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Kinetics of the Friedel–Crafts Sulfonylation of Benzene, Chlorobenzene and Toluene with Aluminum Chloride as Catalyst and Benzenesulfonyl Chloride as Solvent[1,2]

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With benzenesulfonyl chloride as solvent and aluminum chloride as catalyst, the kinetic order of the sulfonylation reaction depends on the reactivity of the aromatic compound. For chlorobenzene the reaction follows the kinetic expression: rate $= k_{3/2}[C_6H_5SO_2Cl\cdot AlCl_3]^{1/2}[C_6H_5Cl]$. In the case of benzene, the kinetic order is mixed, while toluene exhibits second-order kinetics: $k_2[C_6H_5SO_2Cl\cdot AlCl_3][C_6H_5CH_3]$. These results indicate that the reaction with chlorobenzene proceeds *via* free ions, $C_6H_5SO_2^+ + AlCl_4^-$ (predominantly). On the other hand, the reaction with toluene presumably proceeds by a reaction of the aromatic with the addition compound, $C_6H_5SO_2Cl\cdot AlCl_3$, or ion-pairs, $C_6H_5SO_2^+AlCl_4^-$, while the reaction with benzene proceeds simultaneously through both paths.

The Friedel–Crafts sulfonylation reaction, in contrast to the related benzoylation reaction, appears to be a reaction of high "activity" and low "selectivity."[5] Consequently, a comparative study of both of these reactions with respect to the catalytic effectiveness of polyvalent metal halides and the effect of substituents on the rates of aromatic substitution appeared desirable.

Olivier has studied the kinetics of the sulfonylation reaction using various aromatic compounds as solvents,[6] the rates of sulfonylation of benzene (solvent) using various arylsulfonyl chlorides,[7] the kinetics of the reaction using mixtures of sulfonyl chlorides,[8] and the kinetics of the reaction using benzenesulfonyl chloride as solvent.[9] In all cases the rate constants varied markedly with initial aluminum chloride concentration and, in some cases, even during a single kinetic run.

We attempted to avoid these difficulties by using the polar solvent, nitrobenzene, for study of the benzoylation[10] and benzenesulfonylation[11] reactions. However, complicated kinetics were observed. The difficulty appeared to arise from the nature of the aluminum chloride–nitrobenzene solutions, and not from any complexities inherent in the Friedel–Crafts reactions themselves. The benzoylation reaction exhibits simple second-order kinetics in benzoyl chloride solution.[12] We were therefore encouraged to reinvestigate the kinetics of the related benzenesulfonylation reaction in benzenesulfonyl chloride solution, in spite of Olivier's unfavorable experience.

Results

The reactions were followed by isolating and weighing the sulfones produced in the reaction mixture, utilizing a procedure similar to that used by Olivier.[9] It has been previously established[6–9] that the stoichiometry of the reaction is expressed by the equation

$$C_6H_5SO_2Cl\cdot AlCl_3 + ArH \longrightarrow C_6H_5(Ar)SO_2\cdot AlCl_3 + HCl \quad (1)$$

In these acylation reactions one mole of aluminum chloride is utilized per mole of product formed. Consequently, the behavior of aluminum chloride in these reactions is more that of a reactant than that of a true catalyst. However, we have followed common practice in referring to these reactions as being "aluminum chloride-catalyzed."

Benzenesulfonylation of Toluene.—The aluminum chloride-catalyzed reaction exhibits clean second-order kinetics

$$\text{rate} = k_2[AlCl_3][C_6H_5CH_3] \qquad (2)$$

Data for a typical kinetic study are summarized in Table I.

TABLE I

TYPICAL RATE DATA FOR THE ALUMINUM CHLORIDE-CATALYZED BENZENESULFONYLATION OF TOLUENE IN BENZENESULFONYL CHLORIDE SOLUTION AT 25.0°

Time, min.	Phenyl tolyl sulfone G.	Phenyl tolyl sulfone M	Rate constant, k_2[a] l. mole^{-1} min.$^{-1}$
3.2	0.0650	0.056	0.108
11.2	.168	.146	.109
17.9	.218	.189	.107
25.9	.259	.226	.110
32.8	.285	.248[b]	.110
			Mean 0.109 ± 0.001

[a] Initial concentrations: $[AlCl_3] = 0.308$ M; $[CH_3C_6H_5] = 0.613$ M. [b] 81% reaction.

The initial concentration of the toluene was varied from 0.156 to 0.678 M, and that of aluminum chloride was varied from 0.155 to 0.474 M. Only minor changes in the value of the second-order rate constants result, no greater than might be expected in view of the concentrated nature of the solutions and the large changes in their composition. The results are summarized in Table II.

