Aromatic Substitution. XXXI.[1] Friedel–Crafts Sulfonylation of Benzene and Toluene with Alkyl- and Arylsulfonyl Halides and Anhydrides

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Abstract: The aluminum chloride and antimony pentafluoride catalyzed Friedel–Crafts sulfonylation of benzene and toluene with alkyl- and arylsulfonyl chlorides, fluorides, and anhydrides has been studied. The effect of substituents in the sulfonylating agents showed that both the substrate selectivity (as expressed by k_T/k_B rate ratios obtained from both competitive and noncompetitive rate data) and positional selectivity (isomer distribution) were dependent upon the nature of the electrophile involved. The stronger the electrophile, the smaller the k_T/k_B rate ratio, yet the higher the ortho:para isomer ratio, and *vice versa*. The results are discussed in the context of the mechanistic concept of electrophilic aromatic substitution previously developed.

We expressed the view that in electrophilic aromatic substitutions the position of the transition state is not a fixed one but can change with ease from an "early" one resembling starting aromatics thus being of π-complex (benzonium ion) nature, to one of "late" character, *i.e.*, resembling intermediate benzenium ion or σ complex.[3] The behavior depends strongly upon the nature of electrophiles (and substrates). The stronger the electrophile the earlier generally the position of the transition state of the reaction coordinate. Accordingly, both the substrate selectivity, as reflected by $k_{toluene}/k_{benzene}$ (k_T/k_B) rate ratios, and positional selectivities (isomer distributions) are mainly governed by the nature and relative position of the transition states, which in turn are strongly dependent on the nature of the reagents. Little information was so far available on the mechanism of aromatic sulfonylation.

The first limited study of the reaction mechanism of Friedel–Crafts-type aromatic sulfonylation was undertaken in the early 1900's by Oliver,[4] from whose data the relative reactivity ratio of k_T/k_B of 3.7 can be derived for the aluminum chloride catalyzed sulfonylation with *p*-bromobenzenesulfonyl chloride. Later, Truce and Vriesen[5] and subsequently Jensen and Brown[6] studied methanesulfonylation and benzenesulfonylation, respectively. Among the data reported in the literature,[4–9] only two related sets of k_T/k_B rate ratio and isomer distribution data are available (as shown as no. 13 and 16 of Table I). We thus felt it of interest to extend our studies to Friedel–Crafts sulfonylations and particularly to the study of the effect of substituents with sulfonylating agents on the selectivity of the reactions.

(1) Part XXX: G. A. Olah, S. Kobayashi, and M. Tashiro, *J. Amer. Chem. Soc.*, **94**, 7448 (1972).
(2) (a) Postdoctoral Research Associate, 1969–1971; (b) Postdoctoral Research Associate, 1971–1972.
(3) For a summary see G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971), and references given therein.
(4) S. C. J. Oliver, *Recl. Trav. Chim. Pays-Bas*, **33**, 244 (1914).
(5) W. E. Truce and C. W. Vriesen, *J. Amer. Chem. Soc.*, **75**, 5032 (1953).
(6) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 4046 (1958).
(7) For a review see F. R. Jensen and G. Goodman, in "Friedel-Crafts and Related Reaction," Vol. III, G. A. Olah, Ed., pp 1319–1347.
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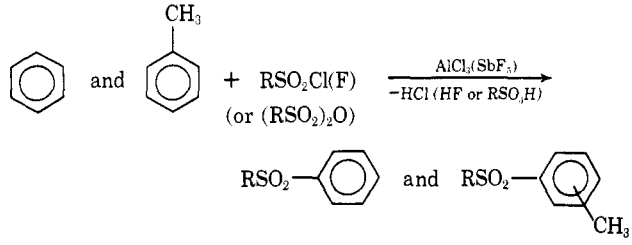
Results and Discussion

We wish to report the study of substituent effects in $AlCl_3$ and SbF_5 catalyzed sulfonylation of benzene and toluene with alkyl- and arylsulfonyl chlorides (fluorides) and sulfonic anhydrides.

Table I summarizes data obtained, using the competitive method of relative rate determination (k_T/k_B) (for details see Experimental Section) along with some available data from the literature. Data of Table I



clearly show the remarkable effect of substituents on both substrate and positional selectivity. Methane- and ethanesulfonylations (reactions no. 1–5) show low substrate selectivities (*i.e.*, small k_T/k_B rate ratios) but at the same time quite high positional selectivities (high ortho/para isomer ratios, with the meta isomer about 12–16%). They can be interpreted as the attacking species being strongly electrophilic, causing a highly exothermic reaction with the transition state of highest energy lying "early" and resembling starting aromatics. On the other hand dimethyl- and diethylaminosulfonyl chlorides, which are expected to be weaker electrophiles (as a consequence of the strong electron-donating ability of the alkylamino group), give higher k_T/k_B ratios and at the same time nearly exclusively the para isomers (expt 6–9).

