Electrophilic Aromatic Substitution. 7. A Kinetic Study of the Aluminum Chloride Catalyzed Desulfonylative Benzylation of Aromatics with Phenylmethanesulfonyl Chloride in Nitromethane

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Kinetic studies have been made of the $AlCl_3$-catalyzed reaction of phenylmethanesulfonyl chloride with benzene or toluene in nitromethane at 20 °C. The reaction follows first-order dependence upon phenylmethanesulfonyl chloride and catalyst but zero-order dependence upon aromatic hydrocarbon. It is proposed that the reaction involves a benzyl cation which is formed in situ. Competitive results are also reported for the reaction with (*p*-chlorophenyl)methanesulfonyl chloride. In both cases, the relative reactivities, k_T/k_B, and toluene isomer product distributions appear to be exceptions to Brown's selectivity relationship.

Introduction

Phenylmethanesulfonyl chloride has been reported to react with benzene, or toluene, in the presence of $AlCl_3/CH_3NO_2$ to form diphenylmethane, or the three isomeric benzyltoluenes, respectively.[2] The curious feature of this reaction is that the reaction is not a sulfonylation but rather a desulfonylative alkylation. The results reported[2] for this reaction at 25 °C, 4.2 for k_T/k_B and isomer percentages of 34.4, 3.3, and 62.4 for ortho, meta, and para products, respectively, appear to be an exception to the Brown selectivity relationship. When $\log p_f = bS_f$ was used, the data yields a b value of 0.76, well outside the 95% confidence limits of the Brown–Stock line ($b = 1.31 \pm 0.20$).[3]

It is not clear in the report whether competitive or noncompetitive methods were used to obtain this data. Therefore, we decided to carry out a thorough kinetic study of this reaction using our improved vacuum line techniques and thoroughly dried solvents. This approach in other alkylation studies yielded reproducible results substantially different from those previously studied.[4,5]

We now report noncompetitive and competitive kinetic results for the $AlCl_3$-catalyzed reaction between phenylmethanesulfonyl chloride and benzene, or toluene, in nitromethane at 20 °C.

Experimental Section

Materials. Methods of analysis, purification, drying, and storage of these materials were described previously: benzene,[4b] toluene[4b] (GC internal standard, bicyclohexyl),[4b] aluminum chloride,[6] and nitromethane.[6]

The phenylmethanesulfonyl chloride (benzylsulfonyl chloride, BSC) was obtained commercially and purified by successive recrystallizations from diethyl ether. The purified material was characterized by IR spectroscopy and yielded a mp (uncorrected) of 89.2–90.1 °C. The BSC was stored in a polyethylene-lined screw-cap amber bottle under N_2 in the dry box.

The (*p*-chlorophenyl)methanesulfonyl chloride (*p*-chlorobenzylsulfonyl chloride, PCBSC) was generously supplied by Dr. Frank S. Abbott[7a] and purified according to Coates procedure.[7b] The purified material yielded a melting point range (uncorrected) of 92–93 °C and was stored in a polyethylene-lined screw-cap amber bottle under N_2 in the dry box.

Stock solutions of both BSC and PCBSC in purified nitromethane were prepared by weighing each component carefully into a N_2-filled septum-capped bottle. The bottle was wrapped in aluminum foil and stored under N_2 in the dry box. Typically, the solutions contained about 1 g of the organic chloride and 10 g of solvent.

Experimental Procedures. Competitive and noncompetitive reactions between $AlCl_3$, phenylmethanesulfonyl chloride (BSC), and benzene and/or toluene in dried purified nitromethane were carried out at 20.00 ± 0.05 °C in a reaction manifold system described in detail elsewhere.[4b] Two changes in procedure are noteworthy. First, the syringe containing the BSC stock solution was thermally equilibrated to the reaction temperature by putting it into a plastic boot and then placing the boot in the water bath for several minutes before injection into the reaction mixture. Generally, the stock solution of BSC was injected last.

Second, gas evolution was characterized by means of a bubbler and a U-shaped gas volume buret (filled with petroleum ether, 90–120 °C) connected together with Teflon tubing and joined via a "T" tube to the reaction vessel with a syringe needle.

Gas–Liquid Chromatographic Analysis. The aliquots of reaction product mixture were quenched with saturated NaCl solution to effect reasonable separation of aqueous and oily phases. The oily phase was then sampled and analyzed by gas–liquid chromatography on a Hewlett-Packard 5710A dual flame-ionization instrument. Typical conditions and retention times for primary products were reported earlier.[4b]

For secondary products, a 9 ft stainless steel column of $^1/_8$ in. O.D., packed with 10% HiEFF 4BP 60/80 mesh Gas Chromasorb Q (from Applied Science Lab., Inc., lot no. 208-902), was found to effect good separation of the three isomeric dibenzylbenzene products. The Hewlett-Packard 5710A instrument was set up with oven 200 °C, injection port 250 °C, and detector 300 °C. With nitrogen carrier gas flow at 20 mL/min, the retention times for the ortho, meta, and para dibenzylbenzene products were 104 min, 116 min, and 143 min, respectively.

