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Aromatic Sulfonylation. I. Kinetics and Kinetic Isotope Effects in the Sulfonylation[*1]

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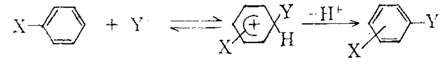
p-Toluenesulfonylation of toluene, chlorobenzene and bromobenzene in the presence of aluminum chloride was investigated in methylene chloride at 0—20°C. The rate was equal to k_3[TsCl][AlCl$_3$][ArH]. Kinetic hydrogen isotope effects were found for *p*-deuteriotoluene ($k_H/k_D=2.8$) and *p*-deuteriochlorobenzene ($k_H/k_D=1.98$). Infrared studies indicated that not a sulfonyl cation but TsCl-AlCl$_3$ complex was present in the medium. Substitution took place exclusively at *para* positions for halobenzenes, but 13.4% *ortho* and 86.6% *para* isomers were obtained for toluene. Partial rate factors for *para* positions were 52.5(PhCH$_3$), 0.224(PhCl) and 0.164(PhBr). A plausible reaction mechanism was proposed, in which the abstraction of proton from the σ-complex was rate-determining.

It is generally understood that electrophilic substitution on an aromatic nucleus involves two steps, *i. e.* formation of a σ-complex and abstraction of proton from the complex.



Kinetic isotope effect has been observed in a few reactions,[1] and for sulfonation the values of $k_H/k_D=1.4$—2.1[2,3] and 1.14—1.34[4] have been reported. Jensen and Brown[5] and Cerfontain[4] studied sulfonylation, which also involves the attack of a positively charged sulfur on an aromatic nucleus. Both groups found no primary isotope effect, and concluded that removal of proton from the intermediate was not the rate-determining step. Jensen and Brown made a through kinetic study of Friedel-Crafts sulfonylation of aromatics with aluminum chloride by using nitrobenzene or benzenesulfonyl chloride as solvent, and estimated that either sulfonyl cation ArSO$_2^+$ or ion-pair ArSO$_2^+$AlCl$_4^-$ was the species attacking aromatics.[6-8] However, their results are rather complicated, and both the reaction order and the mechanism vary with the solvent and the aromatics.

In order to clarify the mechanism of sulfonylation, kinetics and isotope effect of the sulfonylation with

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[*1] Organic Sulfur Compounds. Part XVI.

1) L. Melander, "Isotope Effects on Reaction Rate," Ronald Press, New York (1960); H. Zollinger, "Advances in Physical Organic Chemistry," Vol. II, Academic Press, London and New York (1964), p. 163.

2) L. Melander, *Ark. Kemi*, **2**, 211 (1950).

3) U. Berglund-Larsson and L. Melander, *ibid.*, **6**, 219 (1953); U. Berglund-Larsson, *ibid.*, **10**, 549 (1957).

4) a) H. Cerfontain, H. J. Hofman and A. Teldert *Rec. Trav. Chim.*, **83**, 493 (1964); b) H. Cerfontain and A. Telder, *ibid.*, **84**, 1613 (1965); c) J. K. Bosscher and H. Cerfontain, *ibid.*, **87**, 873 (1968); d) J. K. Bosscher and H. Cerfontain, *J. Chem. Soc.*, *B*, **1968**, 1524.

5) F. R. Jensen and H. C. Brown, *J. Amer. Chem. Soc.*, **80**, 4044, Foot-note 15 (1958).

6) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 4038 (1958).

7) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 4042 (1958).

8) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 4046 (1958).

p-toluenesulfonyl chloride and aluminum chloride have been investigated. Methylene chloride has been used as the solvent. Though it is a solvent of smaller polarity, it dissolves the TsCl-$AlCl_3$ complex well,[9] and thus it enables us to study the sulfonylation in a homogeneous medium under mild conditions. The results of this investigation will be described in this paper.

