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Kinetics of the Friedel–Crafts Sulfonylation of Aromatics with Aluminum Chloride as Catalyst and Nitrobenzene as Solvent[1,2]

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A kinetic study was made of the aluminum chloride-catalyzed reactions of *p*-toluenesulfonyl chloride in nitrobenzene solution with toluene at 25° and with chlorobenzene at 60°. A similar study was made of the corresponding reactions of benzenesulfonyl chloride with benzene, representative monoalkyl- and methylbenzenes. For the reaction with toluene, $\Delta H^{\ddagger} = 19.0$ kcal./mole and $\Delta S^{\ddagger} = -10.6$ e.u. As in the case of the corresponding benzoylation reaction, the rate constants vary with the initial concentration of the aluminum chloride. For a given concentration of aluminum chloride, third-order kinetics are observed for aromatic derivatives of relatively low activity: rate = $k_3[\mathrm{AlCl_3}][\mathrm{ArH}][\mathrm{ArSO_2Cl}]$. However, in the case of the more reactive aromatics, the reaction rate becomes independent of the nature and concentration of the aromatic component and second-order kinetics are followed: rate = $k_2[\mathrm{AlCl_3}][\mathrm{ArSO_2Cl}]$. The reaction is believed to involve ionization of the arylsulfonyl chloride, followed by reaction with the aromatic: $\mathrm{ArSO_2Cl + AlCl_3 \rightarrow ArSO_2{}^+AlCl_4{}^-}$; $\mathrm{ArH + ArSO_2{}^+AlCl_4{}^- \rightarrow ArSO_2Ar{\cdot}AlCl_3 + HCl}$. In the case of the less reactive aromatics, the second stage is rate-controlling. On the other hand, with the more reactive aromatics the ionization stage becomes rate-determining.

The kinetics of the Friedel–Crafts reaction of arylsulfonyl chloride with aromatic derivatives have been studied in considerable detail by Olivier[5] using either the aromatic component or the benzenesulfonyl chloride as solvent. From the published data, the sulfonylation reaction appears to be one of high "activity" and low "selectivity,"[6] in marked contrast to the closely related benzoylation reaction.[7] Consequently, it appeared desirable to compare directive effects realized in the sulfonylation reaction with those established for the benzoylation reaction as a further test of the Selectivity Relationship.[6]

Unfortunately, under the conditions utilized by Olivier[5] the rate constants vary markedly with the initial aluminum chloride concentration. Moreover, even in individual experiments marked drifts in the rate constants were observed. In the hope of avoiding these difficulties, we undertook a kinetic study of the sulfonylation reaction using nitrobenzene as the solvent and aluminum chloride as catalyst.

The reactions were followed by determining the concentration of the residual sulfonyl chloride. Both *p*-toluenesulfonyl chloride and benzenesulfonyl chloride were used as sulfonylation agents and rates were measured for one or the other of these agents with chlorobenzene, benzene and toluene, ethyl-, isopropyl-, *t*-butylbenzene as well as a number of polymethylbenzenes.

Results

The Reaction of *p*-Toluenesulfonyl Chloride with Toluene.—The reaction of *p*-toluenesulfonyl chloride with toluene in nitrobenzene solution proceeds readily at 25° to form the ditolylsulfone (1)

$$p\text{-}\mathrm{CH_3C_6H_4SO_2Cl + C_6H_5CH_3 + AlCl_3 \longrightarrow} \\ p\text{-}\mathrm{CH_3C_6H_4SO_2C_6H_4CH_3{\cdot}AlCl_3 + HCl} \quad (1)$$

One mole of sulfone is formed per mole of aluminum chloride present in solution.[5]

In individual experiments, third-order rate constants are observed, corresponding to the kinetic expression 2

$$\text{rate} = k_3[\mathrm{AlCl_3}][\mathrm{CH_3C_6H_5}][p\text{-}\mathrm{CH_2C_6H_4SO_2Cl}] \quad (2)$$

The reaction is first order in *p*-toluenesulfonyl chloride, and the value of k_3 is independent of the initial concentration of the sulfonyl chloride (Table I).

