C(11)-H(11A)*	109.5
C(11)-H(11C) *	0.9600	O(1)-C(11)-H(11B)*	109.5
C(12)-H(12A)	0.9600	O(1)-C(11)-H(11C)*	109.5
C(12)-H(12B)	0.9600	H(11A)-C(11)-H(11B)*	109.5
C(12)-H(12C)	0.9600	H(11A)-C(11)-H(11C)*	109.5
C(13)-H(13A)	0.9600	H(11B)-C(11)-H(11C)*	109.5
C(13)-H(13B)	0.9600	C(8)-C(12)-H(12A)	109.5
C(13)-H(13C)	0.9600	C(8)-C(12)-H(12B)	109.5
O(1)-S(1)-C(2)	103.58(7)	C(8)-C(12)-H(12C)	109.5
O(4)-S(1)-O(1)	103.92(8)	H(12A)-C(12)-H(12B)	109.5
O(4)-S(1)-C(2)	109.88(7)	H(12A)-C(12)-H(12C)	109.5
O(6)-S(1)-O(1)	109.17(8)	H(12B)-C(12)-H(12C)	109.5
O(6)-S(1)-C(2)	111.27(7)	C(7)-C(13)-H(13A)	109.5
O(6)-S(1)-O(4)	117.82(9)	C(7)-C(13)-H(13B)	109.5
C(11)-O(1)-S(1)	117.12(12)	C(7)-C(13)-H(13C)	109.5

C(5)-C(2)-S(1)	121.23(10)	H(13A)-C(13)-H(13B)	109.5
C(8)-C(2)-S(1)	117.68(10)	H(13A)-C(13)-H(13C)	109.5
C(8)-C(2)-C(5)	121.09(12)	H(13B)-C(13)-H(13C)	109.5
C(5)-C(3)-H(3)	118.5		

* CORRESPONDS TO PROTIUM (^{1}H). ALL UNLABELED HYDROGENS CORRESPOND DEUTERIUM (^{2}H).

TABLE A13.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^{2} \cdot 10^{3}$) FOR METHYL 2,4,6-TRIS[($^{2}H_{3}$)METHYL]($^{2}H_{2}$)BENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	50(1)	38(1)	58(1)	3(1)	4(1)	9(1)
O(1)	78(1)	44(1)	68(1)	12(1)	12(1)	1(1)
C(2)	43(1)	32(1)	45(1)	0(1)	4(1)	3(1)
C(3)	73(1)	32(1)	50(1)	-1(1)	8(1)	3(1)
O(4)	83(1)	49(1)	77(1)	-4(1)	16(1)	23(1)
C(5)	52(1)	36(1)	43(1)	-3(1)	4(1)	-2(1)
O(6)	60(1)	68(1)	86(1)	7(1)	-18(1)	7(1)
C(7)	67(1)	47(1)	49(1)	3(1)	4(1)	16(1)
C(8)	46(1)	40(1)	56(1)	-6(1)	2(1)	-1(1)
C(9)	67(1)	50(1)	72(1)	-10(1)	-10(1)	-11(1)
C(10)	51(1)	57(1)	59(1)	-5(1)	-7(1)	7(1)
C(11)	97(2)	72(1)	67(1)	12(1)	27(1)	13(1)
C(12)	58(1)	48(1)	94(1)	-13(1)	-6(1)	-10(1)
C(13)	95(2)	67(1)	74(1)	14(1)	-2(1)	34(1)

TABLE A13.5 - HYDROGEN COORDINATES (× 10^4) AND ISOTROPIC DISPLACEMENT PARAMETERS (Å^2·10^3) FOR METHYL 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONATE

	X	Y	Z	U(EQ)
H(3)	4037	-1349	7790	62
H(9A)	-168	-205	6911	95
H(9B)	1023	-1058	6657	95
H(9C)	1279	-283	5808	95
H(10)	8110	352	9281	67
H(11A)*	3432	1326	4644	117
H(11B)*	5526	1046	5417	117
H(11C)*	5554	1884	4672	117
H(12A)	6788	2051	7862	100
H(12B)	7694	1755	9129	100
H(12C)	5282	2089	8944	100
H(13A)	7085	-1853	8927	119
H(13B)	7864	-1260	9987	119
H(13C)	9167	-1284	8825	119

* CORRESPONDS TO PROTIUM (^{1}H). ALL UNLABELED HYDROGENS CORRESPOND DEUTERIUM (^{2}H).

TABLE A13.6 - TORSION ANGLES [°]
FOR METHYL 2,4,6-TRIS[($^2H_3$)METHYL]($^2H_2$)BENZENESULFONATE

S(1)-C(2)-C(5)-C(3)	178.56(10)
S(1)-C(2)-C(5)-C(9)	-0.7(2)
S(1)-C(2)-C(8)-C(10)	-178.30(11)
S(1)-C(2)-C(8)-C(12)	1.2(2)
O(1)-S(1)-C(2)-C(5)	-119.21(12)
O(1)-S(1)-C(2)-C(8)	60.12(12)
C(2)-S(1)-O(1)-C(11)	66.06(14)
C(2)-C(8)-C(10)-C(7)	-0.1(2)
C(3)-C(7)-C(10)-C(8)	-1.1(3)
O(4)-S(1)-O(1)-C(11)	-179.08(13)
O(4)-S(1)-C(2)-C(5)	130.27(12)
O(4)-S(1)-C(2)-C(8)	-50.40(13)
C(5)-C(2)-C(8)-C(10)	1.0(2)
C(5)-C(2)-C(8)-C(12)	-179.48(15)
C(5)-C(3)-C(7)-C(10)	1.4(2)
C(5)-C(3)-C(7)-C(13)	-178.01(16)
O(6)-S(1)-O(1)-C(11)	-52.56(15)
O(6)-S(1)-C(2)-C(5)	-2.04(14)
O(6)-S(1)-C(2)-C(8)	177.28(11)
C(7)-C(3)-C(5)-C(2)	-0.5(2)
C(7)-C(3)-C(5)-C(9)	178.86(14)
C(8)-C(2)-C(5)-C(3)	-0.7(2)
C(8)-C(2)-C(5)-C(9)	179.99(14)
C(12)-C(8)-C(10)-C(7)	-179.64(16)
C(13)-C(7)-C(10)-C(8)	178.32(16)

A14- X-RAY ANALYSIS OF ETHYL 4-METHYLBENZENESULFONATE

TABLE A14.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR ETHYL 4-METHYLBENZENESULFONATE

EMPIRICAL FORMULA	$C_9H_{12}O_3S$
FORMULA WEIGHT	200.25
TEMPERATURE	99.65 K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	MONOCLINIC
SPACE GROUP	P 1 21/N 1
UNIT CELL DIMENSIONS	A = 8.031(2) Å, α= 90°.
	B = 7.885(3) Å, β= 98.035(5)°.
	C = 15.625(5) Å, γ = 90°.
VOLUME	979.7(5) Å3
Z	4
DENSITY (CALCULATED)	1.358 MG/M^3
ABSORPTION COEFFICIENT	0.302 MM^{-1}
F(000)	424
CRYSTAL SIZE	0.379 × 0.217 × 0.076 MM^3
THETA RANGE FOR DATA COLLECTION	5.634 TO 30.573°.
INDEX RANGES	-3<=H<=11, -11<=K<=3, -9<=L<=17
REFLECTIONS COLLECTED	2103
INDEPENDENT REFLECTIONS	1891 [R(INT) = 0.0085]
COMPLETENESS TO THETA = 26.000°	70.5 %
ABSORPTION CORRECTION	NONE
MAX. AND MIN. TRANSMISSION	0.7461 AND 0.6794
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	1891 / 0 / 155
GOODNESS-OF-FIT ON F^2	1.047
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0391, WR2 = 0.0967
R INDICES (ALL DATA)	R1 = 0.0449, WR2 = 0.1018
EXTINCTION COEFFICIENT	N/A
LARGEST DIFF. PEAK AND HOLE	0.459 AND -0.304 $E.Å^{-3}$

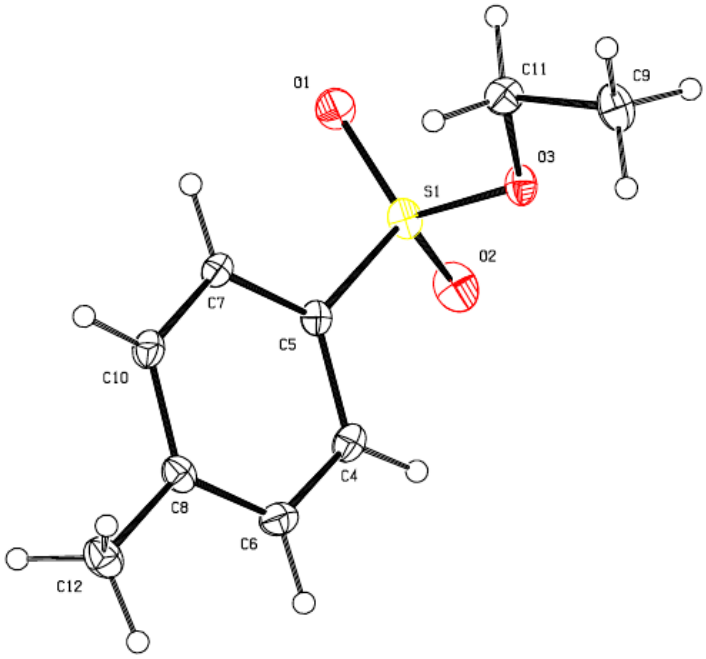


TABLE A14.2.- ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR ETHYL 4-METHYLBENZENESULFONATE