Experimental

Materials. *p*-Toluenesulfonyl chloride was recrystallized twice from *n*-hexane; mp 69°C. Toluene and chlorobenzene were shaken with concentrated sulfuric acid, dried over calcium chloride and then distilled. Bromobenzene was dried over calcium chloride and then distilled. Methylene chloride was dried over calcium chloride and over phosphorus pentoxide, and then distilled. Anhydrous aluminum chloride of first grade was used without further purification.

p-Deuteriochlorobenzene was prepared by hydrolysis of *p*-chlorophenylmagnesium bromide in heavy water (Merck, 99.75%); $n_D^{26.4}$ 1.5201; isotopic purity, 89.7 atom %D (by mass spectrometry). *p*-Deuteriotoluene was prepared by hydrolysis of *p*-tolylmagnesium bromide in heavy water (Asahi Chemicals, 99.80%); bp 110°C; isotopic purity, 80.2 atom %D (by mass spectrometry).

Kinetic Measurements. *p*-Toluenesulfonyl chloride and excess aluminum chloride were stirred in 50 m*l* of methylene chloride for 30 min at room temperature. Excess aluminum chloride undissolved was removed by filtration from the solution of TsCl-$AlCl_3$ complex, which was diluted with methylene chloride to 100 m*l*. This solution and 100 m*l* of a methylene chloride solution of an aromatic compound were placed separately in a constant temperature bath, and the reaction was started by mixing these two solutions after 30 min. For less reactive halobenzenes, 10 m*l* each of the mixed solution was sealed in an ampoule, and then these ampoules were placed in a bath. The time of mixing was regarded as the beginning of the reaction. Samples were taken out after suitable intervals, and the complex was decomposed by dilute hydrochloric acid. The methylene chloride solution was dried over magnesium sulfate, and the amount of aryl *p*-tolyl sulfone produced was determined by means of the absorption at 1320 cm^{-1} (ditolyl sulfone) or at 1325 cm^{-1} (halophenyl tolyl sulfone) by a Hitachi infrared spectrophotometer EPI-G_2. The initial concentration of aluminum chloride was determined gravimetrically by treating a portion of the solution with dilute hydrochloric acid, precipitating aluminum hydroxide with ammonia and then converting into aluminum oxide in a platinum crucible.

Sulfonylation of Toluene. The absence of 860 cm^{-1} band showed the absence of *p*-tolyl *m*-tolyl sulfone in the products. The sulfone mixture was found to contain 13.4% *p*-tolyl *o*-tolyl sulfone and 86.6% di-*p*-tolyl sulfone by gas-chromatographic analysis on a 2 m column packed with Chromosorb-SE30 at 230°C (retention time: *p*-tolyl *o*-tolyl sulfone, 19.9 min, *p*-tolyl *m*-tolyl sulfone, 23.5 min, di-*p*-tolyl sulfone, 24.5 min).

Table 1. Typical data for the sulfonylation of toluene at 5.0°C

Time (sec)	Di-(*p*-tolyl) sulfone ($mol \cdot l^{-1}$)	Rate const. ($l^2 \cdot mol^{-2} \cdot sec^{-1}$)
0.660×10^3	0.0346	1.09×10^{-3}
1.140	0.0577	1.26
1.620	0.0742	1.20
2.040	0.0869	1.22
2.460	0.0930	1.14
2.970	0.1057	1.18
3.360	0.1101	1.16
3.780	0.1193	1.19
4.320	0.1269	1.20
4.830	0.1271	1.24
5.430	0.1378	1.16
	mean	1.19×10^{-3}

Initial concentration: $[TsCl]_0$, 0.2036; $[PhCH_3]_0$, 0.9848; $[AlCl_3]_0$, 0.2887 $mol \cdot l^{-1}$.

The rate of reaction was proportional to the concentration of each of three reactants, and the third order rate constant was nearly constant as illustrated by a typical run in Table 1.

