STRUCTURE-REACTIVITY RELATIONSHIPS AND THE POSITIVE STERIC EFFECT OF *ORTHO* SUBSTITUENTS IN ARENESULFONYL CHLORIDES

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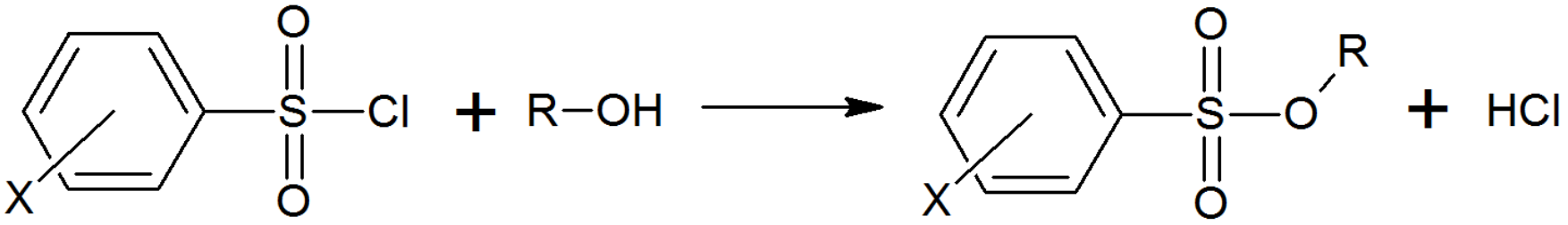
Alcoholysis of arenesulfonyl chlorides



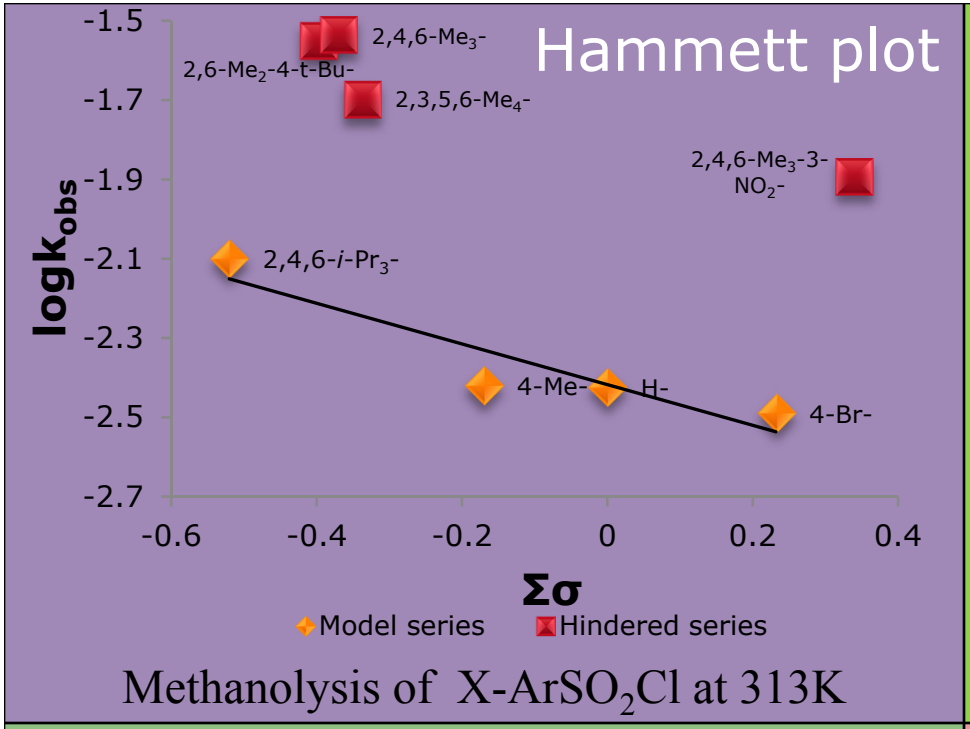
R= Me-, Et-, Pr-; *i*-Pr-

X= 4-Me-; H-;4-Br-; 2,4,6-*i*-Pr_3-; 2,6-Me_2-4-*t*-Bu-;