The $AlCl_3$ catalyzed sulfonylation with methoxysulfonyl chloride and fluoride was also attempted. Although these could be expected to give a stabilized incipient sulfonium ion, $CH_3O{-}SO_2^{\delta+}X^{\delta-} \rightleftharpoons CH_3O^{\delta+}\cdots SO_2X^{\delta-}$, they did not give any sulfonylation of benzene and toluene. Instead, exclusive methylation of benzene and toluene took place in good yield to give toluene and xylenes (isomer distribution: ortho, 47.2%; meta, 18.2%; and para, 34.6%), respectively, in the $AlCl_3$ catalyzed reaction of CH_3OSO_2Cl (a more detailed discussion of methylation of aromatics

Table I. $AlCl_3$ and SbF_5 Catalyzed Sulfonylation of Benzene and Toluene with Sulfonyl Halides and Sulfonic Anhydrides

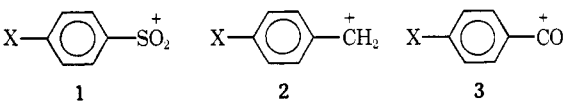
No.	Sulfonylating agent[a]	Catalyst	k_T/k_B[b]	Isomer distribution (%) of tolyl sulfone derivatives Ortho	Meta	Para	Reaction conditions	Analytical method	Ref
1	CH_3SO_2Cl	$AlCl_3$	4.2	54.7	16.6	29.3	60°, 2 hr	Glc	*d*
2	CH_3SO_2Cl			49	15	36	100°, 1 hr	Uv	Ref 8
3	$(CH_3SO_2)_2O$	$AlCl_3$	4.0	53.0	14.1	32.9	60°, 2 hr	Glc	*d*
4	$(CH_3SO_2)_2O$		4.0	52		48	60°, 2 hr	Pmr	*d*
5	$C_2H_5SO_2Cl$	$AlCl_3$	3.8	47.8	12.1	40.1	60°, 2 hr	Glc	*d*
6	$(CH_3)_2NSO_2Cl$	$AlCl_3$	55	1	~0	99	25°, 20 min	Pmr	*d*
7	$(CH_3)_2NSO_2F$	SbF_5	34.5	1	~0	99	25°, 1 hr in Freon-113	Pmr	*d*
8	$(C_2H_5)_2NSO_2Cl$	$AlCl_3$	42	1.5	~0	98.5	25°, 20 min	Pmr	*d*
9	$(C_2H_5)_2NSO_2Cl$	SbF_5	32.0	~1	~0	99	25°, 1 hr in Freon-113	Pmr	*d*
10	*p*-O_2N—Ph—SO_2Cl	$AlCl_3$	2.8	51		49	60°, 2 hr	Pmr	*d*
11	*p*-F—Ph—SO_2Cl	$AlCl_3$	5.4	42		58	60°, 2 hr	Pmr	*d*
12	*p*-Cl—Ph—SO_2Cl	$AlCl_3$	7.5	38		62	60°, 2 hr	Pmr	*d*
13	*p*-Br—Ph—SO_2Cl	$AlCl_3$	3.7[c]				30°		Ref 7
14	Ph—SO_2Cl	$AlCl_3$	8.7	28	7	65	25°, 20 min	Pmr	*d*
15		$AlCl_3$	8.2	28	8	64	60°, 2 hr	Pmr	*d*
16		$AlCl_3$	8.0[c]	28.4	8.7	62.9	25°	Ir	Ref 6
17	Ph—SO_2F	SbF_5	3.9	29	8	63	25°, 1 hr in Freon-113	Pmr	*d*
18	*p*-CH_3—Ph—SO_2Cl	$AlCl_3$	17	17	~3	80	25°, 20 min	Pmr	*d*
19		$AlCl_3$	10.0[c]	13.4	0	86.6	5° in CH_2Cl_2	Ir and glc	Ref 9
20	*p*-CH_3O—Ph—SO_2Cl	$AlCl_3$	82	5.6	~1	93.4	25°, 20 min	Pmr	*d*
21	*p*-CH_3O—Ph—SO_2F	SbF_5	57	7.0	~1	92.0	25°, 1 hr in Freon-113	Pmr	*d*

[a] $AlCl_3$ was catalyst unless otherwise indicated. [b] The values were obtained from the competitive method unless otherwise indicated. [c] Obtained from noncompetitive kinetic study. [d] This work.

including reactions with methyl halosulfates will be published[10]).