Benzenesulfonylation of Chlorobenzene.—The reaction between benzenesulfonyl chloride (solvent) and chlorobenzene under the influence of aluminum chloride was studied previously by Olivier.[9] He believed the reaction to be second order. However, his reported second-order rate constants vary considerably with initial concentration and decrease during the kinetic runs.

The results of the present study reveal that the reaction is three-halves order rather than second

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

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

[6] S. C. J. Olivier, *Rec. trav. chim.*, **33**, 91 (1914).

[7] S. C. J. Olivier, *ibid.*, **33**, 244 (1914).

[8] S. C. J. Olivier, *ibid.*, **35**, 109 (1915).

[9] S. C. J. Olivier, *ibid.*, **35**, 166 (1915).

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

[11] F. R. Jensen and H. C. Brown, THIS JOURNAL, **80**, 4038 (1958).

[12] H. C. Brown and F. R. Jensen, *ibid.*, **80**, 2291 (1958).

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE ALUMINUM CHLORIDE-CATALYZED BENZENESULFONYLATION OF TOLUENE IN BENZENESULFONYL CHLORIDE SOLUTION AT 25.0°

Reactants, M^a [Toluene]	[AlCl$_3$]	Rate constant, k_2 l. mole^{-1} min.$^{-1}$
0.313	0.155	0.125
.310	.310	.123
.318	.474	.121
.156	.312	.133
.310	.309	.128
.310	.310	.123
.613	.308	.109
.678	.450	.109

[a] Initial concentrations.

order. It is first order in chlorobenzene and half order in aluminum chloride (3).

$$\text{rate} = k_{3/2}[\text{AlCl}_3]^{1/2}[\text{C}_6\text{H}_5\text{Cl}] \qquad (3)$$

Rate data for two typical kinetic studies are summarized in Table III, together with both the calculated second-order and three-halves-order rate constants.

TABLE III

TYPICAL RATE DATA FOR THE ALUMINUM CHLORIDE-CATALYZED BENZENESULFONYLATION OF CHLOROBENZENE IN BENZENESULFONYL CHLORIDE SOLUTION AT 25.0°

Time, min.	Chlorodiphenyl sulfone, M	Rate constants × 10^3 k_2, l. mole^{-1} min.$^{-1}$	$k_{3/2}$, l.$^{1/2}$ mole$^{1/2}$min.$^{-1}$
34	0.0090	2.80	1.56
90	.0241	3.38	1.45
190	.0502	3.55	1.50
237	.0614	3.65	1.53
326	.0815	3.81	1.54
		Mean^a	1.52 ± 0.03
61	0.027	(2.1)	(1.3)
231	.086	2.21	1.39
437	.143	2.31	1.37
790	.214	2.47	1.39
		Mean^b	1.38 ± 0.01

[a] Initial concentrations: [AlCl$_3$] = 0.206 M; [C$_6$H$_5$Cl] = 0.448 M. [b] Initial concentrations: [AlCl$_3$] = 0.457 M; [C$_6$H$_5$Cl] = 0.457 M.

The data are in far better agreement with three-halves order kinetics. However, the deviations in the calculated second-order rate constants are not large. Unless the reactions are followed considerably past 50% reaction, it is difficult to differentiate between second-order and three-halves-order reactions from the results of a single experiment.

However, the validity of the three-halves-order treatment is confirmed by an examination of the effects of varying the initial concentrations of the reactants (Table IV). A fivefold change in the initial concentration of the aluminum chloride results in a threefold change in the initial second-order rate constants and less than a 20% change in the three-halves-order rate constants. Increasing the initial concentration of the chlorobenzene concentration causes a larger change in the rate constant than for the corresponding reaction with toluene (Table II). The effect will be discussed later.

TABLE IV

RATE CONSTANTS FOR THE ALUMINUM CHLORIDE-CATALYZED BENZENESULFONYLATION OF CHLOROBENZENE IN BENZENESULFONYL CHLORIDE SOLUTION AT 25.0°

Reactants, M^a [Chlorobenzene]	[AlCl$_3$]	Rate constants × 10^3 k_2(initial), l. mole^{-1} min.$^{-1}$	$k_{3/2}$, l.$^{1/2}$mole$^{-1/2}$ min.$^{-1}$
0.448	0.206	3.87	1.52
.455	.458	2.29	1.40
.453	.999	1.44	1.27
.218	.452	2.58	1.56
.455	.458	2.29	1.40
.993	.453	1.89	1.04

[a] Initial concentrations.