	X	Y	Z	U(EQ)*
S(1)	9610(1)	8545(1)	1708(1)	24(1)
O(1)	9397(2)	8707(2)	2593(1)	32(1)
O(2)	10432(2)	9861(2)	1300(1)	37(1)
O(3)	10691(2)	6917(2)	1593(1)	26(1)
C(4)	7441(2)	8335(2)	208(2)	26(1)
C(5)	7648(2)	8108(2)	1101(1)	20(1)
C(6)	5881(3)	7943(2)	-260(2)	27(1)
C(7)	6356(2)	7510(2)	1515(1)	23(1)
C(8)	4565(2)	7350(2)	136(1)	24(1)
C(9)	11191(3)	3943(2)	1672(2)	33(1)
C(10)	4811(2)	7144(2)	1028(2)	25(1)
C(11)	10351(3)	5374(2)	2071(2)	27(1)
C(12)	2881(2)	6932(2)	-378(2)	32(1)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U^{IJ} TENSOR.

TABLE A14.3 - BOND LENGTHS [Å] AND ANGLES [°] FOR ETHYL 4-METHYLBENZENESULFONATE

S(1)-O(1)	1.4237(19)	C(6)-C(4)-H(4)	122.6(15)
S(1)-O(2)	1.4266(16)	C(4)-C(5)-S(1)	119.18(15)
S(1)-O(3)	1.5736(14)	C(7)-C(5)-S(1)	119.37(15)
S(1)-C(5)	1.7563(16)	C(7)-C(5)-C(4)	121.44(16)
O(3)-C(11)	1.472(2)	C(4)-C(6)-H(6)	116.3(19)
C(4)-C(5)	1.393(3)	C(8)-C(6)-C(4)	122.0(2)
C(4)-C(6)	1.394(3)	C(8)-C(6)-H(6)	121.7(19)
C(4)-H(4)	0.91(3)	C(5)-C(7)-C(10)	119.1(2)
C(5)-C(7)	1.380(3)	C(5)-C(7)-H(7)	122.6(14)
C(6)-C(8)	1.378(3)	C(10)-C(7)-H(7)	118.3(14)
C(6)-H(6)	0.94(3)	C(6)-C(8)-C(10)	118.62(16)
C(7)-C(10)	1.392(2)	C(6)-C(8)-C(12)	121.47(19)
C(7)-H(7)	0.97(3)	C(10)-C(8)-C(12)	119.92(19)
C(8)-C(10)	1.391(3)	C(11)-C(9)-H(9A)	113.1(16)
C(8)-C(12)	1.509(2)	C(11)-C(9)-H(9B)	110.9(15)
C(9)-C(11)	1.494(3)	C(11)-C(9)-H(9C)	106.9(18)
C(9)-H(9A)	0.94(3)	H(9A)-C(9)-H(9B)	106(3)
C(9)-H(9B)	0.96(3)	H(9A)-C(9)-H(9C)	111(2)
C(9)-H(9C)	0.95(3)	H(9B)-C(9)-H(9C)	109(2)
C(10)-H(10)	0.91(3)	C(7)-C(10)-H(10)	118.3(14)
C(11)-H(11A)	0.93(2)	C(8)-C(10)-C(7)	120.9(2)
C(11)-H(11B)	0.94(2)	C(8)-C(10)-H(10)	120.7(14)
C(12)-H(12A)	0.9800	O(3)-C(11)-C(9)	106.7(2)
C(12)-H(12B)	0.9800	O(3)-C(11)-H(11A)	107.2(13)
C(12)-H(12C)	0.9800	O(3)-C(11)-H(11B)	108.0(14)
O(1)-S(1)-O(2)	119.60(9)	C(9)-C(11)-H(11A)	109.5(13)
O(1)-S(1)-O(3)	109.07(8)	C(9)-C(11)-H(11B)	112.4(14)
O(1)-S(1)-C(5)	108.77(10)	H(11A)-C(11)-H(11B)	113(2)
O(2)-S(1)-O(3)	104.24(10)	C(8)-C(12)-H(12A)	109.5
O(2)-S(1)-C(5)	109.79(9)	C(8)-C(12)-H(12B)	109.5
O(3)-S(1)-C(5)	104.25(7)	C(8)-C(12)-H(12C)	109.5
C(11)-O(3)-S(1)	118.21(15)	H(12A)-C(12)-H(12B)	109.5
C(5)-C(4)-C(6)	118.0(2)	H(12A)-C(12)-H(12C)	109.5
C(5)-C(4)-H(4)	119.4(14)	H(12B)-C(12)-H(12C)	109.5

TABLE A14.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR ETHYL 4-METHYLBENZENESULFONATE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	22(1)	17(1)	33(1)	-4(1)	3(1)	-3(1)
O(1)	32(1)	33(1)	29(1)	-13(1)	0(1)	1(1)
O(2)	32(1)	22(1)	56(1)	5(1)	5(1)	-9(1)
O(3)	23(1)	21(1)	34(1)	-1(1)	7(1)	1(1)
C(4)	27(1)	25(1)	27(1)	0(1)	10(1)	-2(1)
C(5)	21(1)	16(1)	25(1)	-2(1)	5(1)	-1(1)
C(6)	34(1)	28(1)	21(1)	0(1)	4(1)	1(1)
C(7)	24(1)	25(1)	22(1)	0(1)	7(1)	0(1)
C(8)	25(1)	18(1)	29(1)	-3(1)	1(1)	3(1)
C(9)	27(1)	24(1)	48(2)	-6(1)	3(1)	1(1)
C(10)	22(1)	27(1)	29(1)	1(1)	9(1)	-2(1)
C(11)	33(1)	21(1)	29(1)	2(1)	7(1)	0(1)
C(12)	27(1)	32(1)	35(2)	-5(1)	-3(1)	1(1)

THE ANISOTROPIC DISPLACEMENT FACTOR EXPONENT TAKES THE FORM: $-2P^2[H^2 A^2 U^{11} + ... + 2 H K A \cdot B \cdot U^{12}]$

TABLE A14.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR ETHYL 4-METHYLBENZENESULFONATE

	X	Y	Z	U(EQ)
H(12A)	2924	7138	-993	48
H(12B)	2011	7650	-183	48
H(12C)	2614	5737	-291	48
H(9A)	10790(40)	3790(30)	1079(18)	41(7)
H(11A)	9190(30)	5210(20)	1985(14)	20(5)
H(6)	5780(40)	8090(30)	-865(19)	50(8)
H(7)	6460(30)	7390(30)	2139(17)	32(6)
H(10)	3970(30)	6730(30)	1307(17)	30(6)
H(11B)	10790(30)	5540(30)	2656(17)	30(6)
H(4)	8330(30)	8700(30)	-49(16)	27(6)
H(9B)	12380(40)	4140(30)	1711(17)	40(7)
H(9C)	11010(30)	2950(30)	1991(18)	41(7)

TABLE A14.6 - TORSION ANGLES [°] FOR ETHYL 4-METHYLBENZENESULFONATE

S(1)-O(3)-C(11)-C(9)	165.09(12)
S(1)-C(5)-C(7)-C(10)	-179.12(13)
O(1)-S(1)-O(3)-C(11)	41.03(14)
O(1)-S(1)-C(5)-C(4)	163.15(14)
O(1)-S(1)-C(5)-C(7)	-18.31(16)
O(2)-S(1)-O(3)-C(11)	169.85(13)
O(2)-S(1)-C(5)-C(4)	30.56(17)
O(2)-S(1)-C(5)-C(7)	-150.90(14)
O(3)-S(1)-C(5)-C(4)	-80.60(15)
O(3)-S(1)-C(5)-C(7)	97.94(15)
C(4)-C(5)-C(7)-C(10)	-0.6(3)
C(4)-C(6)-C(8)-C(10)	0.1(3)
C(4)-C(6)-C(8)-C(12)	179.94(17)
C(5)-S(1)-O(3)-C(11)	-75.01(15)
C(5)-C(4)-C(6)-C(8)	0.1(3)
C(5)-C(7)-C(10)-C(8)	0.9(3)
C(6)-C(4)-C(5)-S(1)	178.64(13)
C(6)-C(4)-C(5)-C(7)	0.1(3)
C(6)-C(8)-C(10)-C(7)	-0.6(3)
C(12)-C(8)-C(10)-C(7)	179.56(16)

SYMMETRY TRANSFORMATIONS USED TO GENERATE EQUIVALENT ATOMS.