In the series of reactions with substituted benzenesulfonyl chlorides, electron-withdrawing substituents such as *p*-NO_2, *p*-F, *p*-Cl, and *p*-Br decrease the k_T/k_B ratios and at the same time increase the ortho isomer contents (expt 10–13) compared with the reaction of benzenesulfonyl chloride (fluoride) (expt 14–17). Electron-donating substituents such as *p*-CH_3 and *p*-OCH_3, on the other hand, increase the k_T/k_B ratio and produce high para isomer contents, exceeding 80% (expt 18–21). These data again can be best interpreted on the basis that with decreasing electrophilicity of the attacking species the transition state increasingly resembles the Wheland intermediate (σ complex). Since the *p*-methyl substituted benzenium ion has greater stability than the ortho (meta being the least stable), para substitution becomes predominant (80–99%) with k_T/k_B being as high as 82 (*p*-OCH_3). When the RSO_2Cl–catalyst complex (incipient sulfonium ion) is strongly electrophilic, the reaction is becoming increasingly more exothermic and the transition state will lie early on the reaction coordinate and resemble starting aromatics (π-complex nature). Accordingly, k_T/k_B is low and the ortho/para isomer ratio is becoming high, reflecting that in this case the transition state resembles more starting hydrocarbons (toluene and benzene) and not the related benzenium ions.

In spite of the fact that the sulfonylation reaction is regarded as a modification of the acylation reaction,[7] it is interesting to note that the para-substituent effect in arenesulfonyl chlorides on both substrate and positional selectivity show rather close similarity to those found in benzylation,[1,11] but not in benzoylation reactions.[12] This finding may be explained by the observation that only with a strongly stabilizing para substituent X (such as CH_3O) are a stable sulfonylium ion 1-CH_3O and a stable benzyl cation 2-CH_3O formed, whereas **1**-H and **2**-H have not so far been observed. On the other hand, the parent benzoyl cation **3**-H itself, as well as its substituted derivatives, were isolated as stable salts. This indicates that substituent effects to stabilize the cations **1** and **2** are much more important than those in the case of cations **3**.



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Noncompetitive Rate Determination. In fast, exothermic electrophilic aromatic substitutions showing low substrate selectivity the question must be considered whether competitive rate data indeed reflect low substrate selectivity differences, or that they are a consequence of the reactions becoming encounter-rate controlled (*i.e.*, diffusion controlled).[3] This question was raised previously in connection with nitration, alkylation, and halogenation data. Whereas nitration of benzene and toluene is generally too fast to allow noncompetitive rate measurements, in the case of benzylation of the same systems it was possible to verify low substrate selectivity data from noncompetitive rate measurements of toluene and benzene. Consequently a similar study was carried out in the present study of sulfonylations.

We obtained pseudo-first-order rate plots in the aluminum chloride catalyzed sulfonylation of benzene and toluene with methanesulfonyl chloride, in nitromethane as solvent, assuming $AlCl_3$ stays constant

(10) G. A. Olah, J. Nishimura, J. DeMember, P. Schilling, and J. A. Olah, in preparation.

(11) G. A. Olah, M. Tashiro, and S. Kobayashi, *ibid.*, **92**, 6369 (1970).

(12) G. A. Olah and S. Kobayashi, *ibid.*, **93**, 6964 (1971).

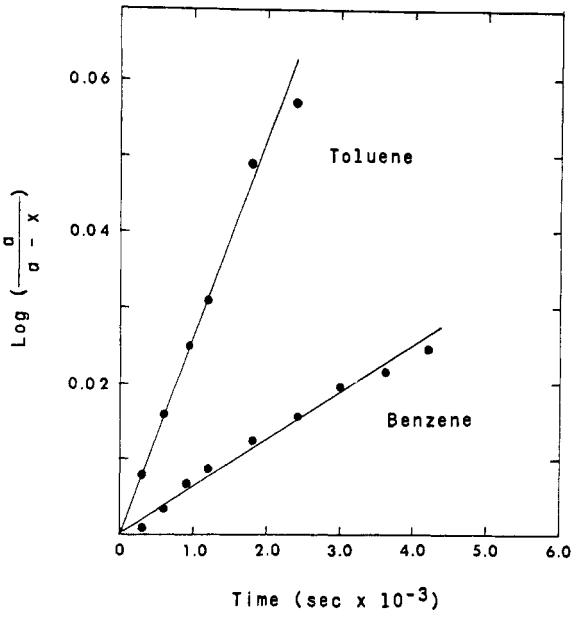


Figure 1. Pseudo-first-order rate plots of methanesulfonylation of toluene and benzene.

and using the aromatics in large excess

$$\frac{\text{d[product]}}{dt} = k'[\text{methanesulfonyl chloride}]$$

where $k' = k[AlCl_3]$ [aromatic].