Table 2. Typical data for the sulfonylation of chlorobenzene at 15.0°C

Time (sec)	*p*-Tolyl *p*-chlorophenyl sulfone ($mol \cdot l^{-1}$)	Rate const. ($l^2 \cdot mol^{-2} \cdot sec^{-1}$)
2.23×10^4	0.0148	1.36×10^{-5}
4.73	0.0233	1.06
6.84	0.0329	1.10
11.40	0.0538	1.26
16.67	0.0666	1.16
25.44	0.0943	1.29
27.78	0.0974	1.30
36.24	0.1135	1.31
	mean	1.23×10^{-5}

Initial concentration: $[TsCl]_0$, 0.2005; $[PhCl]_0$, 1.0004; $[AlCl_3]_0$, 0.2594 $mol \cdot l^{-1}$.

Table 3. Typical data for the sulfonylation of bromobenzene at 15.0°C

Time (sec)	*p*-Tolyl *p*-bromophenyl sulfone ($mol \cdot l^{-1}$)	Rate const. ($l^2 \cdot mol^{-2} \cdot sec^{-1}$)
4.14×10^4	0.0148	1.12×10^{-5}
8.01	0.0254	1.05
12.87	0.0336	1.00
16.55	0.0404	0.88
21.36	0.0516	0.94
25.32	0.0584	0.94
59.76	0.1083	1.09
	mean	1.00×10^{-5}

Initial concentration: $[TsCl]_0$, 0.1996; $[PhBr]_0$: 0.5998; $[AlCl_3]_0$, 0.2898 $mol \cdot l^{-1}$.

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[9] G. Holt and B. Pagdin, *J. Chem. Soc.*, **1960**, 2508; E. C. Dart, G. Holt and K. D. Jeffreys, *ibid.*, **1964**, 5663.

TABLE 4. RATE CONSTANTS OF SULFONYLATION OF SUBSTITUTED BENZENES

X in PhX	Temp. (°C)	Initial concentrations (mol·l^{-1})			k_3 (l^2·mol^{-2}·sec^{-1})	E_a (kcal·mol^{-1})	$\Delta S^{\ddagger}$ at 0°C (e.u.)
		$[TsCl]_0$	$[PhX]_0$	$[AlCl_3]_0$			
CH_3	1.0	0.1996	0.6031	0.2158	0.994* × 10^{-3}	14.8	−20.2
	5.0	0.1994	0.3504	0.2068	1.37		
	5.0	0.2022	0.6013	0.2315	1.26*		
	5.0	0.2036	0.9848	0.2887	1.19		
	7.5	0.2004	0.6052	0.2409	1.74*		
	10.0	0.2016	0.6315	0.2425	2.35*		
H**	0.0	0.3003	0.1905	0.4332	1.16 × 10^{-4}	11.9	−34.6
	0.0	0.2935	0.4484	0.4449	1.07		
	0.0	0.2988	0.6261	0.4544	1.19		
	0.0	0.2370	1.1502	0.4304	1.28		
	7.0	0.2952	0.3254	0.4209	1.92		
	15.5	0.2933	0.4323	0.4721	4.02		
Cl	0.0	0.2004	0.3994	0.2603	0.532 × 10^{-5}	11.0	−42.5
	0.0	0.2005	0.5986	0.2603	0.453		
	0.0	0.2004	1.0000	0.2747	0.425*		
	7.0	0.2007	1.0014	0.2715	0.717*		
	15.0	0.2005	1.0004	0.2594	1.23*		
	20.0	0.1993	0.5993	0.4022	2.01		
	20.0	0.2005	0.9992	0.2354	1.70*		
Br	0.0	0.1993	0.6002	0.2821	0.283 × 10^{-5}	12.1	−41.5
	7.0	0.1995	0.5988	0.2613	0.524		
	15.0	0.1996	0.5998	0.2898	1.00		
	20.0	0.1997	0.6000	0.2704	1.39		

* E_a and $\Delta S^{\ddagger}$ were calculated on the basis of these values.
** Ref. 10.

Sulfonylation of Halobenzenes. Recrystallization of the product of tosylation of chlorobenzene yielded *p*-tolyl *p*-chlorophenyl sulfone (mp 121°C) and a mother liquor, which was found by elution chromatography to be almost completely *p*-tolyl *p*-chlorophenyl sulfone. Thus it was shown that more than 98% of *p*-toluenesulfonyl chloride reacted at *p*-position of chlorobenzene. Similarly it was found that tosylation of bromobenzene took place almost exclusively at *p*-position.