TABLE I

RATE CONSTANTS FOR THE ALUMINUM CHLORIDE-CATALYZED REACTION OF *p*-TOLUENESULFONYL CHLORIDE WITH TOLUENE IN NITROBENZENE SOLUTION AT 25.0°

Reactants, *M* [Toluene]	[*p*-Toluenesulfonyl chloride]	[AlCl$_3$]	Rate constant, k_3, l.^{2} mole^{-2} min.$^{-1}$
0.317	0.0760	0.317	0.0677
.317	.157	.317	.0735
.317	.317	.317	.0798
.317	.317	.317	.0790
.317	.473	.317	.0765
.317	.317	.0793	.13
.317	.317	.171	.0955
.317	.317	.172	.0940
.317	.317	.317	.0794
.317	.317	.525	.0595
.103	.317	.317	.105
.317	.317	.317	.0940
.520	.317	.317	.0598
1.215	.317	.317	.0291
0.317[a]	.317	.317	.0745
.317[b]	.317	.317	.0785

[a] Cyclohexane added, 0.189 *M*. [b] Hexamethylbenzene added, 0.0965 *M*.

For any given initial concentration of aluminum chloride, satisfactory third-order rate constants are obtained. However, if the initial concentrations of the aluminum chloride are increased, the values of the calculated rate constants decrease (Table I). A similar effect has been observed in the related benzoylation reaction.[7]

The latter reaction was cleanly first order in toluene.[7] However, in the present reaction, increases in the initial toluene concentration result in decreases in the calculated values of the third-order rate constants (Table I). Moreover, at

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[1] The Catalytic Halides. XXIII. Directive Effects in Aromatic Substitution. XXIII.

[2] Based upon a thesis submitted by F. R. Jensen in partial fulfillment of the requirements for the Ph.D. degree.

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[4] Research assistant on a project supported by the Atomic Energy Commission, 1953–1954. National Science Foundation Predoctoral Fellow, 1954–1955.

[5] S. J. C. Olivier, *Rec. trav. chim.*, **33**, 91, 244 (1914); **35**, 109, 166 (1915).

[6] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

[7] H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719, 724 (1957).

high toluene concentrations, third-order plots of the kinetic data tend to curve upward.

This change could conceivably be the result of a solvent effect, in view of the high concentrations utilized and the large difference in the polar characteristics of toluene and nitrobenzene. However, addition of 0.189 *M* cyclohexane decreased the rate constant by only 6%, whereas a corresponding increase in the toluene concentration of 0.203 *M* (from 0.317 to 0.520 *M*), decreases the rate constant by 25%. Consequently, although there may be a small solvent effect, it appears that this cannot be responsible for the large decreases in the calculated values of k_3 observed with increasing toluene concentration.

Aromatic compounds form ternary complexes with aluminum chloride and nitrobenzene.[8] To test the possibility that the effect of varying toluene concentration might be due to this cause, the reaction was carried out in the presence of hexamethylbenzene (0.0965 *M*). However, no change in the third-order rate constant was observed (Table I).

The Reaction of *p*-Toluenesulfonyl Chloride with Chlorobenzene.—It appeared that a study of the kinetics of the sulfonylation reaction for a less reactive aromatic derivative might be of diagnostic value. Accordingly, a kinetic study was undertaken with chlorobenzene. The reaction proceeded at a convenient rate at 60°, and the study was therefore made at this temperature.

As in the previous case the reaction is first order in *p*-toluenesulfonyl chloride and of ill-defined order with respect to aluminum chloride (Table II). In this case, the decrease in the value of k_3 with increasing aluminum chloride concentration is so large, that the reaction order appears to be nearly zero in the metal halide, *i.e.*, $k_3 \times [AlCl_3]_0$ is nearly constant.