It was mentioned that Olivier treated his data for the same reaction as a second-order reaction and his reported rate constants vary considerably both with changes in the initial concentration and in the course of individual kinetic runs.[9] From the expression for a second-order reaction (2″) and

$$\text{rate} = k_2[\text{AlCl}_3][\text{C}_6\text{H}_5\text{Cl}] \qquad (2'')$$

equation 3, it is seen readily that $k_{3/2} = k_2\,[\text{AlCl}_3]_0^{1/2}$. In Table V are listed Olivier's second-order rate constants together with the calculated values of the three-halves-order constant.

TABLE V

RECALCULATED THREE-HALVES-ORDER RATE CONSTANTS FROM THE SECOND-ORDER RATE CONSTANTS REPORTED BY OLIVIER[9] FOR THE BENZENESULFONYLATION OF CHLOROBENZENE USING BENZENESULFONYL CHLORIDE AS SOLVENT AT 30°

Reactants, M^a [Chlorobenzene]	[AlCl$_3$]	Rate constants × 10^3 k_2(initial) l. mole^{-1} min.$^{-1}$	$k_{3/2}{}^b$ l.$^{1/2}$ mole$^{-1/2}$ min.$^{-1}$
0.386	0.200	5.97	2.67
.313	.300	4.89	2.68
.724	.300	4.53	2.48
.827	.300	4.16	2.27
.353	.500	3.87	2.73
.784	.500	3.43	2.42
.789	.500	3.44	2.43
.800	.800	2.59	2.31
1.57	.800	2.16	1.93

[a] Initial concentrations. [b] Calculated from the expression, $k_{3/2} = k_2[\text{AlCl}_3]_0^{1/2}$.

The $k_{3/2}$ values are essentially constant, exhibiting only the moderate decrease with large increases in the concentration of chlorobenzene referred to earlier. Olivier's rate constants decreased considerably with time in individual determinations. Consequently the above calculations are based on the initial second-order constants. Our own data do not exhibit a similar decrease (Table III). It is probable that either the aluminum chloride or the benzenesulfonyl chloride used by Olivier was impure and responsible for the observed decrease in the values of the rate constants with time.

In conclusion, the results argue strongly for a three-halves-order kinetic expression in the chlorobenzene reaction, in contrast to the second-order kinetic expression observed for toluene.

Benzenesulfonylation of Benzene.—Olivier[9] had attempted to investigate the kinetics of the reaction with benzene, but failed to obtain satisfactory rate constants. For individual experiments the calculated second-order rate constants decreased sharply as the reaction proceeded, and the initial second-order rate constants varied with changes in the initial concentrations of the reactants. He concluded that the removal of benzene by the evolved hydrogen chloride was responsible for his difficulties.

In the present study, the reaction of benzenesulfonyl chloride with benzene follows second-order kinetics in individual experiments, except when the benzene concentration is small. In that event, a small increase in the calculated rate constants is observed as the reactions proceed. However, the values of the second-order rate constants change with the initial concentrations of the reactants (Table VI).

TABLE VI

RATE CONSTANTS FOR THE ALUMINUM CHLORIDE-CATALYZED BENZENESULFONYLATION OF BENZENE IN BENZENESULFONYL CHLORIDE SOLUTION AT 25.0°

Reactants, M^a [Benzene]	[$AlCl_3$]	Rate constant, k_2, l. mole^{-1} min.$^{-1}$
0.553	0.173	0.0170
.590	.546	.0151
.163	.538	.0208
.190	.548	.0182
.590	.546	.0151

[a] Initial concentrations.

These results are explicable on the assumption that the reaction exhibits mixed kinetics. Because the kinetic study based on the present technique requires high concentrations of reactants, solvent effects introduce an additional complicating factor and render an exact analysis of the kinetics quite difficult. A qualitative analysis of the data, based on the proposed mechanism of the reaction, will be presented in the Discussion.

Replacement of the benzenesulfonyl chloride by cyclohexane (48% by volume) decreased the rate to one-seventh of its original value. Additional cyclohexane (72% by volume) decreased the rate even further, to one-twenty-fifth of its original value.