In plotting log $(a/a - x)$ *vs.* time (Figure 1) in typical rate studies a stands for the initial concentration of methanesulfonyl chloride and x is the concentration of the product.

The systems are homogeneous and there is no isomerization caused by $AlCl_3$. Pseudo-first-order rate constants were obtained from the slope of the kinetic curves which are summarized in Table II.

Table II. Rate Constants of Methanesulfonylation of Benzene and Toluene

Aromatic	Reagent	Catalyst	Reaction temp, °C	Rate constant sec^{-1}
Benzene	CH_3SO_2Cl	$AlCl_3$–CH_3NO_2	80	1.5×10^{-5}
Toluene	CH_3SO_2Cl	$AlCl_3$–CH_3NO_2	80	5.0×10^{-5}
			k_T/k_B = 3.3 (3.8)[a]	

[a] From competitive experiments of identical reaction conditions.

These results show that the methanesulfonylation reaction is not encounter rate or diffusion controlled, but a rather slow reaction. The rate ratio k_T/k_B = 3.3 calculated from individual kinetic data corresponds well with the ratio obtained by the competitive reaction under identical conditions in nitromethane solution at 80° (k_T/k_B = 3.8).

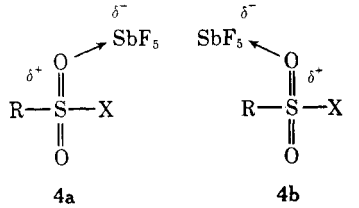
It should be mentioned that Jensen and Brown[6] in their studies of sulfonylation also provided noncompetitive rate data of benzenesulfonylation of toluene and benzene, which shows good agreement with competitive rate studies.

The Nature of Sulfonylating Agents. Concerning the nature of the sulfonylating agents involved, our previous investigations involved an nmr study of sulfonyl halide–antimony pentafluoride complexes under stable ion conditions[13] and indicated only the formation of oxygen-coordinated donor–acceptor complexes, but not sulfonylium ions (sulfonyl cations).

In order to attempt obtaining relationship between the nature of the sulfonylating agents and the inter- and intramolecular selectivity data of the Friedel–Crafts sulfonylation reactions summarized in Table I, we extended our studies to the sulfonyl halide systems which were employed in this work as sulfonylating agents, but not yet studied under ionizing conditions with SbF_5 generally allowing to observe stable ions. It was of particular interest to see whether in case of strongly electron donating substituents (such as CH_3O– and R_2N–) stable sulfonylium ions could be observed.

The samples were prepared by careful addition of the sulfonyl halides dissolved in SO_2 or SO_2ClF into well-stirred superacid solutions at −78°. The pmr data are summarized in Table III. The following sulfonyl fluorides and chlorides were studied in SbF_5–SO_2, SbF_5–SO_2ClF, FSO_3H–SbF_5–SO_2, and FSO_3H–SbF_5–SO_2ClF solutions: methoxy- and ethoxysulfonyl fluoride (methyl and ethyl fluorosulfates), methoxysulfonyl chloride (methyl chlorosulfate), *N,N*-dimethylsulfonyl fluoride and chloride, *N,N*-diethylsulfonyl chloride, and *p*-methoxybenzenesulfonyl fluoride and chloride.

Methoxysulfonyl fluoride (methyl fluorosulfate) in SbF_5–SO_2 at −60° showed two sharp singlets at δ 4.87 and 4.27, respectively, deshielded significantly from the CH_3 shift of the parent compound, indicating two isomeric forms of the oxygen coordinated complex, *i.e.*, **4a** and **4b** (where R = CH_3O–, X = F), as suggested in our previous work for a series of alkylsulfonyl halide–antimony pentafluoride complexes.[13] Raising the temperature to −20° resulted in a broad singlet at δ 4.40 along with a new sharp singlet at δ 5.50. This indicates that two isomeric forms of the donor–acceptor complex **4a** and **4b** (where R = OCH_3, X = F) can be observed at −60°, but the equilibrium between **4a** and **4b** becomes faster at −20° resulting in a broad signal at δ 4.40. The new peak at δ 5.50 is apparently due to the formation of the $CH_3F \rightarrow SbF_5$ complex[14] involving cleavage of the methyl–oxygen bond or ionization to the methoxysulfonyl cation followed by loss of SO_3. In SO_2ClF solution CH_3OSO_2F–SbF_5 shows a sharp singlet at δ 4.98, deshielded about 0.71 ppm from that of the precursor, indicating formation of the donor–acceptor complex. The spectrum shows no significant change from −60 to +20°. After