TABLE II

RATE CONSTANTS FOR THE ALUMINUM CHLORIDE-CATALYZED REACTION OF *p*-TOLUENESULFONYL CHLORIDE WITH CHLOROBENZENE IN NITROBENZENE SOLUTION AT 60°

	Reactants, *M*		
[Chlorobenzene]	[*p*-Toluenesulfonyl chloride]	[$AlCl_3$]	Rate constant, k_3, $l.^2$ $mole^{-2}$ $min.^{-1}$
0.305	0.118	0.305	0.0123
.305	.305	.305	.0121
.305	.821	.305	.0108
.305	.305	.119	.0269
.305	.305	.305	.0121
.305	.305	.805	.00565
.117	.305	.305	.0134
.305	.305	.305	.0121
.831	.305	.305	.0108

In contrast to the toluene results, the calculated third-order rate constant appears to be cleanly first order in the aromatic component (Table II). (The small decrease which is observed is of the magnitude to be expected for a simple solvent effect.)

The Reaction of Benzenesulfonyl Chloride with Toluene.—It appeared desirable to ascertain whether the kinetics would be affected by a change in the sulfonyl chloride used. Accordingly the reaction of benzenesulfonyl chloride with toluene was examined.

The reaction at 25° proceeds at roughly one-fourth of the rate exhibited by *p*-toluenesulfonyl chloride. Otherwise the characteristics of the reaction exhibit no significant difference. From reaction rates at several temperatures, the enthalpy of activation is calculated to be 19.0 kcal./mole and entropy of activation is −10.6 e.u. (Table III).

TABLE III

RATE CONSTANTS AND DERIVED DATA FOR THE ALUMINUM CHLORIDE-CATALYZED BENZENESULFONYLATION OF TOLUENE IN NITROBENZENE SOLUTION

Temp., °C.	25.0	39.9	49.9
Rate constant k_3, $l.^2$ $mole^{-2}$ $min.^{-1}$	0.0213	0.106	0.429
Energy of activation, E_{act}	19.6 kcal./mole		
log *A*	10.9		
Enthalpy of activation, $\Delta H^{\ddagger}$	19.0 kcal./mole		
Entropy of activation, $\Delta S^{\ddagger}$	−10.6 e.u.		

The Reactions of Benzenesulfonyl Chloride with Benzene, the Monoalkylbenzenes and the Polymethylbenzenes.—In spite of the complications in the kinetics, it appeared that the reaction could yield interesting data on the effect of the structure and position of alkyl substituents on the reaction rate. Accordingly, a study was made of the rate of reaction of benzenesulfonyl chloride with benzene and several representative monoalkylbenzenes under identical conditions (Table IV).

TABLE IV

RATE CONSTANTS AND RELATIVE RATES FOR THE ALUMINUM CHLORIDE-CATALYZED BENZENESULFONYLATION OF REPRESENTATIVE MONOALKYLBENZENES IN NITROBENZENE SOLUTION AT 25°[a]

Compound	Rate constant, k_3, $l.^2$ $mole^{-2}$ $min.^{-1}$	Relative rate
Benzene	0.00221, 0.00247, 0.00242	1.00
Toluene	.0205, .0218	9.0
Ethylbenzene	.0160, .0162	6.8
Isopropylbenzene	.0111, .0114	4.8
t-Butylbenzene	.0081, .0084	3.5

[a] The concentrations of benzenesulfonyl chloride, alkylbenzene and aluminum chloride ($AlCl_3$) all equal, 0.222 *M*.

When an attempt was made to extend the reaction to the higher methylbenzenes, it was observed that the calculated third-order rate constants increase as the reactions proceed. Accordingly the initial rates are given in Table V.

It was observed that the rate increased only slightly over that exhibited by toluene, with the most reactive derivatives reacting at essentially the same rate, roughly three times that of toluene. This observation, that in the case of the more reactive aromatics the reaction rate was essentially independent of their structure, suggested that the rate was probably independent of their concentration also. This possibility was examined for mesitylene, and the rate of disappearance of the benzenesulfonyl chloride was indeed independent

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(8) H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 6285 (1953).

