[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Relative Rates and Isomer Distribution in the Aluminum Chloride-catalyzed Benzenesulfonylation of Benzene and Toluene in Benzenesulfonyl Chloride Solution. Partial Rate Factors for the Benzenesulfonylation Reaction[1,2]

BY FREDERICK R. JENSEN[3,4] AND HERBERT C. BROWN

RECEIVED JANUARY 22, 1958

The rate of reaction of benzene with benzenesulfonyl chloride–aluminum chloride in benzenesulfonyl chloride solution at 25.0° has been determined at high benzene concentrations (1.3 *M*). Under these conditions the reaction appears to proceed predominantly through the same reaction path as that of toluene. Under these conditions the relative rate of reaction, k_T/k_B is 8.0 ± 1 and the isomer distribution for the sulfonylation of toluene is: *ortho*, 29.4%; *meta*, 8.7%; and *para*, 62.9%. From these data partial rate factors for the benzenesulfonylation reaction are calculated to be: o_f, 6.8; m_f, 2.1; p_f, 30.2. The partial rate data for the benzenesulfonylation reaction obey the Selectivity Relationship. The marked increase in the degree of *ortho* substitution in benzenesulfonylation as compared to benzoylation suggests that the steric requirements of the substituting moiety must be a function of the selectivity of the substituting reaction as well as of the steric dimensions of the attacking species.

It was proposed recently that the rates of reaction of benzene and toluene could be correlated in a simple manner with the isomer distribution in toluene.[5-7] Numerous reactions have now been demonstrated to obey this Selectivity Relationship.[8]

The aluminum chloride-catalyzed benzoylation and benzenesulfonylation reactions bear numerous points of resemblance,[9] with one major difference. Benzoylation appears to be a reaction of high "selectivity," whereas from the available rate data[9] benzenesulfonylation appears to be of low "selectivity." Benzoylation has been previously demonstrated to obey the Selectivity Relationship, both in nitrobenzene solution[10] and in benzoyl chloride solution.[11] It was of interest to ascertain whether benzenesulfonylation likewise is consistent with the proposed Selectivity Relationship in spite of the apparent major differences in its selectivity characteristics.

The reaction of methanesulfonyl chloride–aluminum chloride with toluene at 100° yields 49% *ortho*, 15% *meta* and 36% *para*.[12] Unfortunately, data are not available for the relative reactivities of toluene and benzene under the same conditions. In the absence of such data, the relative reactivity of benzene and toluene in their reactions with *p*-bromobenzenesulfonyl chloride[13] was adopted as an estimate of this quantity. However, it is clear that this procedure does not provide a satisfactory test of the applicability of the Selectivity Relationship to the sulfonylation reaction.

Since it has been found that the reaction of toluene with benzenesulfonyl chloride–aluminum chloride in benzenesulfonyl chloride solution exhibits reasonably simple second-order kinetics,[14] we were encouraged to undertake a determination of the toluene/benzene relative rates as well as the isomer distribution realized in toluene under these conditions.

Results and Discussion

Relative Rates.—The benzenesulfonylation of chlorobenzene exhibits three-halves-order kinetics and appears to involve the reaction of the aromatic with dissociated benzenesulfonylonium ions ($C_6H_5SO_2^+$) in the rate-determining stage. On the other

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

hand, the corresponding reaction of toluene exhibits second-order kinetics and appears to involve in the rate-determining stage a reaction of the aromatic with the undissociated ion-pair ($C_6H_5SO_2^+AlCl_4^-$) or the un-ionized isomeric form of the addition compound ($C_6H_5SO_2Cl{:}AlCl_3$).[14]

$$\text{rate} = k_2[C_6H_5SO_2Cl \cdot AlCl_3][CH_3C_6H_5]$$

The kinetics observed for benzene in this reaction exhibit peculiarities which suggest that the reaction follows both of these alternative paths, part of the benzene reacting with the separated ions and part reacting with the other reactive species, ion-pairs or the un-ionized addition compound. It is obviously desirable that the relative reactivities be established under conditions whereby the substitution reaction proceeds to a major extent through identical paths for the two aromatics.