A15- X-RAY ANALYSIS OF 2,4,6-TRIMETHYL-3-NITROBENZENE SULFONYL CHLORIDE

TABLE A15.1 -CRYSTAL DATA AND STRUCTURE REFINEMENT FOR 2,4,6-TRIMETHYL-3-NITROBENZENESULFONYL CHLORIDE

EMPIRICAL FORMULA	$C_9H_{10}CLNO_4S$
FORMULA WEIGHT	263.69
TEMPERATURE	272.55 K
WAVELENGTH	0.71073 Å
CRYSTAL SYSTEM	ORTHORHOMBIC
SPACE GROUP	$PNA2_1$
UNIT CELL DIMENSIONS	A = 15.5106(5) Å A= 90°.
	B = 13.1384(4) Å , B= 90°.
	C = 5.7013(2) Å Γ= = 90°.
VOLUME	1161.84(7) $Å^3$
Z	4
DENSITY (CALCULATED)	1.507 MG/M^3
ABSORPTION COEFFICIENT	0.506 MM^{-1}
F(000)	544
CRYSTAL SIZE	0.489×0.255×0.254 MM^3
THETA RANGE FOR DATA COLLECTION	2.626 TO 26.373°.
INDEX RANGES	-19<=H<=19, -16<=K<=16, -7<=L<=7
REFLECTIONS COLLECTED	21736
INDEPENDENT REFLECTIONS	2348 [R(INT) = 0.0271]
COMPLETENESS TO THETA = 26.000°	99.8 %
ABSORPTION CORRECTION	SEMI-EMPIRICAL FROM EQUIVALENTS
MAX. AND MIN. TRANSMISSION	0.7454 AND 0.6887
REFINEMENT METHOD	FULL-MATRIX LEAST-SQUARES ON F^2
DATA / RESTRAINTS / PARAMETERS	2348 / 1 / 148
GOODNESS-OF-FIT ON F^2	1.059
FINAL R INDICES [I>2SIGMA(I)]	R1 = 0.0343, WR2 = 0.0876
R INDICES (ALL DATA)	R1 = 0.0388, WR2 = 0.0908
ABSOLUTE STRUCTURE PARAMETER	0.048(18)
EXTINCTION COEFFICIENT	N/A
LARGEST DIFF. PEAK AND HOLE	0.478 AND -0.349 E. $Å^{-3}$

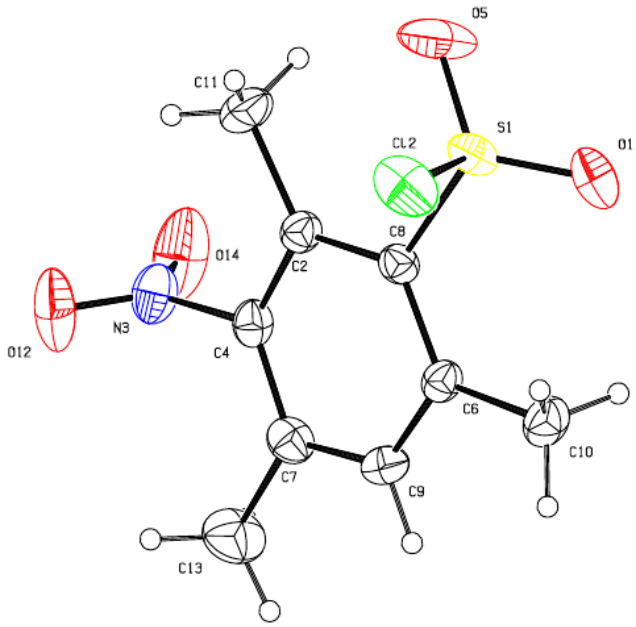


TABLE A15.2.-ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIMETHYL-3-NITROBENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)*
S(1)	4697(1)	2511(1)	2921(2)	48(1)
CL(2)	3683(1)	1827(1)	1278(2)	76(1)
O(1)	4802(2)	1987(2)	5051(5)	70(1)
C(2)	5842(2)	2991(2)	-600(6)	39(1)
N(3)	6907(2)	3492(2)	-3557(6)	57(1)
C(4)	6540(2)	2714(2)	-1991(7)	41(1)
O(5)	4501(2)	3551(2)	3004(8)	92(1)
C(6)	5915(2)	1252(2)	1027(6)	38(1)
C(7)	6928(2)	1764(2)	-2014(7)	46(1)
C(8)	5550(2)	2234(2)	952(6)	36(1)
C(9)	6590(2)	1055(2)	-481(7)	45(1)
C(10)	5641(2)	411(2)	2648(7)	54(1)
C(11)	5458(3)	4038(3)	-865(9)	64(1)
O(12)	6681(3)	3516(3)	-5563(6)	94(1)
C(13)	7673(3)	1500(4)	-3586(11)	75(1)
O(14)	7421(3)	4072(3)	-2718(7)	106(2)

*U(EQ) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED UIJ TENSOR.

TABLE A15.3 - BOND LENGTHS [Å] AND ANGLES [°]FOR 2,4,6-TRIMETHYL-3-NITROBENZENESULFONYL CHLORIDE

S(1)-CL(2)	2.0397(14)	O(12)-N(3)-C(4)	119.1(3)
S(1)-O(1)	1.405(3)	O(12)-N(3)-O(14)	123.9(4)
S(1)-O(5)	1.400(3)	O(14)-N(3)-C(4)	117.1(3)
S(1)-C(8)	1.773(3)	C(2)-C(4)-N(3)	117.7(3)
C(2)-C(4)	1.391(5)	C(7)-C(4)-C(2)	125.4(3)
C(2)-C(8)	1.405(4)	C(7)-C(4)-N(3)	116.9(3)
C(2)-C(11)	1.507(4)	C(8)-C(6)-C(10)	125.4(3)
N(3)-C(4)	1.471(4)	C(9)-C(6)-C(8)	117.2(3)
N(3)-O(12)	1.197(5)	C(9)-C(6)-C(10)	117.4(3)
N(3)-O(14)	1.203(4)	C(4)-C(7)-C(13)	123.2(4)
C(4)-C(7)	1.386(4)	C(9)-C(7)-C(4)	115.9(3)
C(6)-C(8)	1.410(4)	C(9)-C(7)-C(13)	121.0(3)
C(6)-C(9)	1.378(5)	C(2)-C(8)-S(1)	119.6(2)
C(6)-C(10)	1.502(4)	C(2)-C(8)-C(6)	122.5(3)
C(7)-C(9)	1.381(5)	C(6)-C(8)-S(1)	117.9(2)
C(7)-C(13)	1.502(6)	C(6)-C(9)-C(7)	123.8(3)
C(9)-H(9)	0.9300	C(6)-C(9)-H(9)	118.1
C(10)-H(10A)	0.9600	C(7)-C(9)-H(9)	118.1
C(10)-H(10B)	0.9600	C(6)-C(10)-H(10A)	109.5
C(10)-H(10C)	0.9600	C(6)-C(10)-H(10B)	109.5
C(11)-H(11A)	0.9600	C(6)-C(10)-H(10C)	109.5
C(11)-H(11B)	0.9600	H(10A)-C(10)-H(10B)	109.5
C(11)-H(11C)	0.9600	H(10A)-C(10)-H(10C)	109.5
C(13)-H(13A)	0.9600	H(10B)-C(10)-H(10C)	109.5
C(13)-H(13B)	0.9600	C(2)-C(11)-H(11A)	109.5
C(13)-H(13C)	0.9600	C(2)-C(11)-H(11B)	109.5
O(1)-S(1)-CL(2)	105.68(14)	C(2)-C(11)-H(11C)	109.5
O(1)-S(1)-C(8)	111.17(18)	H(11A)-C(11)-H(11B)	109.5
O(5)-S(1)-CL(2)	106.13(19)	H(11A)-C(11)-H(11C)	109.5
O(5)-S(1)-O(1)	118.2(3)	H(11B)-C(11)-H(11C)	109.5
O(5)-S(1)-C(8)	112.54(18)	C(7)-C(13)-H(13A)	109.5
C(8)-S(1)-CL(2)	101.22(11)	C(7)-C(13)-H(13B)	109.5
C(4)-C(2)-C(8)	115.2(3)	C(7)-C(13)-H(13C)	109.5
C(4)-C(2)-C(11)	119.3(3)	H(13A)-C(13)-H(13B)	109.5
C(8)-C(2)-C(11)	125.6(3)	H(13A)-C(13)-H(13C)	109.5
		H(13B)-C(13)-H(13C)	109.5