TABLE V

RATE CONSTANTS AND RELATIVE RATES FOR THE ALUMINUM CHLORIDE-CATALYZED BENZENESULFONYLATION OF THE METHYLBENZENES IN NITROBENZENE SOLUTION AT 25°[a]

Compound	Rate constant, k_3,[b] l.^{2} mole^{-2} min.$^{-1}$	Relative rate	Rate constant, k_2,[c] l. mole^{-1} min.$^{-1}$
Benzene	0.00235	0.11	
Toluene	.0212	1.00	
1,2,4,5-Tetramethylbenzene	.0178, 0.0173	0.84	
o-Xylene	.041, .043	2.0	
p-Xylene	.045, .042	2.1	
m-Xylene	.047, .052	2.4	
Pentamethylbenzene	.058, .055	2.7	
1,2,3-Trimethylbenzene	.064	3.0	1.42
1,2,4-Trimethylbenzene	.071	3.4	1.58
1,3,5-Trimethylbenzene	.069, 0.072	3.3	1.56

[a] The concentrations of benzenesulfonyl chloride, alkylbenzene and aluminum chloride ($AlCl_3$) all equal, 0.222 *M*. [b] Initial rate constants. [c] Obtained by multiplying k_3 by the initial concentration of the hydrocarbon, 0.222 *M*.

TABLE VI

DATA SHOWING CHANGE IN CONCENTRATION OF BENZENESULFONYL CHLORIDE WITH TIME IN REACTION MIXTURES OF VARYING INITIAL CONCENTRATIONS OF MESITYLENE[a]

Time, min.	Initial concentration of mesitylene 0.22 *M* [$C_6H_5SO_2Cl$]	0.40 *M* [$C_6H_5SO_2Cl$]	0.70 *M* [$C_6H_5SO_2Cl$]
64	0.185	0.188	0.183
246	.135	.132	.127
758	.076	.072	.067
1360	.053	.049	.048

[a] The concentrations of benzenesulfonyl chloride and aluminum chloride equal, 0.222 *M*.

of the initial concentration of the hydrocarbon (Table VI).

From the above data, good second-order rate constants may be obtained, corresponding to the rate expression

$$\text{rate} = k_2[AlCl_3][ArSO_2Cl] \qquad (3)$$

Consequently, it appears that the reaction order changes from third for the less reactive aromatics to second for the more reactive derivatives, with mixed orders probable for those of intermediate reactivity. Second-order rate constants for the more reactive aromatics are listed in Table V.

Discussion

The order of the reaction with respect to aluminum chloride is ill-defined. The behavior is quite similar to that previously observed for the benzoylation reaction in nitrobenzene solution[7] and for the aluminum chloride-catalyzed reaction of cyclohexyl chloride with benzene.[9]

Lebedev noted that the apparent order with respect to aluminum chloride varies with the composition of the solvent, from approximately 0.5 in pure nitrobenzene to approximately 2 in benzene.[10] He accounted for the 0.5 order in terms of a complex dissociation of aluminum chloride in nitrobenzene solution with one of the dissociation products being the active catalyst. Unfortunately, there are insufficient data now available on the nature of nitrobenzene solutions of aluminum chloride to permit a reasonably firm decision as to the ionic and molecular species present which may be responsible for the unusual order with respect to the catalyst.

In the case of the benzoylation reaction, it was concluded that the complex kinetics (with respect to aluminum chloride) were not the result of any peculiarity of the acylation reaction, but the result of peculiarities of the aluminum chloride–nitrobenzene solution.[7] We believe that the situation is similar in the arylsulfonylation reaction examined in the present study and shall proceed on this basis. In the absence of contrary evidence as to the precise nature of the molecular or ionic species derived from aluminum chloride which may be responsible for its catalytic activity, we shall discuss the reaction mechanism in terms of the parent molecule, $AlCl_3$, associated with the various bases present in the reaction mixtures.