X = F or Cl

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(14) (a) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **92**, 2112 (1970); (b) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, **94**, 156 (1972).

Table III. Pmr Spectral Data[a] of the Parent, Complexed, and Protonated Sulfonyl Halides and Stable Sulfonium Ion

Precursor	Solvent[b]	Temp. °C	H_1	H_2	Aromatic
$CH_3^1OSO_2F$	A	−30	4.05		
	B	−30	4.27		
	C	−60	4.87		
			4.27		
	D	−60	4.98		
	E	−60	4.87		
			4.27		
	E	−20	5.50		
			4.40, br		
	F	−60	4.95		
			4.65		
	F	−20	4.80, br		
$CH_3^1OSO_2Cl$	A	−30	4.02		
	C	−60	4.66		
			4.20		
	C	−20	4.60, br		
$CH_3^1CH_2^2OSO_2F$	A	−30	4.60 (q, 7.0)	1.40 (t, 7.0)	
	B	−30	4.83 (q, 7.0)	1.58 (t, 7.0)	
	E	−60	4.80 (q, 7.2)	1.53 (t, 7.2)	
			5.41 (q, 7.2)	1.75 (t, 7.2)	
			6.20 (q, 7.3)	1.90 (t, 7.3)	
	F	−60	5.55 (q, 7.0)	1.95 (t, 7.0)	
$(CH_3^1)_2NSO_2F$	A	−30	2.80 (d, 2.2)		
	B	−30	3.10 (d, 2.2)		
	C	−60	3.75 (d, 5.2)		
			3.32 (d, 3.6)		
	D	−60	3.85 (d, 5.0)		
			3.53 (d, 3.4)		
$(CH_3^1)_2NSO_2Cl$	A	−30	2.72		
	C	−60	3.75 (d, 5.2)		
			3.32 (d, 3.6)		
$(CH_3^2CH_2^1)_2NSO_2Cl$	A	−30	3.54 (q, 8.0)	1.17 (t, 8.0)	
	C	−60	4.02 (q, 8.0)	1.47 (t, 8.0)	
p-CH_3^1O—Ph—SO_2F	A	−30	4.03		7.30[c] 8.15[c]
p-CH_3^1O—Ph—SO_2Cl	D	−60	5.12		8.30[d] 8.80[d]

[a] Chemical shifts are in parts per million from external TMS. Coupling constants in hertz are given in parentheses following the multiplicities: d = doublet; t = triplet; q = quartet. [b] A = SO_2; B = SO_2ClF; C = SbF_5–SO_2; D = SbF_5–SO_2ClF; E = FSO_3H–SbF_5–SO_2; F = FSO_3H–SbF_5–SO_2ClF. [c] AB quartet. $J_{AB} \approx 9$ Hz. [d] AB quartet. $J_{AB} \approx 11$ Hz.

standing for 1 day, two singlet absorptions were observed at 4.98 and 4.63, respectively. Using 1:1 magic acid[R] (FSO_3H–SbF_5) in both SO_2 and SO_2ClF solvents showed the same behavior as found in SbF_5–SO_2 and SbF_5–SO_2ClF systems.

Methoxysulfonyl chloride (methyl chlorosulfate) in SbF_5–SO_2 also showed at −60° two sharp singlets at δ 4.66 and 4.20 indicating two isomers (**4a** and **4b** where the halogen is chlorine). The chemical shift difference in SbF_5–SO_2 solution at −60° between CH_3OSO_2F (δ 4.87 and 4.27) and CH_3OSO_2Cl (δ 4.66 and 4.20, respectively) clearly indicates that the chlorine atom of CH_3OSO_2Cl is still attached to the sulfur atom. In other words, no Cl–F exchange reaction of CH_3OSO_2Cl takes place at −60 to −20° in the medium. Furthermore, this is proven by ^{19}F nmr, indicating no fluorine signal in the $-SO_2F$ region.