The higher the concentration of the aluminum chloride, the smaller should be the ratio of dissociated ions to ion-pairs (or addition compound). The difference in the kinetics exhibited by chlorobenzene and toluene suggests that the rate of formation of dissociated ions is in a critical range, such that the process cannot compete with their removal by the reactive aromatic. It follows that a large increase in the concentration of the less reactive species, benzene, should likewise serve to remove the dissociated ions faster than they can be generated. Consequently, high concentrations of aluminum chloride and of benzene should reduce that portion of the reaction proceeding through dissociated ions to a negligible fraction of the total reaction, and permit an estimation of the relative

---

(1) Directive Effects in Aromatic Substitution. XXV.

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

(3) Department of Chemistry, University of California, Berkeley, Calif.

(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) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300 (1955).

(7) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

(8) A critical examination of all of the available data is in preparation (with L. M. Stock) and will be submitted for publication shortly.

(9) S. C. J. Olivier, *Rec. trav. chim.*, **33**, 91 (1914); **37**, 205 (1918).

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

(11) H. C. Brown and F. R. Jensen, THIS JOURNAL, **80**, 2296 (1958).

(12) W. E. Truce and C. W. Vriesen, *ibid.*, **75**, 5032 (1953).

(13) S. C. J. Olivier, *Rec. trav. chim.*, **33**, 163 (1914).

(14) F. R. Jensen and H. C. Brown, THIS JOURNAL, **80**, 4042 (1958).

reactivity from a direct comparison of the relative rates.

Rate constants obtained from such studies are summarized in Table I, together with related data for toluene to facilitate comparison.

TABLE I

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

Reactants, M[a]		Rate constant, k_2,[b] l. mole^{-1} min.$^{-1}$	Reactants, M[a]		Rate constant, k_2, l. mole^{-1} min.$^{-1}$
[Benzene]	[AlCl$_3$]		[Toluene]	[AlCl$_3$]	
0.590	0.546	0.0151[c]	0.318	0.474	0.121[c]
.601	1.201	.0127	.568	.527	.112
.691	0.462	.0186	.322	.796	.109
.811	.780	.0153	.613	.308	.109[c]
1.31	.406	.0129	.678	.450	.109[c]
1.26	.526	.0118			

[a] Initial concentrations. [b] Note discussion of the benzene reaction in text. [c] From ref. 14.

Although the reactions with benzene utilizing low or moderate concentrations of reactants exhibit irregularities in the treatment as a second-order reaction,[14] presumably due to the presence of competing paths, the reactions at the high concentrations follow the second-order rate expression quite closely. Consequently, it appears safe to conclude that in the experiments with high benzene concentration [1.26 to 1.31 M], the reactions are following predominantly a single path, with only minor contributions from the alternative path involving dissociated ions. We may adopt the value $k_2 = 0.0118$ as an upper limit, recognizing that it probably still contains a minor component of the undesired reaction path.

Unfortunately, the reactivity of toluene is such that it was not possible to determine the rates at the same high concentration of hydrocarbon. We therefore extrapolated the decreasing values of k_2 with increasing concentration of hydrocarbon[14] to 1.25 M and arrived at an estimated value of $k_2 = 0.095$.

The ratio of k_T/k_B for the identical reaction path then becomes 0.095/0.0118 or 8.0.

In arriving at this value for the relative rates, a number of corrections have had to be introduced into the experimental data. Fortunately, the corrections are relatively small. Consequently, we estimate that the value 8.0 ± 1.0 will cover the probable range of uncertainty.

An alternative procedure for determining the relative rate is based upon a competition of the two aromatic hydrocarbons for a limited quantity of the substituting agent. Unfortunately, this procedure involves the implicit assumption that the two aromatic hydrocarbons are reacting by identical paths. Considering both the greater analytical difficulties and the possible uncertainties in this assumption it did not appear that the competitive procedure would be of assistance in establishing the relative rate value with greater precision than that realized by the present approach.