Nitrobenzene forms a 1:1 addition compound, $C_6H_5NO_2 \cdot AlCl_3$, which exhibits the simple monomeric molecular weight in nitrobenzene solution.[11] Molecular weight studies of solutions of benzoyl chloride and aluminum chloride in nitrobenzene indicate that the aluminum chloride is preferentially associated with the nitrobenzene solvent.[12] Arylsulfonic acids are far stronger than the corresponding benzoic acids. Consequently, it appears safe to conclude that arylsulfonyl chloride must be less basic than the benzoyl chlorides, so that in solutions of arylsulfonyl chlorides and aluminum chloride in nitrobenzene the metal halide will be primarily associated with the nitrobenzene, in equilibrium with a minor amount of a derivative containing the aluminum chloride associated with the sulfonyl chloride.

In the benzoylation reaction the metal halide appears to function through conversion of the acyl halide into the acylonium ion.[13,14] In the absence of experimental data requiring an alternative interpretation, we shall assume that the metal halide performs a similar function in the sulfonylation reaction. On this basis we can write for the mechanism the reactions

$$RSO_2Cl + AlCl_3 \cdot O_2NC_6H_5 \underset{k'_{-1}}{\overset{k'_1}{\rightleftarrows}} RSO_2Cl \cdot AlCl_3 + O_2NC_6H_5 \qquad (4)$$

$$RSO_2Cl \cdot AlCl_3 \underset{k'_{-2}}{\overset{k'_2}{\rightleftarrows}} RSO_2{}^+AlCl_4{}^- \qquad (5)$$

$$ArH + RSO_2{}^+AlCl_4{}^- \xrightarrow{k'_3} ArSO_2R \cdot AlCl_3 + HCl \qquad (6)$$

This mechanism is consistent with all of our observations (with the exception of the change in rate constant with change in the initial aluminum chloride concentration discussed previously). Thus, in the case of the less reactive aromatics, the reaction of the ionized species with the aromatic (6) is rate-determining and the reaction exhibits third-order kinetics (2). On the other hand, with

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(9) N. N. Lebedev, *J. Gen. Chem.* (*U.S.S.R.*), **24**, 664 (1954).

(10) In the aluminum chloride-catalyzed benzylation of benzene and toluene in nitrobenzene solution the order with respect to the catalyst was close to one (ref. 8).

(11) R. E. Van Dyke and H. E. Crawford, THIS JOURNAL, **73**, 2018 (1951).

(12) Unpublished observations with Dr. Sang Up Choi.

(13) G. Baddeley and D. Voss, *J. Chem. Soc.*, 418 (1954).

(14) F. R. Jensen and H. C. Brown, THIS JOURNAL, **80**, 3039 (1958).

reactive aromatics, the ionization stage 5 becomes rate-determining and the reaction rate becomes independent of the specific structure and concentration of the aromatic. The reaction then follows second-order kinetics (3). In terms of this mechanism the second-order constants (k_2) listed in Table V are the product of the equilibrium constant for step 4 and the rate constant (k'_2) for the ionization of the arylsulfonyl chloride–aluminum chloride addition compound.

In presenting the above mechanism we have avoided consideration of some of the finer details, such as the structure of the arylsulfonyl chloride–aluminum chloride addition compound and the question whether the ionized species reacts in the form of ion-pairs, separated ions, or both. In view of the state of our knowledge of these molecular addition compounds and their nature in nitrobenzene solution, such a discussion is best deferred. The above mechanism is not the only possible interpretation of the available facts. However, it is consistent with all of the available data, as well as with the known facts for the closely related benzoylation reaction.

It should be pointed out that in the reaction of aromatics with nitric acid, in solvents such as nitromethane and acetic acid, Ingold and his coworkers had previously observed the reaction to change from first order for less reactive aromatic compounds to zero order for the more reactive derivatives.[15] Here also the interpretation was based on an ionization of the reagent, nitric acid, into a reactive intermediate, nitronium ion, with this ionization becoming the rate-determining stage in the case of the more reactive aromatic substrates.