TABLE A15.4. - ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIMETHYL-3-NITROBENZENESULFONYL CHLORIDE

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	51(1)	44(1)	49(1)	-11(1)	12(1)	-3(1)
CL(2)	45(1)	105(1)	77(1)	-21(1)	0(1)	-4(1)
O(1)	79(2)	92(2)	40(2)	-4(2)	13(1)	-6(2)
C(2)	43(2)	35(2)	40(2)	1(1)	-3(1)	-1(1)
N(3)	53(2)	63(2)	56(2)	17(2)	0(2)	-14(2)
C(4)	44(2)	42(2)	38(2)	4(2)	-2(2)	-9(1)
O(5)	102(2)	48(1)	126(3)	-23(2)	55(3)	5(2)
C(6)	42(2)	33(1)	40(2)	3(2)	-4(2)	-3(1)
C(7)	38(1)	56(2)	46(2)	-4(2)	4(2)	-1(1)
C(8)	40(1)	35(1)	34(2)	-4(1)	1(1)	-3(1)
C(9)	44(2)	38(2)	53(2)	-2(2)	-1(2)	9(1)
C(10)	65(2)	41(2)	55(2)	11(2)	-1(2)	-5(2)
C(11)	83(3)	37(2)	73(3)	12(2)	9(2)	11(2)
O(12)	121(3)	118(3)	43(2)	26(2)	-8(2)	-40(2)
C(13)	58(2)	85(3)	83(3)	-4(3)	25(3)	5(2)
O(14)	109(3)	113(3)	97(3)	47(2)	-32(2)	-73(2)

THE ANISOTROPIC DISPLACEMENT FACTOR EXPONENT TAKES THE FORM: $-2P^2[H^2 A^2 U^{11} + ... + 2 H K A \cdot B \cdot U^{12}]$

TABLE A15.5 - HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \cdot 10^3$) FOR 2,4,6-TRIMETHYL-3-NITROBENZENESULFONYL CHLORIDE

	X	Y	Z	U(EQ)
H(9)	6830	407	-465	54
H(10A)	5831	561	4213	81
H(10B)	5894	-219	2140	81
H(10C)	5024	352	2626	81
H(11A)	5602	4442	481	97
H(11B)	4843	3984	-995	97
H(11C)	5685	4354	-2252	97
H(13A)	7517	1631	-5188	113
H(13B)	7814	793	-3404	113
H(13C)	8163	1908	-3172	113

TABLE A15.6 - TORSION ANGLES [°] FOR 2,4,6-TRIMETHYL-3-NITROBENZENESULFONYL CHLORIDE

CL(2)-S(1)-C(8)-C(2)	101.8(2)
CL(2)-S(1)-C(8)-C(6)	-78.7(2)
O(1)-S(1)-C(8)-C(2)	-146.3(3)
O(1)-S(1)-C(8)-C(6)	33.2(3)
C(2)-C(4)-C(7)-C(9)	-1.2(6)
C(2)-C(4)-C(7)-C(13)	178.9(4)
N(3)-C(4)-C(7)-C(9)	178.2(3)
N(3)-C(4)-C(7)-C(13)	-1.7(6)
C(4)-C(2)-C(8)-S(1)	177.0(2)
C(4)-C(2)-C(8)-C(6)	-2.5(5)
C(4)-C(7)-C(9)-C(6)	-0.8(5)
O(5)-S(1)-C(8)-C(2)	-11.1(4)
O(5)-S(1)-C(8)-C(6)	168.5(3)
C(8)-C(2)-C(4)-N(3)	-176.6(3)
C(8)-C(2)-C(4)-C(7)	2.8(5)
C(8)-C(6)-C(9)-C(7)	0.9(5)
C(9)-C(6)-C(8)-S(1)	-178.7(2)
C(9)-C(6)-C(8)-C(2)	0.8(5)
C(10)-C(6)-C(8)-S(1)	0.0(4)
C(10)-C(6)-C(8)-C(2)	179.5(3)
C(10)-C(6)-C(9)-C(7)	-177.9(3)
C(11)-C(2)-C(4)-N(3)	4.0(5)
C(11)-C(2)-C(4)-C(7)	-176.6(4)
C(11)-C(2)-C(8)-S(1)	-3.7(5)
C(11)-C(2)-C(8)-C(6)	176.9(4)
O(12)-N(3)-C(4)-C(2)	-96.2(5)
O(12)-N(3)-C(4)-C(7)	84.3(5)
C(13)-C(7)-C(9)-C(6)	179.1(4)
O(14)-N(3)-C(4)-C(2)	83.6(5)
O(14)-N(3)-C(4)-C(7)	-95.8(5)

SYMMETRY TRANSFORMATIONS USED TO GENERATE EQUIVALENT ATOMS.

Isotope Effects in the Solvolysis of Sterically Hindered Arenesulfonyl Chlorides

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Received 22 March 2015; revised 5 August 2015; accepted 7 August 2015

DOI 10.1002/kin.20945
Published online 22 September 2015 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Solvent isotope effects in the ethanolysis of sterically hindered arenesulfonyl chlorides ruled out a proton transfer in the rate-determining step and agreed with a S_N2 mechanism involving at least a second solvent molecule in the transition state (TS). The lack of a secondary kinetic isotope effect in the *o*-alkyl groups allows us to disregard the possible contribution of $\sigma-\pi$ hyperconjugation. The measured activation parameters are consistent with a S_N2 mechanism involving the participation of solvent molecules in the TS, possibly forming a cyclic TS through a chain of solvent molecules. © 2015 Wiley Periodicals, Inc. Int J Chem Kinet 47: 744–750, 2015

INTRODUCTION

Despite the existence of a large corpus of research on solvolytic processes near sulfonyl centers [1–23], details on the mechanism of this nucleophilic substitution remain unclear. A number of authors have proposed S_N2 [2–6,9–15] or borderline S_N1–S_N2 mechanisms for this process [16–19]. However, sterically hindered derivatives of aromatic sulfonic acids that contain *o*-alkyl groups show kinetic features that pose questions on the classical view of the bimolecular substitution mechanism [4–8,12].

o-Alkyl derivatives of benzenesulfonyl chlorides show increased reactivity in solvolysis processes [4–8,12]. In this respect, as shown in Scheme 1, the feasibility of uni- [6] and bimolecular mechanisms [20], structural modifications of the S_N2-type transition state (TS) involving a second molecule of nucleophile (S_N3-mechanism) [2,21,22], the stabilization of the bimolecular TS by intramolecular interactions, hyperconjugation effects [23], or stereochemical rearrangements during the nucleophilic attack [4,8] have been discussed.

In addition, the effect of substitution at sterically hindered sulfonyl center is usually considered a minor effect, which is not always the case.

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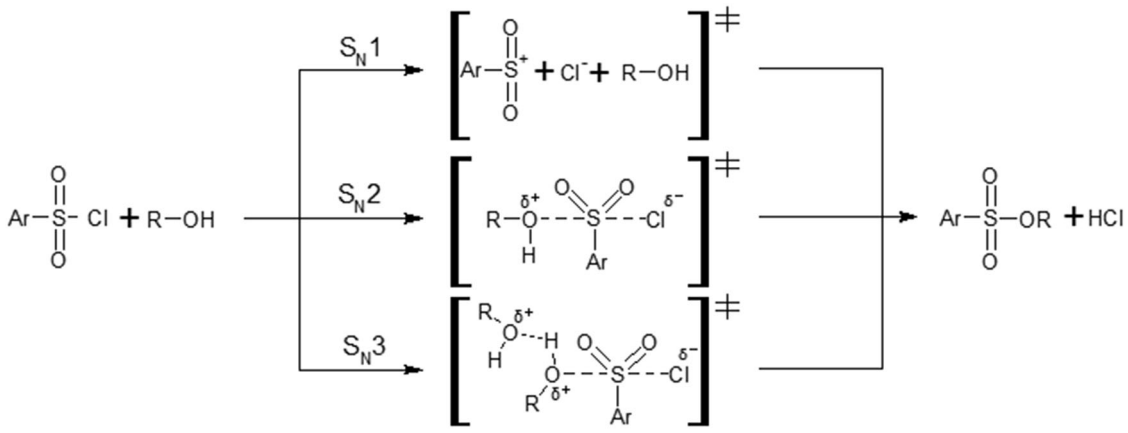
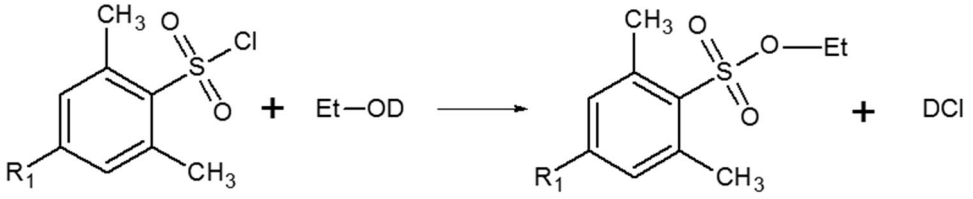
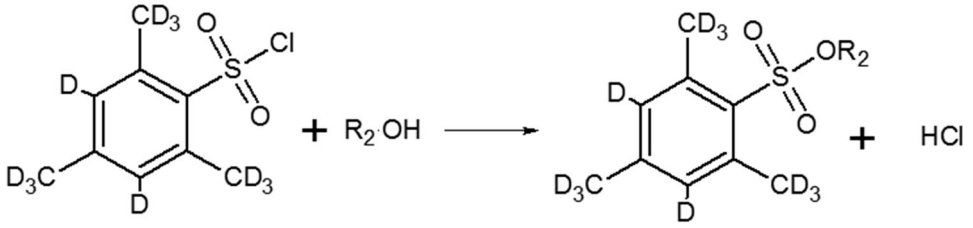
Supporting Information is available in the online issue at www.wileyonlinelibrary.com.