Ethoxysulfonyl Fluoride (Ethyl Fluorosulfate). Two isomeric forms of the donor–acceptor complex of ethoxysulfonyl fluoride–SbF_5 were also observed in SO_2 solution at −70°. Even at this temperature the complex undergoes partial ethyl–oxygen cleavage to give the $CH_3CH_2F \rightarrow SbF_5$ complex,[14b] with absorptions of CH_3 (triplet) at δ 1.90 and CH_2 (quartet) at δ 6.20. The ethoxysulfonyl fluoride–SbF_5 complex is thermally less stable than its methyl homolog. The observed structure of the complexes and this ease of cleavage are in accordance with their chemical reactions; they are alkylating and not alkoxysulfonylating agents in their Friedel–Crafts reactions with benzene and alkylbenzenes (more reactive aromatics, such as phenols, are, however, alkoxysulfonylated).

Both ***N,N*-dimethylsulfamoyl fluoride** and **chloride** showed identical pmr and ^{19}F spectra in SbF_5–SO_2 at −60°. In the pmr spectra two doublets were observed at δ 3.75 (J_{HF} = 5.2 Hz) and δ 3.32 (J_{HF} = 3.6 Hz) indicating the formation of the donor–acceptor complexes of **4a** and **4b** (where R = $(CH_3)_2N$, X = F) in which the Cl atom of $(CH_3)_2NSO_2Cl$ is replaced by the F atom. Two multiplets were observed in the ^{19}F spectra at ϕ = −45.4 and −40.0 which correspond to those of the two isomers, **4a** and **4b**. The S–F bond is not cleaved in the complexes; thus no sulfonyl cation is formed.

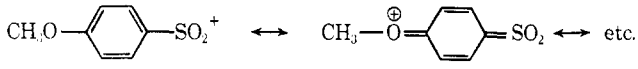
***N,N*-Diethylsulfamoyl chloride** in SbF_5–SO_2 at −60° showed deshielded ethyl groups whose methylene and methyl protons appeared as a quartet at δ 4.02 and a triplet at δ 1.47, respectively.

Our preceding studies[13] of arylsulfonyl halide–antimony pentafluoride systems showed only the formation of donor–acceptor complexes and gave no indication of arylsulfonylium on formation. We have, however, now extended these studies to arylsulfonyl halides containing strongly electron donating para substituents, such as methoxy.

Both ***p*-methoxybenzenesulfonyl fluoride** and **chloride** in SbF_5–SO_2Cl at −60° gave identical pmr spectra showing a sharp singlet of the methoxy protons at δ

5.12 (1.09 ppm deshielded from that of the precursor) and the aromatic AB quartet at δ 8.30 and 8.80 (the corresponding signals of the precursor are at δ 7.30 and 8.15, respectively).

Whereas the ^{19}F spectrum of *p*-methoxybenzenesulfonyl fluoride in SO_2ClF showed a sharp singlet at ϕ = 66.4, the absence of a fluorine resonance of the *p*-$CH_3OC_6H_4SO_2F$–SbF_5–SO_2ClF system in the $-SO_2F$ region could imply that the fluoride atom was ionized and is not bonded anymore to the sulfur atom. Alternatively a fast-exchanging system should give the same result, but in arylsulfonyl fluoride–antimony pentafluoride donor–acceptor complexes no such exchange was previously observed. Data of both the pmr and ^{19}F nmr taken together strongly indicate the formation of *p*-methoxybenzenesulfonylium ion **1**-CH_3O which



1-CH_3O-a **1**-CH_3O-b

is highly stabilized by the contribution of the resonance from **1**-CH_3O-b. The *p*-methoxyphenylsulfonylium ion **1**-CH_3O can be compared with the *p*-dimethylaminophenylsulfonylium ion **1**-$(CH_3)_2N$-(*p*-$(CH_3)_2NC_6H_4SO_2^+$), which was obtained by Lindner and Weber[15] by the metathetic reaction of the sulfonyl chloride with silver salts.

Reactivity of Sulfonylating Agents. Based on the data obtained in the present work, as well as preceding studies, it seems possible to classify sulfonyl halides into three groups with respect to the reactivity of the sulfonylating agents in SbF_5–SO_2 or SbF_5–SO_2ClF solutions: (A) no halogen exchange with SbF_5 at low temperatures (CH_3SO_2X, $C_2H_5SO_2X$, CH_3OSO_2X, $C_2H_5OSO_2X$, $C_6H_5SO_2X$, $CH_3C_6H_4SO_2X$, etc.); (B) halogen exchange with SbF_5 at low temperatures ($(CH_3)_2NSO_2X$, $(C_2H_5)_2NSO_2X$); and (C) sulfonylium ion formation (*p*-$CH_3OC_6H_4SO_2^+$, *p*-$(CH_3)_2NC_6H_4SO_2^+$).