The reactions were of third order, and the third order rate constants calculated were nearly constant till about 50% reaction as illustrated by typical runs in Tables 2 and 3.

Results and Discussion

Results of kinctic studies of tosylation are summarized in Table 4. Rate constants are larger for the runs with lower concentrations of a substituted benzene. This can be ascribed to the solvent effect due to the decrease of the less polar substance in the medium. Therefore, the activation parameters were obtained on the basis of the runs with similar compositions.

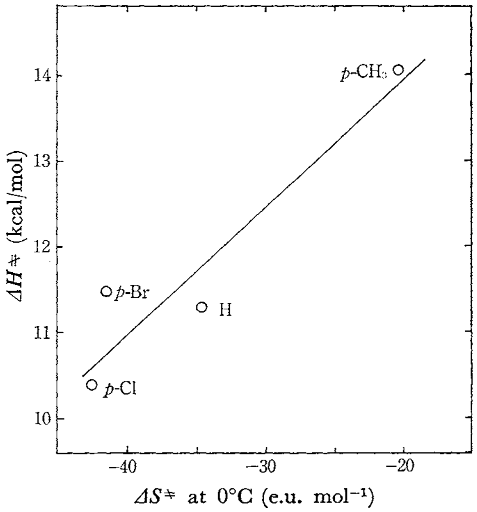


Fig. 1. Isokinetic relationship for the sulfonylation (β=152°K).

In Fig. 1 values of activation enthalpy were plotted *versus* values of activation entropy, and it was shown that an isokinetic relationship holds with r=0.95. The isokinetic temperature, β, was 152°K.

The partial rate factors of *para* positions at 7.0°C were calculated. They were 52.5 for *p*-CH$_3$, 0.224 for *p*-Cl and 0.164 for *p*-Br. Figure 2 shows

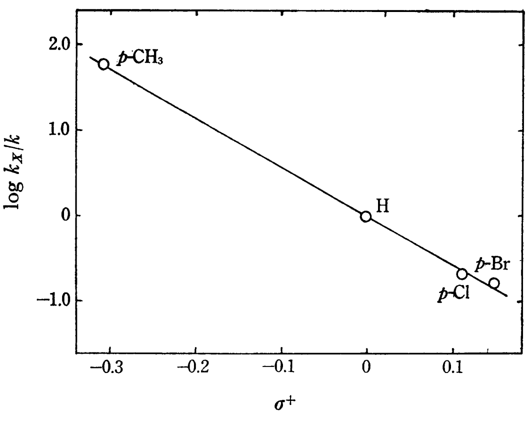
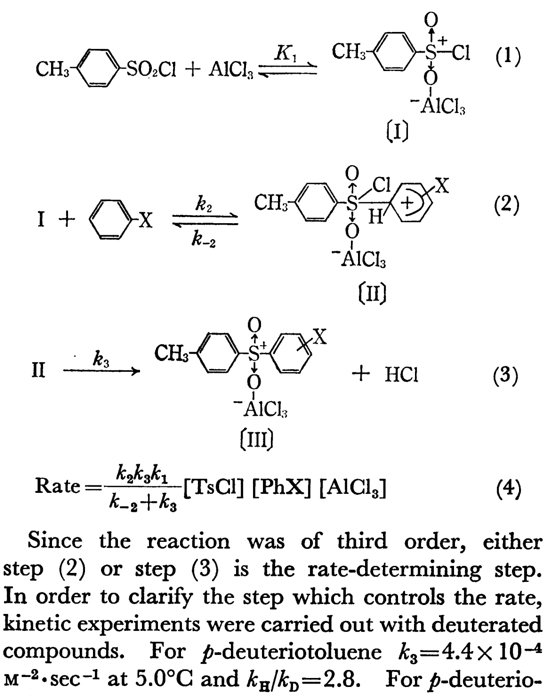


Fig. 2. Hammett plots for the sulfonylation at 7.0°C ($\rho=-5.6$).

that a good linear relationship holds between these values and σ^+ ($\rho=-5.6$).