Scheme 1 Mechanistic possibilities for solvolytic processes at a sulfonyl center.



Scheme 2 SIE on the ethanolysis of sterically hindered arenesulfonyl chlorides (R_1 = Me(**2**), *t*-Bu(**1**)).



Scheme 3 SKIE on the solvolysis of sterically hindered arenesulfonyl chlorides **2** and **2D** (R_2 = H-, Me-, Et-, Pr-, *i*-Pr-).

Here, we analyze the mechanism of solvolysis, hydrolysis, and alcoholysis of sterically hindered arenesulfonyl chlorides in the light of new results of solvent isotope effects (SIE; Scheme 2) and secondary kinetic isotope effects (SKIE; Scheme 3) in the temperature range 303–323 K.

EXPERIMENTAL

Kinetic runs were spectrophotometrically monitored under pseudo–first-order conditions with respect to the nucleophile on a Cary 1E UV–VIS spectrophotometer, in thermostated quartz cuvettes at temperatures between 303 and 323 K. Examples of UV–VIS spectra and time-resolved absorbance profiles are shown in the Supporting Information.

All solvents were thoroughly purified and tested for the presence of water impurities immediately before the kinetic experiments [24]. The acceptable water content was considered <0.002%.

Analytical-grade alcohols were purchased from Sigma-Aldrich (St. Louis, MO, USA). Molecular sieves (3 Å) were used for dehydration. All alcohols were redistilled immediately before the kinetic experiments at the temperatures specified in the literature (bp_{MeOH} = 64,4°C; bp_{EtOH} = 78.32°C; bp_{PrOH} = 97.15°C; $bp_{i\text{-}PrOH}$ = 82,6°C at 760 mmHg). Water obtained from the distiller Auga ELIX-Q was used for the hydrolysis.

Deuterated ethanol was obtained by the reaction of sodium ethoxide with pure heavy water. The initial ethoxide was prepared by dissolving of metal sodium in ethanol. Furthermore, after the alcohol distilling off,

Table I SIE Observed in the Ethanolysis of X-$ArSO_2Cl$

X-	T (K)	$k_{Et\text{-}OD} \times 10^4$ (s^{-1})	$k_{Et\text{-}OH} \times 10^4$ (s^{-1})	SIE = ($k_{Et\text{-}OH}/k_{Et\text{-}OD}$)
(**1**) 2,6-Me_2-4-*t*Bu-	303	1.78 ± 0.01	2.25 ± 0.01	1.26 ± 0.02
	313	4.00 ± 0.02	5.70 ± 0.04	1.42 ± 0.06
	323	8.04 ± 0.05	11.3 ± 0.1	1.41 ± 0.06
(**2**) 2,4,6-Me_3-	303	1.63 ± 0.01	2.24 ± 0.01	1.37 ± 0.02
	313	3.57 ± 0.01	4.99 ± 0.01	1.40 ± 0.02
	323	7.60 ± 0.04	10.2 ± 0.1	1.34 ± 0.02
(**3**) 4-Me-	303	0.26 ± 0.01	0.36 ± 0.01	1.39 ± 0.02
	313	0.66 ± 0.01	0.82 ± 0.01	1.24 ± 0.02
	323	1.42 ± 0.01	1.91 ± 0.01	1.35 ± 0.02

the residue was dried under vacuum. Heavy water in a fourfold excess was added to ethoxide; the reaction mixture was boiled under reflux (for 30 min) and distilled with a reflux condenser. Further purification corresponds to the methods mentioned previously.

2,4,6-Me_3-benzenesulfonyl chloride (**2**) and 4-Me-benzenesulfonyl chloride (**3**) were obtained from Sigma-Aldrich and recrystallized from hexane prior to its use.

Deuterated mesitylene sulfonyl chloride (**2D**) was synthesized from deuterated mesitylene [mesitylene-d_{12} (98 atom%D); Sigma-Aldrich] as follows [25]: The reaction was carried out under constant stirring at 273 K, 1 mol of NaCl was added to 1 mol of the mesitylene in 450 mL of an inert solvent ($CHCl_3$, CCl_4, hexane); then 5 mol of chlorosulfonic acid were slowly added dropwise for half an hour. After 3–4 h, the reaction mixture was poured onto ice, treated with chloroform; the extract was dried over Na_2SO_4 and filtered. The filtrate was evaporated under vacuum. The resulting deuterated sulfonyl chloride (**2D**), the middle fraction, was collected, and the product recrystallized from hexane with a yield of 80%, mp = 66.5–67°C. As there is no isotopic exchange, the percentage of deuteration in **2D** must be the same as in the parent mesitylene-d_{12}.

2,6-Me_2-4-*t*Bu-benzenesulfonyl chloride (**1**) was synthesized analogously from the 1-*tert*-butyl-3,5-dimethylbenzene with a yield of 85%; mp = 66–67°C.

The structure and purity of the obtained sulfonyl compounds were confirmed by NMR spectroscopy and monocrystal X-ray diffraction (see the Supporting Information).

RESULTS AND DISCUSSION

The SIE was studied to check the catalytic assistance of the solvent as a nucleophile in the ethanolysis of X-$ArSO_2Cl$ in the range 303–323 K [2]; the observed rate constants and the corresponding SIE are collected in Table I.

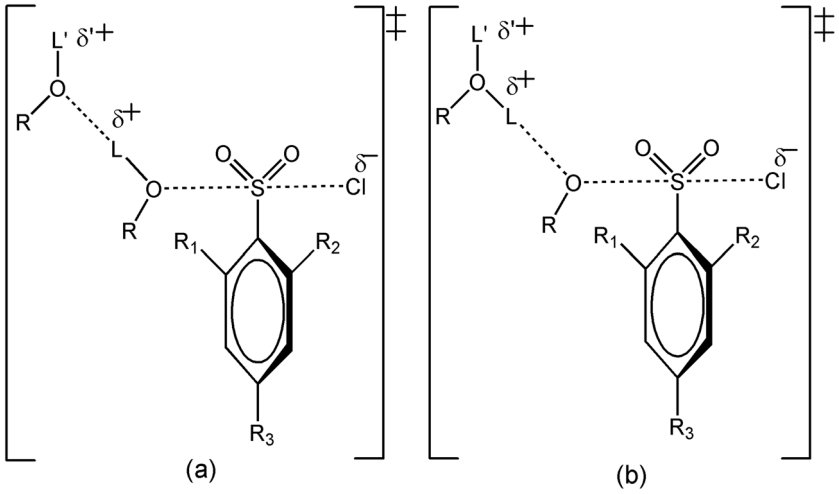
Ortho-methylated substrates show increased reactivity toward solvolysis in all cases (Table I). Change from protonated to deuterated solvent causes a slight decrease in the observed solvolytic rate constants. For compound **3**, adopted as a model compound, SIE ranges between 1.24 and 1.39 (Table I). SIE for hindered substrates **1** and **2** shows a similar range of SIE, 1.26–1.42, in agreement with previous observations for the methanolysis of sulfonyl chlorides [9,26]. The observed SIEs are comparable when considering different compounds and temperatures. For the methanolysis of **2** and **3** SIE ($k_{Me\text{-}OH}/k_{Me\text{-}OD}$) are, respectively, 1.68 and 1.72, in good agreement with those observed here [9,26]. Similar SIEs, ranging from 1.2 to 1.6, are typical for S_N2 processes at sulfonyl centers [9,26–29]. These results point to a SKIE of the alcoholic proton, the proton transfer between the oxygen of the attacking alcohol and that of a solvent molecule, not taking place in the rate-determining step.

The analysis of the SIE could be done in terms of fractionation factors:

$$\mathrm{SIE} = \frac{k_{\mathrm{EtoH}}}{k_{\mathrm{EtOD}}} = \frac{\phi_{\mathrm{EtOL}}}{\Pi_i \phi_i^{\ddagger}}$$

where ϕ_{EtOL} is the fractionation factor of the alcoholic hydrogen/deuterium of ethanol, whereas $\phi^{\ddagger}$ is/are the fractionation factor(s) of the alcoholic hydrogen/deuterium atom(s) involved in the TS.