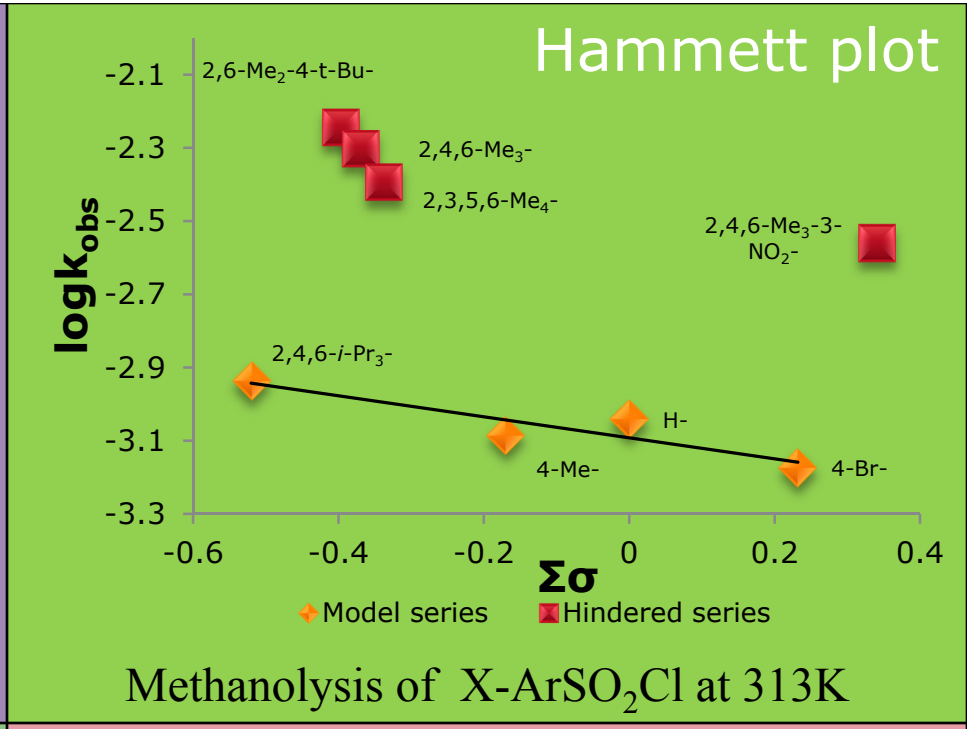
2,4,6-Me_3-; 2,3,5,6-Me_4-; 2,4,6-Me_3-3-NO_2-