Since the rate was proportional to the concentration of each of TsCl, $AlCl_3$ and PhX, the following mechainsm appeared plausible.



$$\text{Rate}=\frac{k_2k_3k_1}{k_{-2}+k_3}[\text{TsCl}]\,[\text{PhX}]\,[\text{AlCl}_3] \qquad (4)$$

Since the reaction was of third order, either step (2) or step (3) is the rate-determining step. In order to clarify the step which controls the rate, kinetic experiments were carried out with deuterated compounds. For p-deuteriotoluene $k_3=4.4\times10^{-4}$ $\text{M}^{-2}\cdot\text{sec}^{-1}$ at 5.0°C and $k_H/k_D=2.8$. For p-deuteriochlorobenzene $k_3=8.58\times10^{-6}\text{M}^{-2}\cdot\text{sec}^{-1}$ at 20.0°C and $k_H/k_D=1.98\pm0.3$. The values previously given were $k_H/k_D=2.0$ for hexadeuteriobenzene and $k_H/k_D=1.77\pm0.2$ for p-deuteriobromobenzene.[10] These data clearly confirmed that the hydrogen-abstraction step was the rate-determining step. This conclusion is in contrast with the finding of Jensen and Brown that in benzenesulfonyl chloride as the solvent there was no kinetic isotope effect.[5] Bosscher and Cerfontain reported a very small isotope effect ($k_H/k_D=1.1$) for the sulfonylation occurring as a side reaction in the sulfonation of benzene with sulfur trioxide in trichlorofluoromethane at −35°C.[4d]

The formation of TsCl•$AlCl_3$ complex and Ts•Ar•$AlCl_3$ complex was checked by means of infrared spctroscopy. The absorptions of asymmetric and symmetric stretching vibrations of the SO_2 group of p-toluenesulfonyl chloride in methylene chloride were observed at 1375 and 1175 cm^{-1}, whereas they appeared at 1365 and 1175 cm^{-1} when aluminum chloride was present in the medium. The absorptions due to the SO_2 group in p-tolyl p-chlorophenyl sulfone in methylene chloride were observed at 1325 and 1160 cm^{-1}, whereas these absorptions shifted to 1305 and 1105 cm^{-1} when aluminum chloride was added to the medium. Lindner and Weber reported that p-dimethylaminobenzenesulfonyl chloride absorbed at 1367 and 1160 cm^{-1} and its sulfonyl cation absorbed at 1418 and 1195 cm^{-1}. These facts indicate that not a sulfonyl cation but complexes such as shown in structure I and II are present in the reaction medium and the sulfone produced is also present as the complex III.

Since the rate of sulfonylation of toluene was greater faster than those of halobenzenes, it was expected that the rate of sulfonylation of anisole would be much greater. However, it was found that the rate was extremely solw with anisole. When a methylene chloride solution of anisole, aluminum chloride and p-toluenesulfonyl chloride was viewed in infrared, no shift in the sulfonyl absorption was observed, indicating the absence of TsCl-$AlCl_3$ complex. Formation of $PhOCH_3$-$AlCl_3$ complex was suspected, and a solution of anisole and aluminum chloride was compared with a solution of anisole alone by infrared, ultraviolet and nuclear magnetic resonance spectroscopy. The results are shown in Table 5. These spectroscopic observations are consistent with the formation of $PhOCH_3$-$AlCl_3$ complex. Apparently the following equilibrium exists, and the $PhOCH_3$-$AlCl_3$ complex predominates.

$$\text{TsCl} + \text{PhOCH}_3\text{-AlCl}_3 \rightleftharpoons \text{PhOCH}_3 + \text{TsCl-AlCl}_3$$

TABLE 5. SPECTRA OF ANISOLE-ALUMINUM CHLORIDE-COMPLEX IN CH_2Cl_2

	$PhOCH_3$	$PhOCH_3$-$AlCl_3$
UV λ_{max}	280 mμ	410 mμ 497 mμ
NMR OCH_3	6.22 τ (s)	5.55 τ (s)
aromatic -H	3 τ (m)	2.65 τ (s)
IR =C-O-CH_3	1240 cm^{-1}	1135 cm^{-1}

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10) M. Kobayashi, K. Honda and A. Yamaguchi, *Tetrahedron Lett.*, **1968**, 487.