The fractionation factor of any hydrogen/deuterium, which behaves like a hydrogen/deuterium of the solvent, is equal to one, whereas that of the corresponding lyonium ion is lower than unity, for example, $\phi(L_3O^+) = 0.69$ [30] or $\phi(MeOL_2{}^+) = 0.60$ [31], where L designates either H or D. From there, it follows that the more charge on the hydrogen/deuterium, the lower is the value of its fractionation factor, i.e. the value of the

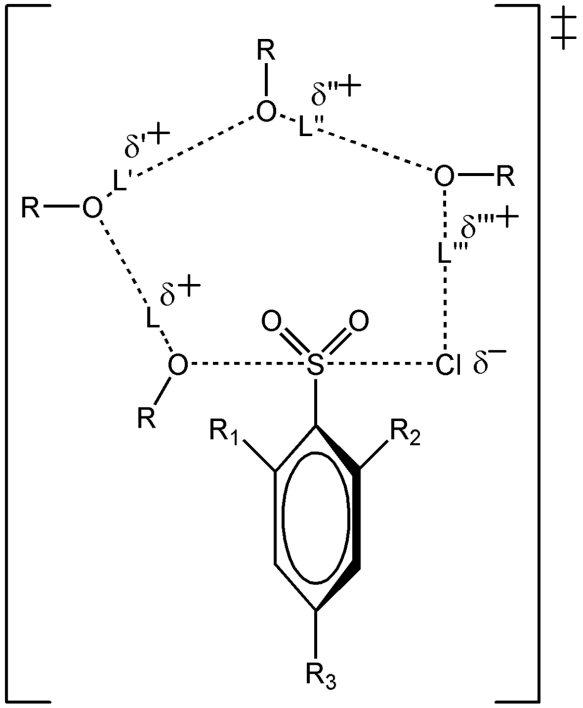


Scheme 4 "Early" (a) and "late" (b) TSs for the S_N2 mechanism of arenesulfonyl chlorides solvolysis with general base catalysis by a second solvent molecule.

fractionation factor gives information on the amount of charge on the hydrogen/deuterium relative to the solvent.

The value of the SIE could be consistent, regardless of the position of the hydrogen/deuterium, with both "early" (Scheme 4a) or "late" (Scheme 4b) S_N2 TSs. When the extreme "early" TS is considered, the hydrogen/deuterium is only starting to be transferred to another solvent molecule, and assuming the fractionation factor of the alcoholic hydrogen/deuterium should be similar to that of $MeOL_2^+$ (ϕ_L^+ca. 0.60 relative to MeOL) [31], a SIE = (k_{EtOH}/k_{EtOD} = 1/0.60) ca. 1.6 would be expected; in this case, the hydrogen/deuterium should resemble that of protonated alcohol. Under the same assumption, SIE = (k_{EtOH}/k_{EtOD} = $1/0.60^2$) ca. 2.8 would be expected for the extreme "late" TS, where the hydrogen/deuterium has been almost fully transferred to another solvent molecule, so two hydrogens/deuteriums contribute to the SIE.

The observed SIE is ca. 1.35 (Table I), which implies the TS lies in between the "early" and "late" TSs for the S_N2 mechanism described above (Scheme 4), the product of the fractionation factors of the hydrogens/deuteriums involved in the TS being ≈0.74. It could be the value for only one hydrogen/deuterium (i.e., $\phi^{\ddagger}_L = 0.74$) that of the alcohol molecule bonded to the sulfur atom at the TS, or the product of several of them somehow participating in the TS; such figure is compatible even with a cyclic one involving several solvent molecules as shown in Scheme 5, i.e., $0.74 = (\phi_L \cdot \phi_{L'} \cdot \phi_{L''} \cdot \phi_{L'''})^{\ddagger}$ with ($\phi_L < \phi_{L'} \approx \phi_{L''} \approx \phi_{L'''} \leq 1$). These results support the participation of, at least, a second solvent molecule in the TS, through a general-base catalysis mechanism [2]. There is strong evidence in the literature for this kind of mechanism, with participation of solvent chains [32–35]. It has been found that there are an optimal number of solvent molecules that facilitates the mechanism, for example, via linear proton transfer in the TS [34].



Scheme 5 TS for the general-base catalyzed S_N2 mechanism for solvolysis of arenesulfonyl chlorides involving a chain of solvent. molecules.

Table II Activation Parameters for X-$ArSO_2Cl$ Ethanolysis in EtOH and EtOD

X-	Solvent	$\Delta H^{\ddagger}$ (kJ·mol^{-1})[a]	$\Delta S^{\ddagger}$ (J·mol^{-1}·K^{-1})[a]	$\Delta G^{\ddagger}$ (kJ·mol^{-1})[a,b]
(**1**) 2,6-Me_2–4-*t*Bu-	Et-OD	59 ± 2	–146 ± 5	105 ± 1
	Et-OH	64 ± 4	–126 ± 14	104 ± 9
(**2**) 2,4,6-Me_3-	Et-OD	60 ± 1	–143 ± 2	105 ± 3
	Et-OH	57 ± 3	–150 ± 8	104 ± 5
(**3**) 4-Me-	Et-OD	66 ± 3	–137 ± 9	109 ± 6
	Et-OH	66 ± 2	–137 ± 6	109 ± 3

[a]Estimated considering the second-order constant, i.e., $k_2 = k_{obs}$/[solvent].
[b]Value calculated at 313 K.

Activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$) are within statistical error when the solvent is isotopically modified, i.e. EtOD instead of EtOH (Table II). Sterically hindered substrates **1**, **2** show slightly lower $\Delta G^{\ddagger}$ ~ (104–105 kJ·mol^{-1}) in comparison with the less sterically hindered **3** [31,36,37], which provides additional evidence against proton transfer in the rate-determining step.

On the other hand, the large negative $\Delta S^{\ddagger}$ values are consistent with highly ordered TSs, which support the participation of solvent molecules in the TS, as is shown in Scheme 4. The low and similar $\Delta H^{\ddagger}$ values

Table III Effective Rate Constants and Activation Parameters for Solvolysis of **2** and Deuterated-**2 (2D)** using Different Solvents as Nucleophiles

Compound	Nucleophile	T (K)	$k_{obs} \times 10^4$ (s^{-1})	$\Delta H^{\ddagger}$ (kJ·mol^{-1})[a]	$\Delta S^{\ddagger}$ (J·mol^{-1}·K^{-1})[a]	$\Delta G^{\ddagger}$ (kJ·mol^{-1})[a,b]
2	H_2O	293	505 ± 8	49 ± 2	–134 ± 7	91 ± 5
		298	746 ± 25			
		303	1090 ± 42			
		308	1640 ± 57			
		313	2000 ± 31			
		318	2650 ± 116			
	EtOH	303	2.24 ± 0.01	57 ± 3	–150 ± 8	104 ± 5
		313	4.99 ± 0.02			
		318	7.06 ± 0.01			
		323	10.2 ± 0.1			
		328	14.2 ± 0.01			
	MeOH	303	13.2 ± 0.1	54 ± 4	–148 ± 13	100 ± 8
	PrOH	323	6.13 ± 0.02	59 ± 1	–147 ± 2	105 ± 1
	i-PrOH	323	0.84 ± 0.01	55 ± 2	–173 ± 5	110 ± 3
2D	H_2O	293	493 ± 2	51 ± 2	–128 ± 5	91 ± 3
		298	764 ± 10			
		303	1120 ± 35			
		308	1550 ± 27			
		313	2140 ± 37			
		318	2790 ± 81			
	EtOH	303	2.23 ± 0.01	59 ± 2	–143 ± 7	104 ± 4
		313	4.95 ± 0.01			
		318	7.59 ± 0.01			
		323	10.2 ± 0.01			
		328	13.8 ± 0.01			
	MeOH	303	12.5 ± 0.1	–	–	–
	PrOH	323	5.83 ± 0.01	–	–	–
	i-PrOH	323	0.87 ± 0.01	–	–	–

[a]Estimated considering the second-order constant, i.e., $k_2 = k_{obs}$/[solvent].
[b]Value calculated at 313 K.

Table IV SKIE Observed for the Solvolysis of **2** and **2D** with Different Solvents as Nucleophiles between 303 and 323 K

Nucleophile	T (K)	SKIE (k_2/k_{2D})
H_2O	293	1.03 ± 0.01
	298	0.98 ± 0.01
	303	0.97 ± 0.01
	308	1.06 ± 0.02
	313	0.93 ± 0.02
	318	0.95 ± 0.02
EtOH	303	1.00 ± 0.01
	313	1.01 ± 0.01
	318	0.93 ± 0.02
	323	1.00 ± 0.01
	328	1.03 ± 0.01
MeOH	303	1.06 ± 0.01
PrOH	323	1.05 ± 0.01
i-PrOH	323	0.96 ± 0.02

point to a highly concerted TS, which would support the hypothesis of formation of solvent chains as in Scheme 5.

To check for nonbonding intramolecular interactions between the hydrogens of the *ortho*-methyl groups and the oxygens of the sulfonyl groups, activation parameters and SKIEs were investigated for the solvolysis of mesitylene sulfonyl chloride, 2,4,6-$(CH_3)_3$-$C_6H_2SO_2Cl$ (**2**) and its deuterated analog 2,4,6-$(CD_3)_3$-$C_6D_2SO_2Cl$ (**2D**) (SKIE $= k_2/k_{2D}$), using different solvents as nucleophiles. Comparable results were obtained in both cases (Tables III and IV).