Observed rate constants for alcoholysis of arenesulfonyl chlorides at 313K

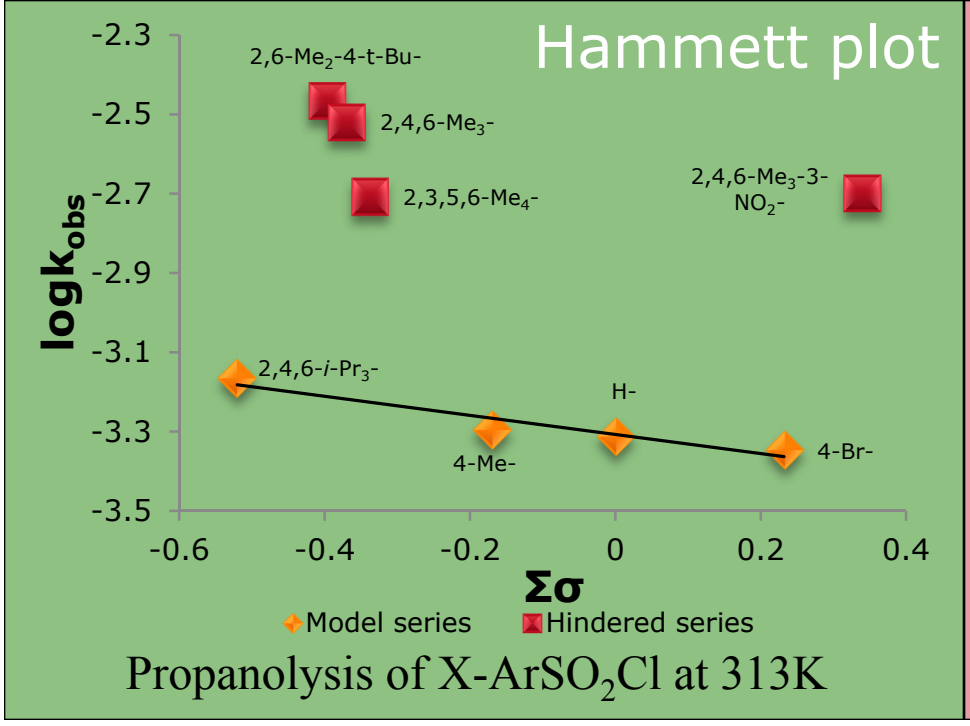
X	$k_{obs} \cdot 10^4$ / s^{-1}			
	MeOH	EtOH	PrOH	*i*-PrOH
4-Me-	3.80±0.02	0.82±0.01	0.506±0.002	0.066±0.008
H-	3.76±0.01	0.91±0.01	0.488±0.003	0.08±0.01
4-Br-	3.24±0.02	0.67±0.01	0.450±0.007	0.099±0.001
2,4,6-*i*-Pr_3-	7.94±0.04	1.16±0.01	0.684±0.001	0.070±0.005
2,6-Me_2-4-*t*-Bu-	28.1±0.2	5.70±0.80	3.43±0.01	0.47±0.01
2,4,6-Me_3-	29.1±0.2	4.99±0.02	3.03±0.01	0.44±0.01
2,3,5,6-Me_4-	20.1±0.1	4.05±0.05	1.96±0.01	0.31±0.01
2,4,6-Me_3-3-NO_2-	12.8±0.2	2.76±0.01	2.00±0.02	0.38±0.03