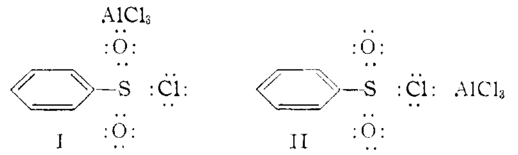
Discussion

Olivier demonstrated the existence of 1:1 addition compounds of aluminum chloride with benzenesulfonyl chloride, $C_6H_5SO_2Cl \cdot AlCl_3$, and with diphenyl sulfone, $(C_6H_5)_2SO_2 \cdot AlCl_3$.[9] In benzenesulfonyl chloride solution, aluminum chloride exhibits a molecular weight corresponding to its monomeric formula, $AlCl_3$, and must exist in the form of its 1:1 addition compound, $C_6H_5SO_2Cl \cdot AlCl_3$. It follows that the experimental rate expressions, 2 and 3, should be revised to show this addition compound as one of the reactants.

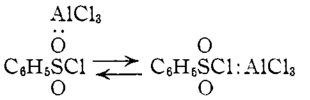
$$\text{rate} = k_2[C_6H_5SO_2Cl \cdot AlCl_3][CH_3C_6H_5] \qquad (2')$$

$$\text{rate} = k_{3/2}[C_6H_5SO_2Cl \cdot AlCl_3]^{1/2}[C_6H_5Cl] \qquad (3')$$

In the case of the related benzoyl chloride–aluminum chloride derivative, the available evidence indicates that the aluminum chloride is bonded to the oxygen atom of the carbonyl group rather than to chlorine.[13,14] Although similar studies have not been made for the benzenesulfonyl chloride derivative, it appears probable that here also the aluminum chloride is associated with the more basic oxygen atom (I), rather than the less basic chlorine atom (II).



In the case of chlorobenzene, three-halves-order kinetics were observed. The only reasonable mechanism which is consistent with a three-halves order is a dissociation of the addition compound into ions, followed by reaction of the ionic intermediate with the aromatic derivative. Consequently, the following ionic mechanism (7″, 8), appears to be called for by the chlorobenzene results.



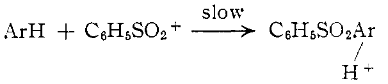
$$C_6H_5SO_2Cl \rightleftarrows C_6H_5SO_2Cl:AlCl_3 \qquad (4)$$

$$C_6H_5SO_2Cl:AlCl_3 \rightleftarrows C_6H_5SO_2{}^+AlCl_4{}^- \qquad (5)$$

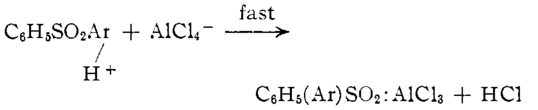
$$C_6H_5SO_2{}^+AlCl_4{}^- \rightleftarrows C_6H_5SO_2{}^+ + AlCl_4{}^- \qquad (6)$$

$$ArH + C_6H_5SO_2Cl:AlCl_3 \longrightarrow C_6H_5(Ar)SO_2:AlCl_3 + HCl \qquad (7)$$

$$ArH + C_6H_5SO_2{}^+AlCl_4{}^- \longrightarrow C_6H_5(Ar)SO_2:AlCl_3 + HCl \qquad (7')$$



$$ArH + C_6H_5SO_2{}^+ \xrightarrow{\text{slow}} C_6H_5SO_2Ar\,H^+ \qquad (7'')$$



$$C_6H_5SO_2Ar\,H^+ + AlCl_4{}^- \xrightarrow{\text{fast}} C_6H_5(Ar)SO_2:AlCl_3 + HCl \qquad (8)$$

With step 7″ slow (ArH = chlorobenzene), the rate will be proportional to the concentrations of $C_6H_5SO_2{}^+$ and the aromatic. Since $[C_6H_5SO_2{}^+] = [AlCl_4{}^-] = K[C_6H_5SO_2Cl \cdot AlCl_3]^{1/2}$, this mechanism leads to the kinetics observed for the relatively inert aromatic, chlorobenzene.

The more reactive aromatic toluene exhibits second-order kinetics. Such a change in kinetics could arise in several ways. If step 7″ becomes sufficiently fast (ArH reactive), it could become comparable in velocity with step 8. Then the rate will be proportional to the concentrations of both $[C_6H_5SO_2{}^+]$ and $[AlCl_4{}^-]$, resulting in a first-order dependence on $[C_6H_5SO_2Cl \cdot AlCl_3]$. However, failure to realize any significant isotope effects in the benzenesulfonylation of deuterated aromatics leads us to discard this possibility in favor of another interpretation.[15]

Alternatively, the reactive aromatic could react directly with the ion-pair (7′), or even with the isomeric form of the addition compound (7), with a resulting first-order dependence on the concentration of the addition compound. In the case of benzene, a considerable decrease in rate accompanied the replacement of a portion of the benzenesulfonyl chloride solvent by the less polar material cyclohexane. On this basis we tend to favor the paths

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(13) N. N. Lebedev, *J. Gen. Chem.* (*U.S.S.R.*), **21**, 1788 (1951).