Isomer Distribution and Partial Rate Factors.—The three isomeric phenyl tolyl sulfones were synthesized from the reaction of the isomeric toluenesulfonyl chlorides with benzene under the influence of aluminum chloride. Synthetic mixtures were prepared and it was established that they could be analyzed with satisfactory precision in carbon disulfide solution by infrared absorption.

The reaction product from the benzenesulfonylation of toluene was isolated from a typical kinetic run and analyzed in this way. The analysis indicated the presence of 28.4% *o*-, 8.7% *m*- and 62.9% *p*-tolyl phenyl sulfone.

The relative rate and the observed isomer distribution led to the partial rate factors: o_f, 6.8; m_f, 2.1; p_f, 30.2.

Utilizing the Selectivity Relationship, it is possible to calculate the partial rate factors and the toluene/benzene relative rate directly from the isomer distribution.[7] The calculated and observed values are summarized in Table II.

TABLE II

OBSERVED AND CALCULATED VALUES OF THE PARTIAL RATE FACTORS FOR THE ALUMINUM CHLORIDE-CATALYZED BENZENESULFONYLATION REACTION IN BENZENESULFONYL CHLORIDE SOLUTION AT 25°

	Partial rate factors			Relative rate,
	o_f	m_f	p_f	k_T/k_B
Observed[a]	6.8	2.1	30.2	8.0 ± 1.0
Calculated[b]	7.3	2.3	33.0	8.7

[a] This study. [b] Ref. 7.

The agreement is good, well within the probable experimental uncertainty in the relative rate value.

The results clearly indicate that benzenesulfonylation is a far less selective substitution reaction than the otherwise closely related benzoylation reaction. Nevertheless, in spite of the marked difference in selectivity of the two reactions, both are correlated with satisfactory precision by the Selectivity Relationship.

Steric Requirements as a Function of Selectivity.—The benzoylation of toluene leads to the formation of only 9.3% of the *ortho* isomer, as compared to 89.3% of the *para* compound. The relatively low degree of *ortho* substitution was considered to be indicative of large steric requirements for the substituting species far greater than appear reasonable for the simple benzoylonium ion, $C_6H_5CO^+$. It was therefore suggested that the Friedel–Crafts acylation reaction might not proceed through such ionic intermediates.[10,15]

However, the observation that the orientation is independent of the specific metal halide used as catalyst ($AlCl_3$, $GaCl_3$, $SnCl_4$, $SbCl_5$),[16] argues strongly that the same or very similar substituting species must be involved in these reactions.[16] The only reasonable intermediate which fulfills this requirement is the benzoylonium ion or ion-pair. We are thereby forced to the conclusion that despite the low degree of *ortho* substitution, the benzoylation reaction must proceed through the benzoylonium ion or ion-pair.

The corresponding benzenesulfonylation of toluene yields 28.4% *ortho*, 8.7% *meta* and 62.9% *para*. Here also the evidence favors the benzenesul-

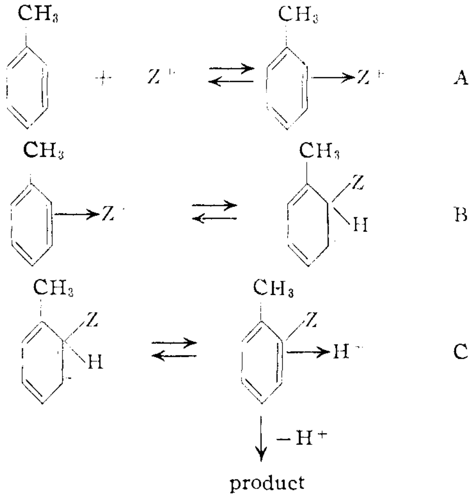
---

(15) H. C. Brown and W. H. Bonner, THIS JOURNAL, **76**, 605 (1954).

(16) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 3039 (1958).

fonylonium ion or ion-pair as the substituting species.[14] A consideration of the two structures suggests that there should be no major difference in the steric requirements of the benzoylonium ($C_6H_5CO^+$) and the benzenesulfonylonium ($C_6H_5SO_2^+$) ions or ion-pairs, with the latter having the larger such requirements, if a significant difference exists. Yet the reaction involving the latter intermediate exhibits the smaller steric effect[17]: benzoylation, $(o_f/p_f) = 0.052$; benzenesulfonylation, $(o_f/p_f) = 0.20$.