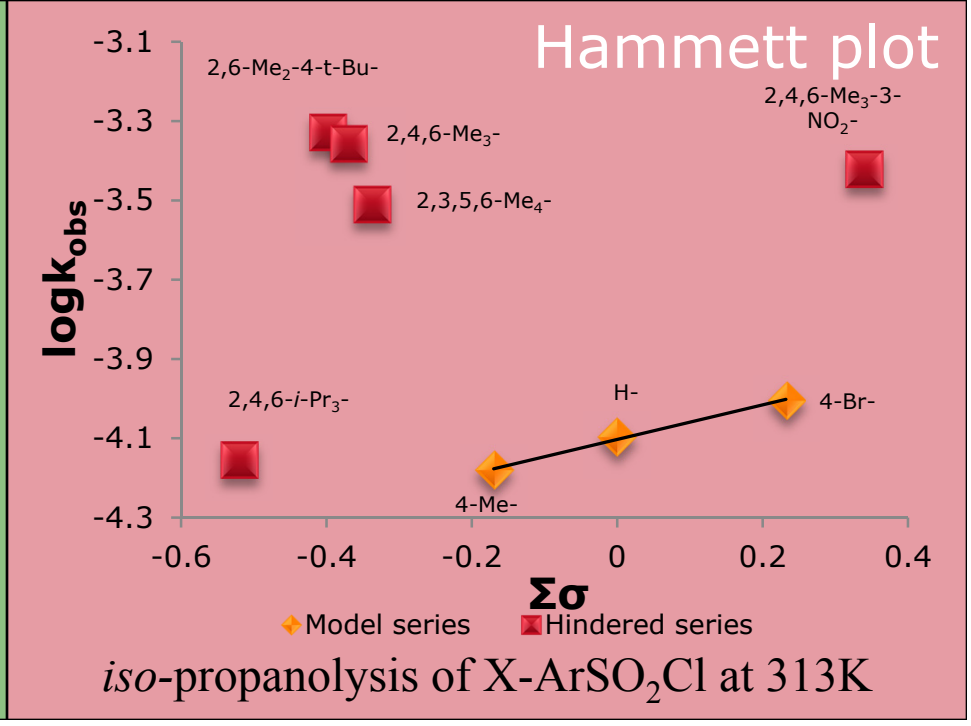
Methanolysis of X-$ArSO_2Cl$ at 313K



Methanolysis of X-$ArSO_2Cl$ at 313K



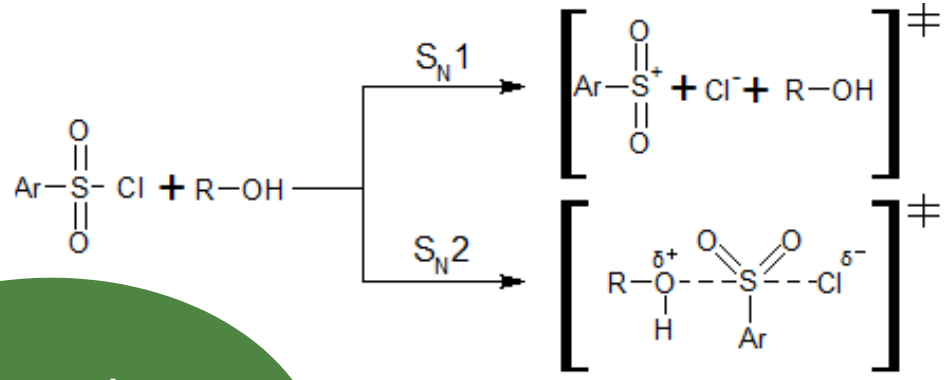
Propanolysis of X-$ArSO_2Cl$ at 313K



iso-propanolysis of X-$ArSO_2Cl$ at 313K

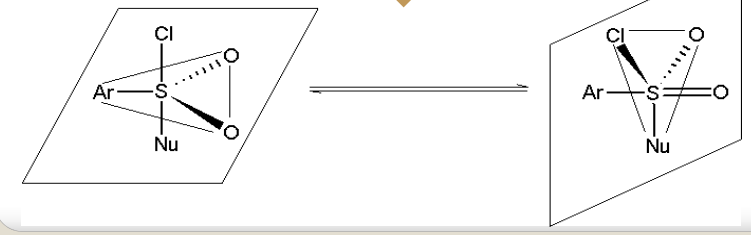
Mechanism change