(14) B. P. Susz and I. Cooke, *Helv. Chim. Acta*, **37**, 1273 (1954); I. Cooke, B. P. Susz and C. Herschmann, *ibid.*, **37**, 1280 (1954).

(15) Unpublished investigations of F. R. Jensen.

involving ionic intermediates (7′ or 7″ and 8) over that involving the isomeric addition compound (7).

High concentrations of chlorobenzene or toluene result in decreases in the rate constants. These decreases are explicable in terms of a solvent effect similar to that observed in replacing a portion of the benzenesulfonyl chloride solvent by cyclohexane. It was observed that high concentrations of chlorobenzene (Table IV) result in larger decreases in the rate constant than do high concentrations of toluene (Table II). This observation is also consistent with the proposed mechanism. A reaction which proceeds through dissociated ions (chlorobenzene) would be expected to be more sensitive to decreases in the dielectric constant of the medium than a reaction which proceeds through an attack of the aromatic (toluene) on ion-pairs or the isomeric form of the addition compound.

In nitrobenzene solution the benzenesulfonylation reaction was independent of the concentration of the aromatic.[11] It is probable that under the present conditions highly reactive aromatics would follow first-order kinetics, independent of the concentration of the aromatic.

$$\text{rate} = k_1[C_6H_5SO_2Cl{\cdot}AlCl_3] \qquad (9)$$

Such kinetics should be observed in cases where the reaction of the aromatic with the reactive species (7, 7′ or 7″) is faster than the rate of formation of the intermediate (4, 5 or 6).

The results with benzene support the proposed interpretation of the kinetics. At low benzene concentrations, the calculated second-order rate constants (Table VI) are large because the reaction proceeds largely through the path involving dissociated ions (7″). Under these conditions the calculated second-order rate constants within single experiments increase slightly as the reaction proceeds, indicating that the assumed reaction order is too high, *i. e.*, less than two. In other words, at low benzene concentrations a significant fraction of the reaction must proceed through the reaction path favored by chlorobenzene, with the reaction kinetics representing mixed orders, both three-halves and second.

As the initial benzene concentration is increased, the calculated second-order rate constants decreased rapidly at first and then leveled off. Also, excellent second-order constants are realized throughout each kinetic experiment involving high benzene concentrations. Under these conditions of high benzene concentration, the reaction must proceed predominantly through the path favored by toluene (presumably 7′).

In summary, the three-halves-order kinetics observed for chlorobenzene appear to require the proposed mechanism involving dissociated ions ($C_6H_5SO_2^+$, $AlCl_4^-$). As the reactivity (and concentration) of the aromatic is increased, other stages in the reaction become rate determining and the kinetics undergo a gradual change to mixed order for benzene (second order at high concentrations), second order for toluene, presumably involving ion-pairs ($C_6H_5SO_2^+AlCl_4^-$), and first order (predicted) for sufficiently reactive aromatics. The fact that alternative intermediates may be involved must be kept in mind in utilizing benzenesulfonylation rate data for a comparison of relative reactivities.

Experimental Part

Materials.—The benzene, toluene and chlorobenzene were purified by standard methods and were established to have purities of at least 99.5% by cooling curve analysis.

The benzenesulfonyl chloride used both as solvent and reactant required rigorous purification for satisfactory results. The freshly distilled material was treated with 3 mole % toluene and 3 mole % aluminum chloride, and allowed to stand overnight. The free benzenesulfonyl chloride was taken off at 1 mm., and then refractionated carefully at 10 mm. in an all-glass column rated at 50 plates. Three fractionations, collecting only the constant-boiling center fractions, yielded a product of satisfactory purity, as judged by the progress of test reactions to 100% completion and the reproducibility of the kinetics.

Aluminum chloride was purified as previously described.[12] Solutions of aluminum chloride in benzenesulfonyl chloride were prepared and handled utilizing the techniques and apparatus previously developed for the similar benzoyl chloride solutions.[12] These solutions were colorless and, protected from light, appeared to be stable indefinitely. However, the kinetic measurements were carried out with freshly prepared solutions, no older than ten days as a maximum.

Kinetic Procedure.—The rates were followed by hydrolyzing the benzenesulfonyl chloride, isolating the sulfone product, and weighing it. The procedure was similar to that used in the benzoylation study.[12] However, because of the lower volatility of the products it was satisfactory to bring them to constant weight at 1.0 mm.

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