The reactivities of **2** and **2D** are similar, within statistical error, for all solvolytic processes. Similarly activation parameters are statistically indistinguishable (Table III). Values of SKIE are in all cases very close to unity, within statistical error, for all studied nucleophiles (Table IV). Thus, it follows that noncovalent intramolecular interactions between the *ortho*-methyl hydrogens and oxygen atoms of the sulfonyl group are not a significant factor in the stabilization of the S_N2-transition state. This conclusion also poses serious doubts on the applicability of the idea of $\sigma-\pi$ hyperconjugation to this particular case [8].

CONCLUSIONS

SIE in the ethanolysis of sterically hindered arenesulfonyl chlorides slows the reaction rate by ca. 35%. Such a result rules out a proton transfer in the rate-determining step, and the analysis of the SIE in terms of fractionation factors agrees with a S_N2 mechanism involving at least a second solvent molecule in the TS. No SKIE is observed when hydrogens of the *o*-alkyl groups are replaced by deuteriums, which discard $\sigma-\pi$ hyperconjugation. Activation parameters are similar regardless of the steric hindrance of the substrates, which points to a similar reaction mechanism for all of them. Large negative $\Delta S^{\ddagger}$ and low comparable $\Delta H^{\ddagger}$ are consistent with a S_N2 mechanism with participation of, at least, a second solvent molecule in the TS, and most possibly with a cyclic TS in which a reduced number of solvent molecules form chains, in a general-base catalysis mechanism. The reasons for the "positive steric effect" of *o*-alkyl (methyl) groups should be attributed to structural features of the S_N2 transition state. Further experimental and computational studies are in progress to clarify this point.

Authors gratefully acknowledge EU financial support for the mobility of MI to the UDC within the trans-European mobility Erasmus Mundus action TEMPO (372283–1–2012–1-PT-ERA MUNDUS-EMA21).

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Isotope Effects in the Solvolysis of Sterically Hindered Arenesulfonyl Chlorides

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SUPPORTING INFORMATION

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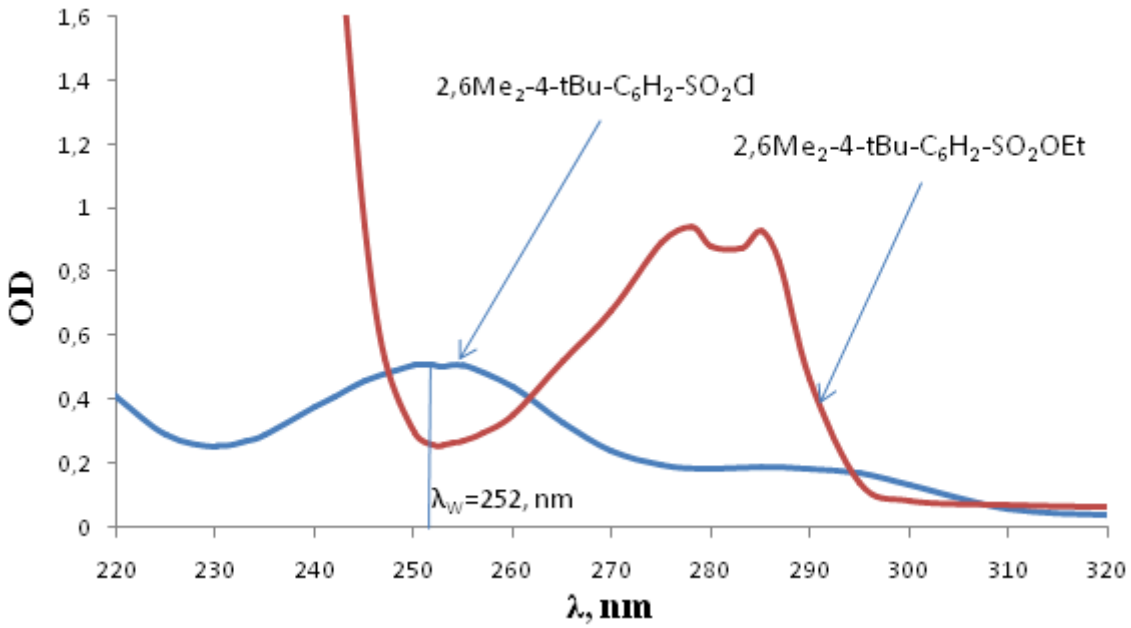


Figure S1. UV spectra of 2,6-Me_2-4-*t*Bu-benzenesulfonyl chloride (**1**) and that of its ethanolysis product. Solvent: Ethanol. λ_w in the working wavelength. [2,6Me_2-4-*t*Bu-C_6H_2-SO_2Cl]=$1.0\cdot10^{-4}$ mol·dm^{-3}; [2,6Me_2-4-*t*Bu-C_6H_2-SO_2OEt] = $4.7\cdot10^{-4}$ mol·dm^{-3}.

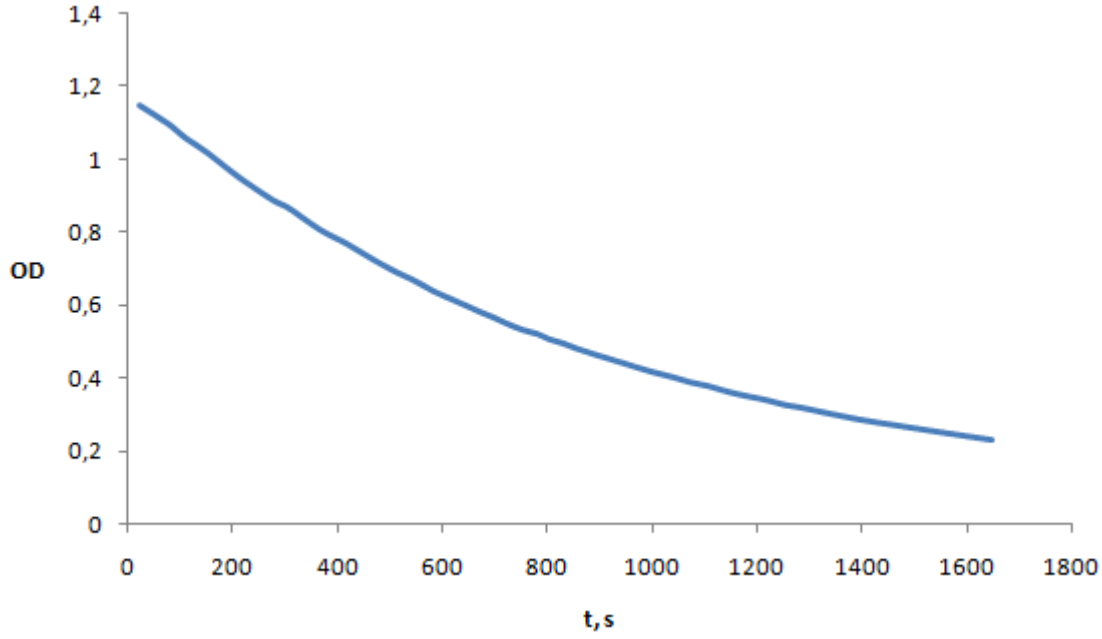


Figure S2. Time resolved absorbance profile for the ethanolysis of 2,6-Me_2-4-*t*Bu-benzenesulfonyl chloride (**1**). [2,6Me_2-4-*t*Bu-C_6H_2-SO_2Cl] = $2.4\cdot10^{-4}$ mol·dm^{-3}; Solvent: Ethanol. λ = 252 nm. T = 323K.

Table S1. NMR chemical shifts of 4-*tert*-butyl-2,6-dimethylbenzenesulfonyl chloride (**1**) and 2,4,6-tris [($^2H_3$)methyl]($^2H_2$) benzenesulfonyl chloride (**2D**)