from S_N2 to S_N1

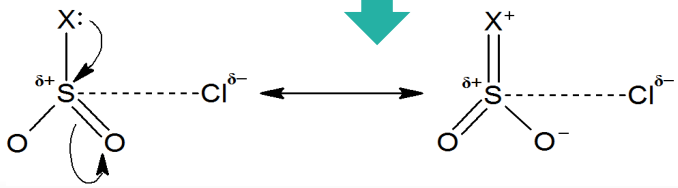


Explanations of positive *ortho*-effect

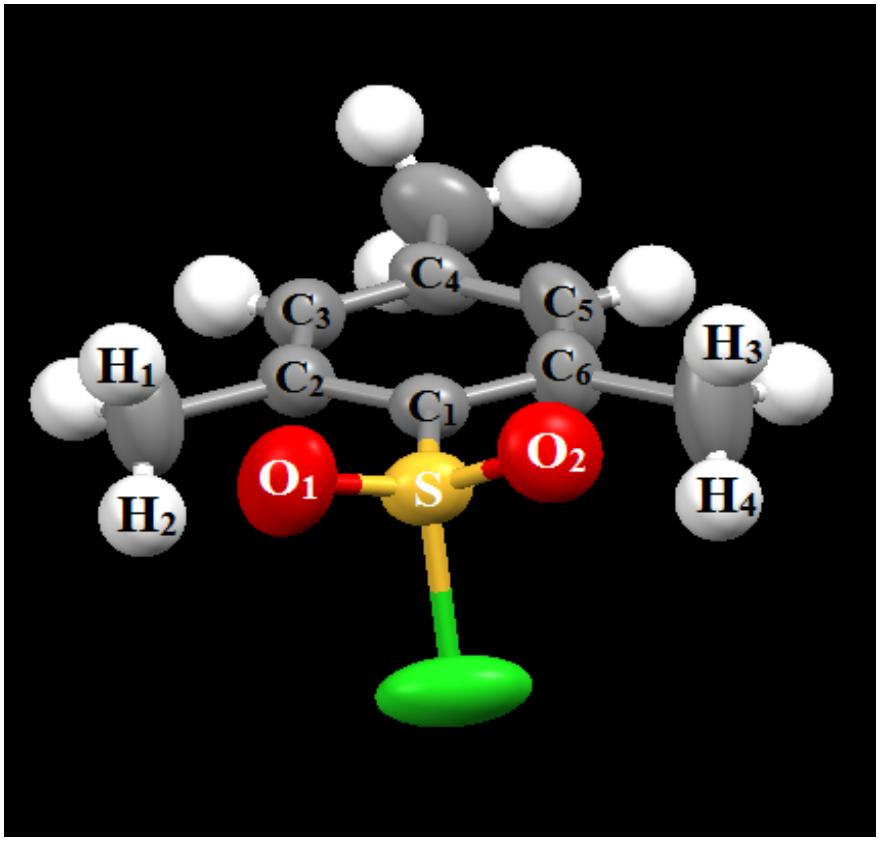
Berry's pseudo rotation mechanism

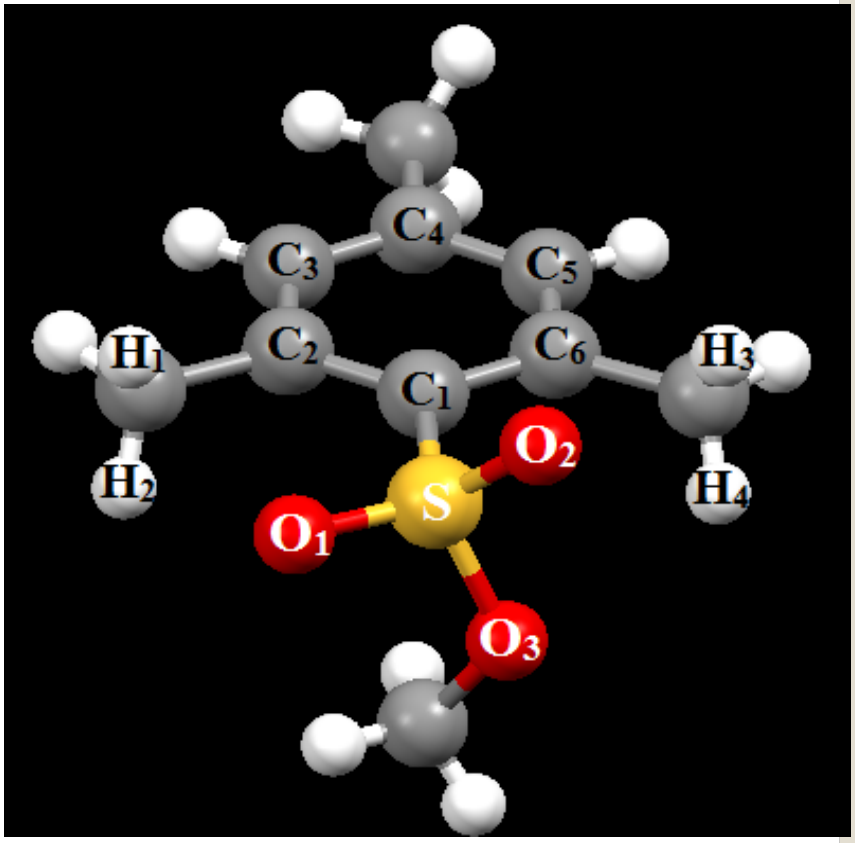


Hyperconjugation



X-ray structures of some derivatives of hindered arenesulfonic compounds.