Among the A group, methyl and ethyl fluorosulfate and chlorosulfate undergo preferentially alkyl–oxygen cleavage reactions. These findings may explain the failure of $AlCl_3$ catalyzed Friedel–Crafts alkoxysulfonylation of benzene and toluene, the reactions resulting only in alkylation of aromatics. More reactive aromatics, such as phenols, are, however, preferentially alkoxysylfonylated (results to be published separately).

In terms of the importance of the nature of the sulfonylating agents to affect the substrate and positional selectivity, the preceding classification well explains the results of Friedel–Crafts sulfonylation as shown in Table I: (A) strong electrophiles, giving low k_T/k_B rate ratios, yet high ortho/para ratios; (B) weaker electrophiles, giving higher k_T/k_B ratios and lower ortho/para ratios; and (C) weak electrophiles, giving high k_T/k_B ratios and low ortho/para ratios.

Conclusions

A series of low substrate, but high positional selectivity, electrophilic aromatic substitutions was observed in our preceding work[3] and present study, as well as in the studies of Nakane[16] and other investigators.[3] The question has been raised that in fast exothermic reactions with strongly electrophilic reagents, low substrate selectivities could be due to diffusion or encounter control of the reactions.[17] As, however, we have succeeded in measuring *noncompetitive rates* of a number of low substrate, but high positional selectivity, substitutions of toluene and benzene, including present studies, these data clearly indicate that we are, indeed, dealing not with experimental artifacts, but an important new aspect of aromatic substitution.

The present work affirms our conviction that in electrophilic aromatic substitutions the nature of the electrophile can substantially influence both substrate and positional selectivity. Introduction of suitable groups (R = alkyl, amino, or substituted phenyl) into the sulfonyl chloride (fluoride) can change the nature of attacking species (*i.e.*, incipient sulfonylium ions) through affecting the electron deficiency of the sulfonylating agent in a systematic way, and thus cause a regular shift of the position of the transition state from an "early" to a "late" one. Positional and substrate selectivities reflect these changes. Our mechanistic conclusions, including the question of substrate selectivity and directing effects (positional selectivity), were discussed in our preceding publication[1] and are in accord with present data.

Experimental Section

Materials. Benzene, toluene, and 1,1,2-trichlorotrifluoroethane, Freon-113, were commercially available and distilled before use. Methane-, ethane-, *p*-nitrobenzene-, *p*-fluorobenzene-, *p*-chlorobenzene-, benzene-, *p*-methylbenzene-, and *p*-methoxybenzenesulfonyl and *N*,*N*-dimethylsulfamoyl chlorides, methanesulfonic anhydride, benzenesulfonyl fluoride, and methyl andethyl fluorosulfate were commercial products of highest purity. *N*,*N*-Diethylsulfamoyl chloride was obtained by the reaction of diethylamine hydrochloride with sulfuryl chloride, bp 65–68° (4 mm). *N*,*N*-Dimethyl- and *N*,*N*-diethylsulfamoyl fluorides and *p*-methoxybenzenesulfonyl fluoride were prepared by heating the corresponding chlorides with anhydrous KHF_2 in acetonitrile solution. Methyl chlorosulfate was prepared by the reaction of sulfuryl chloride with methanol, bp 50° (48 mm).

General Procedure for Competitive Sulfonylation. (a) With aluminum chloride catalyst in excess aromatics as solvent. To a mixture of benzene (0.1 mol), toluene (0.1 mol), and $AlCl_3$ (0.022 mol), 0.02 mol of sulfonyl chloride was added in a constant temperature bath (25 or 60°), dropwise and with stirring, over a period of 5 min. The reaction was allowed to proceed further for another 20 min at 25° (or 2 hr at 60°). It was then poured into ice water, extracted with ether, dried over Na_2SO_4, concentrated, and analyzed by gas–liquid chromatography or by pmr spectroscopy. (b) With antimony pentafluoride catalyst in Freon-113 solvent. Into a mixture of 0.1 mol of benzene, 0.1 mol of toluene, and 0.02 mol of sulfonyl fluoride diluted with 30 ml of Freon-113, 0.022 mol of SbF_5 dissolved in 20 ml of Freon-113 was added slowly with vigorous stirring at 25° over a period of 10 min. The reaction was allowed to proceed for another 1 hr, then quenched with ice water, extracted with ether, dried over Na_2SO_4 and analyzed.