11) E. Lindner and H. Weber, *Chem. Ber.*, **101**, 2832 (1968).

TABLE 6. COMPARISON OF SULFONYLATIONS IN DIFFERENT SOLVENTS

Reactant	Solvent	Rate	Reaction step*	Orientation	Partial rate factor	k_H/k_D
$PhSO_2Cl$, $AlCl_3$, Mesitylene	$PhNO_2$	k_2 $[PhSO_2Cl][AlCl_3]$	(5), $\underline{(6)}$, (7)			
$PhSO_2Cl$, $AlCl_3$, $PhCH_3$	$PhNO_2$	k_3 $[PhSO_2Cl][AlCl_3][PhCH_3]$	(5), (6), $\underline{(7)}$			
$PhSO_2Cl$, $AlCl_3$, PhCl	$PhNO_2$	k_3 $[PhSO_2Cl][AlCl_3][PhCl]$	(5), (6), $\underline{(7)}$			
$PhSO_2Cl$, $AlCl_3$, $PhCH_3$	$PhSO_2Cl$	k_2 $[PhSO_2Cl\text{-}AlCl_3][PhCH_3]$	(6), $\underline{(7)}$	$o=28.4\%$ $m=8.7$ $p=62.9$	$o_f=6.8$ $m_f=2.1$ $p_f=30.2$	1
$PhSO_2Cl$, $AlCl_3$, PhCl	$PhSO_2Cl$	$k_{3/2}$ $[PhSO_2Cl\text{-}AlCl_3]^{-1/2}[PhCl]$	(6), $\underline{(8)}$			
TsCl, $AlCl_3$, $PhCH_3$	CH_2Cl_2	k_3 $[TsCl][AlCl_3][PhCH_3]$	(1), (2), $\underline{(3)}$	$o=13.4\%$ $m=0$ $p=86.6$	$p_f=52.5$	2.8
TsCl, $AlCl_3$, PhH	CH_2Cl_2	k_3 $[TsCl][AlCl_3][PhH]$	(1), (2), $\underline{(3)}$			2.0
TsCl, $AlCl_3$, PhCl	CH_2Cl_2	k_3 $[TsCl][AlCl_3][PhCl]$	(1), (2), $\underline{(3)}$		$p_f=0.224$	1.98
TsCl, $AlCl_3$, PhBr	CH_2Cl_2	k_3 $[TsCl][AlCl_3][PhBr]$	(1), (2), $\underline{(3)}$		$p_f=0.164$	1.77

* Rate-determining step proposed were underlined.

The findings of this investigation must be compared with those of the thorough study made by Jensen and Brown. They found that in nitrobenzene the rate was equal to $k_2[PhSO_2Cl][AlCl_3]$ for reactive aromatics whereas the rate was equal to $k_3[ArH][PhSO_2Cl][AlCl_3]$ for less reactive aromatics. The following reaction sequence was proposed, in which step (6) is rate-determining for more reactive aromatics and step (7) is rate-determining for less reactive aromatics.[6]

$$PhSO_2Cl + PhNO_2\cdot AlCl_3 \rightleftharpoons PhSO_2Cl\cdot AlCl_3 + PhNO_2 \qquad (5)$$

$$PhSO_2Cl\cdot AlCl_3 \rightleftharpoons PhSO_2{}^+AlCl_4{}^- \qquad (6)$$

$$ArH + PhSO_2{}^+AlCl_4{}^- \longrightarrow ArSO_2Ph\cdot AlCl_3 + HCl \qquad (7)$$