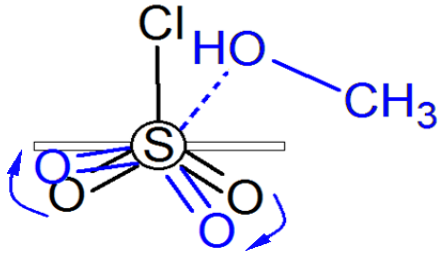
$\angle(O_1SO_2) \approx 118^\circ$

$2.30 < l_{(O1\cdots H1)}, [Å] < 2.70$ $\quad$ $2.36 < l_{(O2\cdots H3)}, [Å] < 2.59$

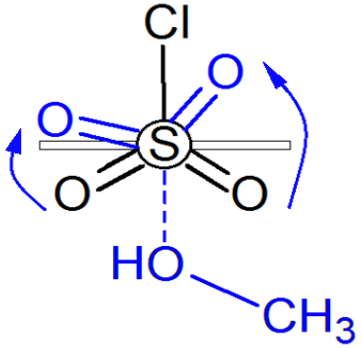
$2.48 < l_{(O1\cdots H2)}, [Å] < 2.66$ $\quad$ $2.57 < l_{(O2\cdots H4)}, [Å] < 3.80$

Weak intramolecular C-H···O interaction.

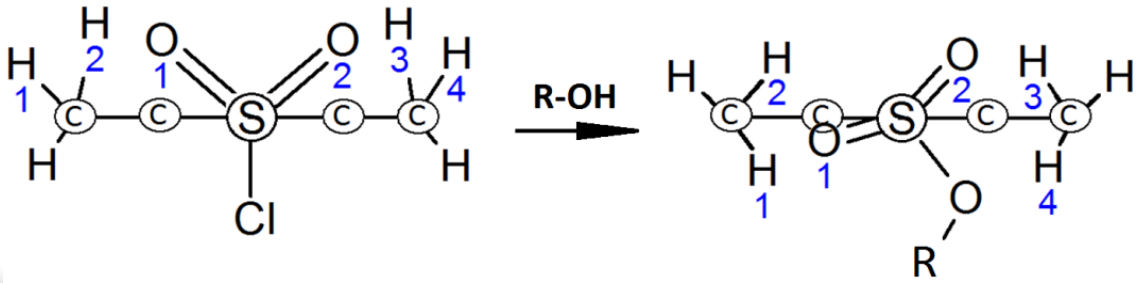
a.