Procedure for Noncompetitive Kinetic Studies. The mixture of 0.2 mol of benzene (or toluene) and 0.170 g of methyl *p*-tolyl sulfone (or 0.156 g of methyl phenyl sulfone in the case of toluene), added as internal standard, was placed into a 100-ml round-bottom flask equipped with a magnetic stirring bar and heated in a constant-temperature bath to 80°. $AlCl_3$ (10 ml of 1 *M*) in nitromethane solution was added to the mixture, and after the system reached the constant temperature, 1.15 g of methanesulfonyl chloride was added at once with vigorous stirring. Samples were withdrawn

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Table IV. Data of Methanesulfonylation of Benzene and Toluene

Run no.	1 Time, sec	1 Log A^a	2 Time, sec	2 Log A	3 Time, sec	3 Log A
		(a) Methanesulfonylation of Benzene				
1	300	0.0026			300	0.0008
2	600	0.0032	600	0.0054	600	0.0032
3	900	0.0072			900	0.0068
4	1200	0.0080	1200	0.0097	1200	0.0087
5					1500	0.0096
6	1800	0.0122	1800	0.0142	1800	0.0124
7	2400	0.0154			2400	0.0158
8	3000	0.0196			3000	0.0199
9	3720	0.0255	3600	0.0247	3600	0.0216
10	5400	0.0312	5400	0.0344	4200	0.0247
11	11400	0.0516	7200	0.0441		
k' (sec^{-1})	1.5×10^{-5}		1.6×10^{-5}		1.5×10^{-5}	
		(b) Methanesulfonylation of Toluene				
1			300	0.0081	300	0.0058
2	600	0.0154	600	0.0162	600	0.0114
3			960	0.0254	900	0.0182
4	1200	0.0305	1200	0.0313	1200	0.0234
5	1800	0.0467	1800	0.0491	1800	0.0295
6					2100	0.0357
7			2400	0.0579	2400	0.0397
8	3600	0.0738				
9	5400	0.1092				
k' (sec^{-1})	4.7×10^{-5}		6.0×10^{-5}		4.4×10^{-5}	

(c) Competitive Rate Determination Under Identical Conditions

	Run 1	Run 2	Run 3
k_T/k_B	4.00	3.60	3.67

[a] $A = a/(a - x)$.

periodically, quenched with ice water, dried over $MgSO_4$, and analyzed by gas–liquid chromatography. Pseudo-first-order rates were obtained.[18]

Analytical Procedure. k_T/k_B rate ratios and isomer distributions were determined either by glc or by pmr spectroscopic determination. The k_T/k_B ratios were obtained by integration of the peak area ratios of the aromatic protons and methyl protons of tolyl group. The *o*-methyl protons (relative to the sulfonyl group) appear at lower field than do the *m*- and *p*-methyl protons. Thus, integration of the methyl signals allows us to obtain isomer distribution data although the meta and para isomers do not separate well from each other (as does the ortho). However, in some cases, the meta isomer content was possible to be calculated from the aromatic proton signal patterns. Data obtained by pmr spectroscopic determination were in good agreement with those obtained by the glc method (see no. 3 and 4, Table IV).

The gas–liquid chromatographic analysis of the products of sulfonylation of benzene and toluene was carried out by using a Perkin-Elmer Model 226 gas chromatograph equipped with a hydrogen flame ionization detector system and open tabular capillary columns.

For glc analysis of methyl phenyl and methyl tolyl sulfones, a stainless-steel capillary column coated with butanediol succinate (150-ft length, 0.01-in. diameter) was used at a column temperature of 160° and the carrier gas (helium) pressure of 30 psi. The retention time was as follows: methyl phenyl sulfone 12.4 min; methyl *o*-tolyl sulfone 14.2 min; methyl *m*-tolyl sulfone 16.9 min; and methyl *p*-tolyl sulfone 18.4 min. The same column was used for the analysis of ethyl phenyl and ethyl tolyl sulfones at a column temperature of 180° and the carrier gas pressure of 40 psi. The retention time was as follows: ethyl phenyl sulfone 18.6 min; ethyl *o*-tolyl sulfone 19.6 min: ethyl *m*-tolyl sulfone 23.0 min; and ethyl *p*-tolyl sulfone 24.8 min. Relative response data were determined as reported previously.

(18) Rate constants were determined from the initial 10% conversion part of the kinetic runs, as under these conditions the systems are entirely free of any possible side reactions.

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