It is probable that this phenomenon is the result of the large difference in the selectivities of the two reactions. It may be that a reaction such as benzoylation which is highly sensitive to the electronic contributions of the substituents in the aromatic ring, is likewise highly sensitive to the steric requirements of that substituent. On the other hand, a reaction which is of low selectivity, may be much less sensitive to the steric requirements of the substituent.



This phenomenon appears to be explicable in terms of present concepts of aromatic substitution.[18] It now appears that aromatic substitution occurs through the intermediate formation of π- and σ-complexes.

In cases where no important isotope effect exists, the transition state would be expected to be intermediate between A and B. In cases with a significant isotope effect, the transition state would lie between B and C. A reaction which is highly selective presumably requires a large degree of bonding in the transition state.[5,19] This should therefore resemble the σ-complex closely.[18] On the other hand, reactions of low selectivity should not require much bonding with the aromatic in the transition state and the latter is expected to approach the π-complex in structure. It is reasonable that the steric factor should be far greater in the σ-complex than in the π-complex.

Experimental Part

Kinetic Measurement.—The procedures were identical to those described in the preceding publication.[14]

Isomer Distribution.—The preparation of the three tolyl phenyl sulfones followed procedures identical to that described for *p*-tolyl phenyl sulfone.

p-Toluenesulfonyl chloride was recrystallized from petroleum ether (b.p. 90–100°), followed by ethyl ether. The product, m.p. 69°, 94.2 g., was dissolved in 200 ml. of benzene, n^{20}_{D} 1.5009. To this reaction mixture 60.0 g. of powdered aluminum chloride was added in small portions. After two hours at room temperature, the mixture was poured into excess 6 *M* sodium hydroxide to hydrolyze the aluminum chloride. To remove residual traces of the sulfonyl chloride, 10 ml. of pyridine was added, the mixture shaken vigorously, and the sulfone was taken up in chloroform. The chloroform extracts were washed with water and the chloroform taken off under vacuum. The crude sulfone was dissolved in pyridine, 2 *M* sodium hydroxide was added until the solution became strongly basic (the solution becomes scarlet in color at this stage), and then a large amount of water was added slowly. The solid was filtered off, dissolved in ethanol, treated with Norite carbon, and then recrystallized 3 times from ethanol.

In all cases the final products were obtained in the form of large colorless crystals: *p*-tolyl phenyl sulfone,[20] m.p. 126.5-126.8°; *m*-tolyl phenyl sulfone,[21] m.p. 120.3–120.7°; *o*-tolyl phenyl sulfone,[22] m.p. 81.4–81.8°.

The infrared spectra were obtained with a Perkin–Elmer model 21 double beam recording spectrophotometer using carbon disulfide as solvent and 0.1-mm. matched sodium chloride cells. The following wave lengths were utilized for the analysis: *meta*, 11.6 μ; *para*, 12.28 μ; and *ortho*, 13.2 and 13.3 μ. In analyzing for the *ortho* isomer, it was necessary to correct for absorption by the other isomers. The procedures were similar to those utilized in the corresponding analysis of the isomeric methylbenzophenones.[11]

LAFAYETTE, IND.

---

[17] The ratio, o_f/p_f, should be nearly equal to unity for reactions with no significant steric factor.

[18] For discussion and pertinent references, see K. L. Nelson and H. C. Brown, "Aromatic Substitution—Theory and Mechanism," Chapter 56 in "The Chemistry of Petroleum Hydrocarbons," ed. by B. T. Brooks, *et al.*, Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955.

[19] E. Berliner and F. Berliner, THIS JOURNAL, **76**, 6179 (1954).

[20] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953), report m.p. 127.0–127.5°.

[21] W. E. Truce and M. F. Amos, *ibid.*, **73**, 3013 (1959), report m.p. 119–120.5°.

[22] F. Ullmann and A. Lehner, *Ber.*, **38**, 729 (1905), report m.p. 80°.