The marked increase in the rates of benzenesulfonylation of toluene over benzene, $k_T/k_B = 9.0$, supports the view that the benzenesulfonylation reaction is far more "active" and presumably less "selective" than the related benzoylation reaction. Since the available evidence favors the conclusion that both reactions proceed through ionic intermediates, it would appear that the benzoylonium ion is considerably more stable than the corresponding benzenesulfonylonium ion. Presumably this is related to the greater stability of resonance structures with multiple bonds involving carbon as compared to sulfur.

Toluenesulfonyl chloride reacts with toluene at approximately 4 times the rate exhibited by benzenesulfonyl chloride. Two possible explanations for the difference in rate appear possible. The *p*-methyl substituent could stabilize the arylsulfonylonium ion and favor the ionization stage 5. Alternatively, the inductive effect of the methyl group might result in a more favorable equilibrium in the pre-equilibrium stage 4. Unfortunately, it is not possible at this time to assess the relative importance of these two factors.

The decrease in rate in the series, toluene, ethylbenzene, isopropylbenzene and *t*-butylbenzene, is similar to that observed in other electrophilic substitution reactions.[16] In the absence of isomer distribution data, it is not possible to calculate the partial rate factors. However, the decrease is so large it appears probable that the *para* partial rate factor, p_f, must decrease with increasing branching of the alkyl group. Such a decrease has been observed for all electrophilic substitution reactions with one exception, nitration.[17] The decrease is presumably due to the smaller hyperconjugative contributions of α-carbon-to-carbon as compared to α-carbon-to-hydrogen bonds[18,19] in the σ-complex.

The moderate increase in apparent rate of substitution of the higher methylbenzenes is not a measure of their relative reactivities, since the substitution stage is no longer rate-determining. The determination of the relative reactivities of these derivatives under present conditions would require competition experiments rather than direct rate measurements.

Experimental Part

Materials.—The purification of aluminum chloride, nitrobenzene and the various aromatic derivatives has been described in previous publications in this series. Benzenesulfonyl chloride and toluenesulfonyl chloride were fractionated under reduced pressures in efficient all-glass fractionating columns.

Kinetic Procedure.—Solutions were prepared and handled under strictly anhydrous conditions using the techniques previously described.[16] Reactions were followed to approximately 60% completion except where the concentrations were low and the rates were relatively slow. In these cases the reactions were followed to approximately 30% completion.

The following procedure was utilized for determination of the residual arylsulfonyl chloride. It was tested thoroughly on synthetic mixtures. The aliquot was removed with a fast-delivery pipet (calibrated for the solution) from the reaction vessel and introduced into a separatory funnel containing 15 ml. of distilled water and 20 g. of ice chips. The mixture was immediately shaken to destroy the aluminum chloride and to stop the reaction. After allowing the solution to settle, the nitrobenzene was drained off and the aqueous layer twice extracted with 2-ml. portions of chloroform. Ten ml. of ice-water was then added to the combined nitrobenzene and chloroform extracts, the mixture shaken, 2 drops of 1% phenolphthalein in acetone added to the aqueous phase, and the latter neutralized with 0.03 *M* sodium hydroxide. Five ml. of pyridine was added, the solution was covered, heated to boiling, and allowed to cool. After cooling, 50 ml. of ethanol was added and the hydrochloric acid and arylsulfonic acid titrated (in the presence of the pyridine) to the phenolphthalein end-point with standard base (0.1 *M*). The titrations were corrected by appropriate blank determinations.

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(15) G. A. Benford and C. K. Ingold, *J. Chem. Soc.*, 929 (1938); E. D. Hughes, C. K. Ingold and R. I. Reed, *ibid.*, 2400 (1950).

(16) For a summary of the literature see H. C. Brown, F. R. Jensen and B. A. Bolto, *J. Org. Chem.*, **23**, 414 (1958).

(17) H. Cohn, E. D. Hughes, M. H. Jones and M. G. Peeling, *Nature*, **169**, 291 (1952).

(18) E. Berliner and F. Berliner, THIS JOURNAL, **72**, 222, 3417 (1950).

(19) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957).