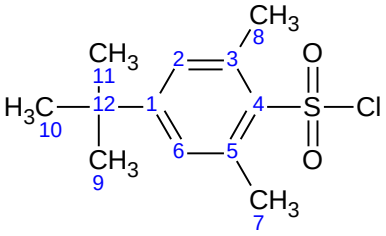
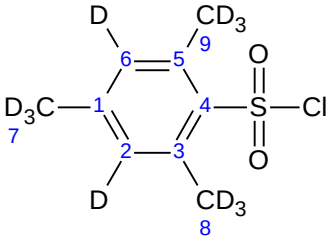
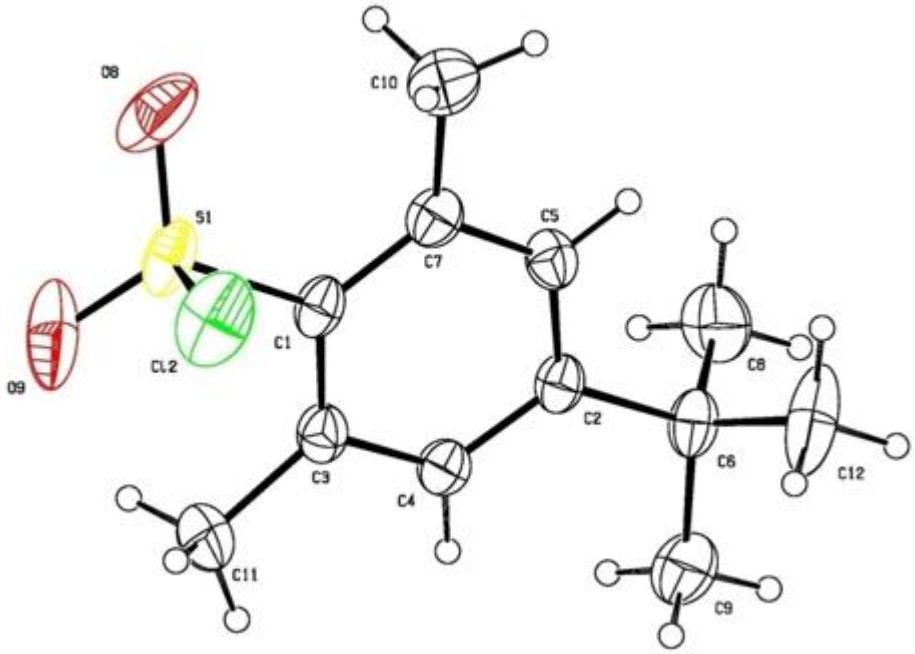
Compound	Structure & chemical shift
1 (4-*tert*-butyl-2,6-dimethylbenzenesulfonyl chloride)	
NMR-^{1}H δ (ppm)	(300 MHz, $CDCl_3$): δ =1,33(s,*J = 7,5 Hz*, 9 $H_{9,\ 10,\ 11}$), 2,76 (s,*J = 7,5 Hz*, 6 $H_{7,8}$),7,20(s,*J = 7,5 Hz*, 2 $H_{2,6}$),
NMR-^{13}C δ (ppm)	(300 MHz, $CDCl_3$): δ = 23,44(C_7=C_8), 30,94 (C_9=C_{10}=C_{11}), 35,85 (C_{12}), 128,94 (C_2=C_6), 139,41 (C_1), 140,54 (C_3=C_5), 158,165 (C_4)
2D (2,4,6-tris [($^2H_3$)methyl]($^2H_2$) benzene sulfonyl chloride)	
NMR-^{1}H δ (ppm)	No relevant signals
NMR-^{13}C δ (ppm)	(300 MHz, $CDCl_3$): δ = 22,11 (C_7), 22,63 (C_8=C_9), 132,27 (C_2=C_6), 139,37 (C_1), 140,07 (C_3=C_5), 145,29(C_4).

Table S2. X-Ray data of 4-*tert*-butyl-2,6-dimethylbenzenesulfonyl chloride (**1**)

Crystal data and structure refinement

Empirical formula	$C_{12}H_{17}ClO_2S$
Formula weight	260.76
Temperature	269(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 6.5256(3) Å, α= 78.477(2)°.
	b = 9.9665(4) Å, β= 84.787(2)°.
	c = 10.5782(4) Å, γ= 81.078(2)°.
Volume	664.68(5) $Å^3$
Z	2
Density (calculated)	1.303 Mg/m^3
Absorption coefficient	0.428 mm^{-1}
F(000)	276
Crystal size	0.500 × 0.450 × 0.420 mm^3
Theta range for data collection	1.969 to 28.315°.
Index ranges	-8<=h<=8, -13<=k<=13, -13<=l<=14
Reflections collected	31013
Independent reflections	3278 [R(int) = 0.0298]
Completeness to theta = 26.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6560
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3278 / 0 / 151
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1588
R indices (all data)	R1 = 0.0685, wR2 = 0.1725
Extinction coefficient	0.163(13)
Largest diff. peak and hole	0.687 and -0.568 e.$Å^{-3}$



ORTEP diagram of 4-*tert*-butyl-2,6-dimethylbenzenesulfonyl chloride (**1**)

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \cdot 10^3$)

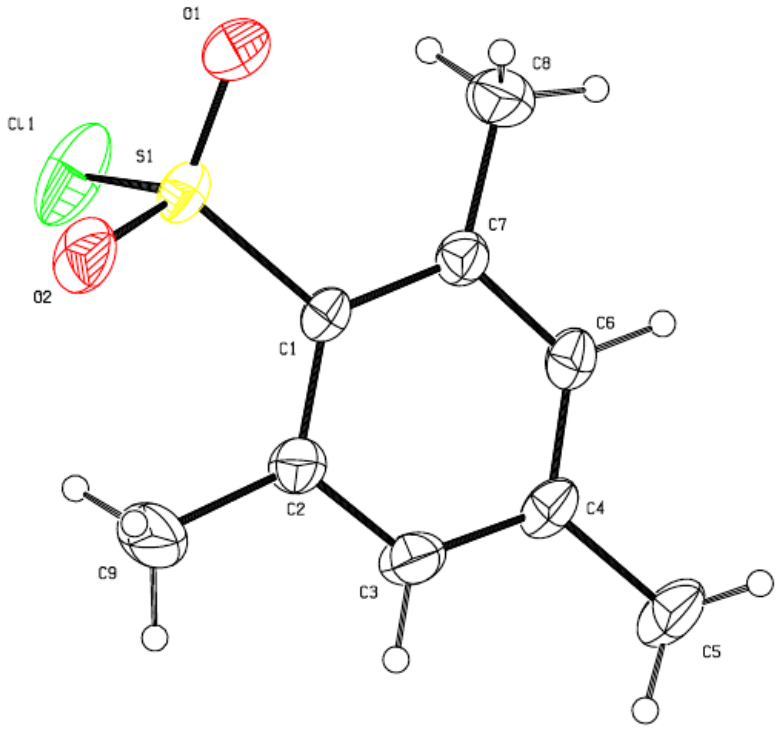
	x	y	z	U(eq)*
S(1)	2285(1)	8481(1)	7505(1)	65(1)
Cl(2)	1349(2)	8079(1)	5873(1)	98(1)
C(1)	783(3)	10088(2)	7616(2)	48(1)
C(2)	-1587(3)	12639(2)	7739(2)	45(1)
C(3)	-1081(3)	10129(2)	8378(2)	49(1)
C(4)	-2212(3)	11424(2)	8415(2)	49(1)
C(5)	269(4)	12539(2)	6999(2)	51(1)
C(6)	-2864(4)	14054(2)	7780(2)	56(1)
C(7)	1490(3)	11296(2)	6904(2)	52(1)
O(8)	4408(3)	8603(3)	7234(3)	109(1)
O(9)	1730(5)	7418(2)	8505(2)	113(1)
C(10)	3426(5)	11348(4)	6009(3)	82(1)
C(11)	-1992(5)	8895(3)	9165(3)	73(1)
C(8)	-1650(6)	14877(3)	8429(4)	85(1)
C(9)	-4933(5)	13930(3)	8576(4)	83(1)
C(12)	-3313(8)	14779(4)	6418(3)	113(2)

*U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S3. X-Ray data of 2,4,6-tris[($^2H_3$)methyl]($^2H_2$)benzenesulfonyl chloride (**2D**)

Crystal data and structure refinement

Empirical formula	$C_9D_{11}ClO_2S$
Formula weight	218.69
Temperature	271.95 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.8768(2) Å, α= 65.7430(10)°.
	b = 7.9571(2) Å, β= 79.3400(10)°.
	c = 9.2502(2) Å, γ = 77.3870(10)°.
Volume	512.86(2) $Å^3$
Z	2
Density (calculated)	1.416 Mg/m^3
Absorption coefficient	0.540 mm^{-1}
F(000)	228
Crystal size	0.44 × 0.42 × 0.23 mm^3
Theta range for data collection	2.429 to 30.555°.
Index ranges	-11<=h<=11, -11<=k<=11, -13<=l<=13
Reflections collected	21493
Independent reflections	3125 [R(int) = 0.0196]
Completeness to theta = 25.242°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.7105
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3125 / 0 / 121
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1308
R indices (all data)	R1 = 0.0518, wR2 = 0.1369
Extinction coefficient	n/a
Largest diff. peak and hole	0.536 and -0.451 e.$Å^{-3}$



ORTEP diagram of 2,4,6-tris[($^2H_3$)methyl]($^2H_2$)benzenesulfonyl chloride (**2D**)

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \cdot 10^3$)

	x	y	z	U(eq)
Cl(1)	12561(1)	-1296(1)	5383(1)	101(1)
S(1)	12367(1)	-1563(1)	7692(1)	48(1)
O(1)	12007(2)	-3387(2)	8621(2)	78(1)
O(2)	13927(2)	-1108(2)	7869(2)	71(1)
C(1)	10549(2)	162(2)	7764(2)	39(1)
C(2)	10819(2)	2011(2)	7251(2)	53(1)
C(3)	9356(2)	3327(2)	7328(3)	61(1)
C(4)	7696(2)	2881(2)	7876(2)	50(1)
C(5)	6141(3)	4354(3)	7939(3)	71(1)
C(6)	7491(2)	1054(2)	8337(2)	47(1)
C(7)	8878(2)	-348(2)	8291(2)	43(1)
C(8)	8439(3)	-2271(3)	8774(4)	77(1)
C(9)	12557(3)	2690(3)	6600(4)	97(1)