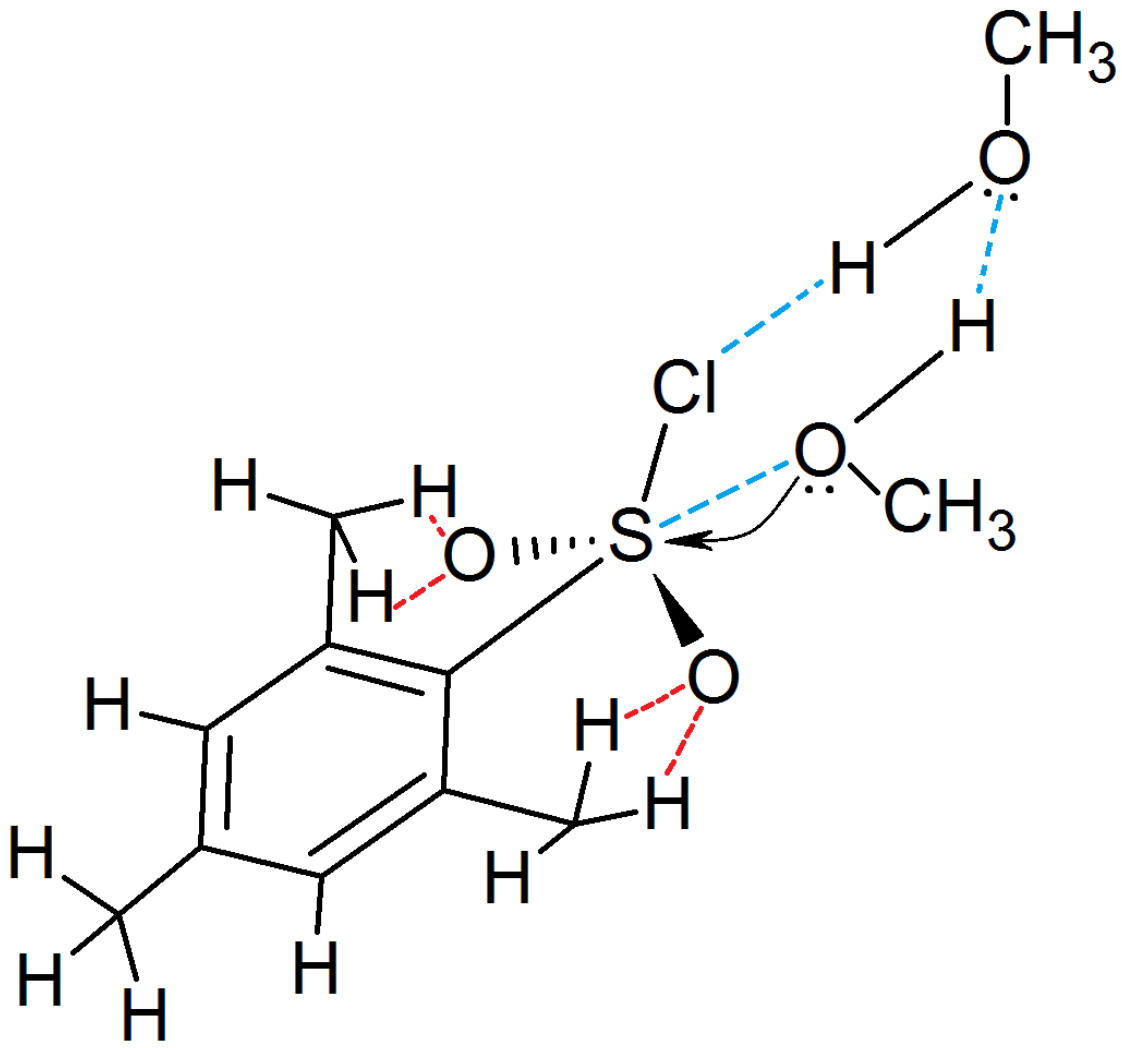


b.



Types of nucleophilic attack at the reaction center during arenesulfonyl chloride methanolysis. a. axial attack; b. backside frontal attack.





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

Conclusions

❑ In methanol, ethanol, propanol an increase of electron withdrawing effect of -*X* in unhindered compounds leads to lower reactivity, contrary to the prediction for typical S_N2 reactions. The kinetics of neutral *iso*-propanolysis of aromatic sulfonyl chlorides has shown the opposite tendency relative to unbranched alcohols.

❑ Sterically-hindered compounds (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-) show anomalous acceleration of the solvolysis reaction rate for all alcohols.

❑ X-ray analysis shown that the distance between the hydrogen atom of the *o*-alkyl group and the nearest oxygen of the sulfonyl group, $l_{(O\cdots H)}$, is comparable to the length of typical hydrogen bonds (2.30-2.70 Å), *i.e.* weak intramolecular (C-H···O) interaction.

❑ *o*-alkyl groups limit the backside approach of the nucleophile whereby creating preconditions for a frontal attack on the sulfur atom, that may be the possible reason of the positive steric effect.


THANK
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