Jensen and Brown reported that in benzenesulfonyl chloride the rate was equal to $k_2[PhSO_2Cl\cdot AlCl_3][PhCH_3]$ with toluene and the attacking species was $ArSO_2{}^+AlCl_4{}^-$, whereas with chlorobenzene the rate was equal to $k_{3/2}[PhSO_2Cl\cdot AlCl_3]^{1/2}[PhCl]$ and the attacking species was $ArSO_2{}^+$ cation.[7]

$$PhSO_2{}^+AlCl_4{}^- \rightleftharpoons PhSO_2{}^+ + AlCl_4{}^- \qquad (8)$$

The findings of Jensen and Brown are compared with the findings of this investigtaion in Table 6.

A comparison of the orientation and the partial rate factors in Table 6 indicates that both intra- and intermolecular selectivity are greater with $TsCl\text{-}AlCl_3\text{-}ArH\text{-}CH_2Cl_2$ than with $PhSO_2Cl\text{-}AlCl_3\text{-}ArH$. The ρ value in CH_2Cl_2 was -5.6, whereas the ρ value calculated from the data in $PhSO_2Cl$ was -4.8. It is reasonable that in solvents of greater polarity such as nitrobenzene (dielectric constant, 34.092 at 25°C) and benzenesulfonyl chloride the reaction intermediates formed are ion pair $ArSO_2{}^+$ $AlCl_4{}^-$ or free cation, which are more reactive and less selective than complex II formed in

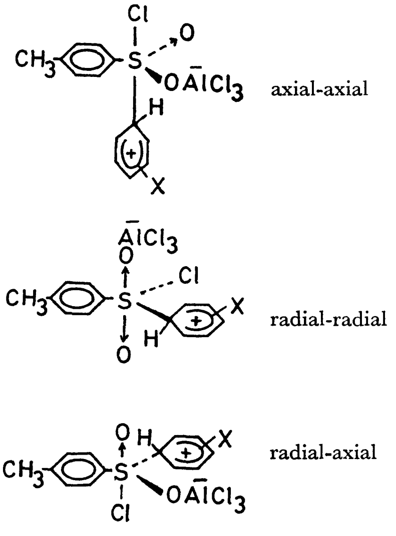

Fig. 4. Transition state of the sulfonylation.

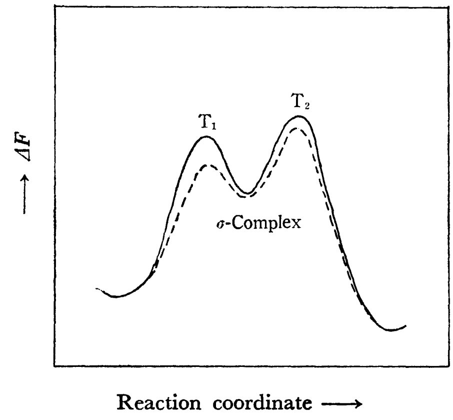

Fig. 3. Energy profile for the sulfonylation.
——: halobenzene -----: toluene

methylene chloride (dielectric constants, 9.08 at 20°C).

The isotope effect found for toluene was greater than that for benzene, chlorobenzene or bromobenzene. This finding may be explained by the energy profile shown in Fig. 3.

It is plausible that the presence of electron-releasing methyl group lowers the transition state T_1 considerably but affects the transition state T_2 very little. If so, k_{-2} as well as k_2 will be greater and k_{-2}/k_3 will be greater with toluene than with halobenzenes, and consequently the isotope effect with toluene is expected to be greater than that with halobenzenes.

It should be pointed out that three different structures are possible for the transition state from complex I to complex II, as shown in Fig. 4. However, at present it is not possible to determine which structure is more advantageous for the addition-elimination reaction discussed here.

On the basis of the reaction rate, reaction orders, activation parameters, orientations, partial rate factors, Hammett's plot, spectroscopic observations and kinetic hydrogen isotope effects, it was concluded that the reaction sequence (1), (2) and (3) best represent the reactions taking place in mixtures of *p*-toluenesulfonyl chloride, aluminum chloride and aromatic compounds in methylene chloride.