Data Reduction. Calculations were carried out on a NOVA mini computer using programs prepared in this lab. Initial

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Table I. Rate Constants and Initial Rates for the $AlCl_3$-Catalyzed Reaction of Phenylmethanesulfonyl Chloride (BSC) with Benzene and Toluene in Nitromethane at 20 °C

reactants, M				initial rates,[a] 10^5M s^{-1}	10^3k_{app},[b] s^{-1}	$10^2k_{app}/[AlCl_3]_0$,[b] M^{-1} s^{-1}
$[C_6H_6]$	$[C_6H_5CH_3]$	[BSC]	$[AlCl_3]$			
0.514		0.0431	0.0467	7.6 ± 2.0[c]	1.7 ± 0.1[c]	3.5 ± 0.2[c]
0.419		0.0416	0.0466	6.6 ± 0.9	1.44 ± 0.03	3.09 ± 0.06
0.242		0.0441	0.0540	8.2 ± 2.0	1.5 ± 0.5	2.8 ± 0.1
0.528		0.0521	0.0206	3.1 ± 0.9	0.73 ± 0.5	3.5 ± 0.4
0.530		0.0259	0.0603	6.8 ± 2.0	2.81 ± 0.03	4.66 ± 0.05
0.446		0.0593	0.0361	5.5 ± 2.0	1.2 ± 0.1	3.4 ± 0.3
0.235		0.0634	0.0313	4.5 ± 0.6	0.74 ± 0.07	2.4 ± 0.2
0.438		0.0622	0.0158	1.9 ± 0.2	0.29 ± 0.01	1.8 ± 0.1
					av	3.14 ± 0.85[d]
	0.413	0.0636	0.0442	9.3 ± 2.0	2.4 ± 0.6	5.4 ± 1.4
	0.368	0.0598	0.0602	16.8 ± 0.7	3.1 ± 0.9	5.1 ± 1.5
	0.429	0.0255	0.0297	3.2 ± 0.6	1.54 ± 0.09	5.19 ± 0.03
	0.2085	0.0216	0.0268	2.2 ± 1.1	1.4 ± 0.4	4.8 ± 1.5
					av	5.12 ± 0.25[d]

[a] ≤10% reaction. [b] ≤20% reaction. [c] ±95% confidence limits. [d] Standard deviation.

Table II. Competitive Data Rate Ratios and Product Isomer Percentages for the $AlCl_3$-Catalyzed Reaction of Phenylmethanesulfonyl Chloride (BSC) with Benzene and Toluene at 20 °C

$[C_6H_6]$ M	$[C_6H_5CH_3]$ M	[BSC] M	$[AlCl_3]$ M	k_T/k_B	% ortho	% meta	% para
0.308	0.321	0.0593	0.0594	2.21 ± 0.03[a]	46.8 ± 0.5[a]	6.0 ± 0.2[a]	47.3 ± 0.3[a]
0.238	0.0203	0.0264	0.0353	2.2 ± 0.1	46.8 ± 2.1	5.4 ± 0.3	47.8 ± 1.9
0.236[b]	0.231	0.0119	0.0277	2.20 ± 0.09	46.5 ± 0.9	5.7 ± 0.1	47.8 ± 0.9
0.243[c]	0.0232	0.0220	0.0726	1.8 ± 0.2	48.6 ± 3.8	7.0 ± 0.4	44.4 ± 4.1

[a] Standard deviation. [b] Stirring via L & R Maxomatic ultrasonic cleaner. [c] Stirring via Brinkmann Polytron homogenizer.

concentrations were calculated after correction for moles in the gas phase at 20 °C. Moles of product produced as a function of time were obtained using GLC techniques and used to calculate initial rates. Graphs of various first-order, second-order, and third-order correlations of reactant concentrations to product concentrations produced plotted against time were prepared and inspected for consistency and linearity. All initial rates and rate constants were calculated as slopes, using the least-squares method, along with 95% confidence limits and linear correlation coefficients.

Results

The benzylation of benzene, or toluene, by phenylmethanesulfonyl chloride (BSC) in the presence of $AlCl_3$ is readily followed at 20 °C in nitromethane.

$$PhCH_2SO_2Cl + ArH \xrightarrow[20\ °C]{AlCl_3} PhCH_2Ar + SO_2 + HCl \quad (1)$$

where Ar = aromatic hydrocarbon. However, the reaction is not without complications. In the presence of $AlCl_3$, BSC undergoes polymerization, with concomitant loss of SO_2 whenever its concentration is comparable to that of the aromatic hydrocarbon reagent. This is avoidable if the hydrocarbon concentration is in at least 5-fold excess and if BSC is added last to the reaction mixture. Further, secondary product formation is significant beyond about 30% reaction (based upon primary product). This limits convenient evaluation of kinetic data to less than 30% reaction.

The initial rate data, Table I, points to a second-order rate law, first order in initial concentrations of BSC and $AlCl_3$.[8] For runs in which the initial $AlCl_3$ concentration was much less than that of BSC, the moles of product formed exceeded by several fold the moles of $AlCl_3$ used. This shows that $AlCl_3$ functions as a true catalyst in this reaction. The indicated rate law then is

$$\text{rate} = k_{app}[BSC] \quad (2)$$

where $k_{app} = k_2[AlCl_3]_0$. Significantly, the rate law is zero order in aromatic hydrocarbon.

Graphs of various first-, second-, and third-order correlations of reactant concentrations to product concentrations plotted against time were prepared and inspected for consistency and linearity. All plots showed curvature toward slower rates at longer times. The curvature can be explained in part on the basis of secondary product formation. Indeed, curvature is less pronounced when the secondary product concentration is taken into account. Syringe needle intrusion has already been discussed as another factor inducing curvature.[6] In any case, there was no significant curvature up to 20% reaction in any graph.

The rate law based on initial rate data is supported by the constancy of the second-order rate constants, k_2, defined as $k_{app}/[AlCl_3]_0$, where k_{app} is obtained from pseudo-first-order (in BSC) plots. Both k_{app} and k_2 values are included in Table I.

Individual product isomer percentages were evaluated from gas chromatographic analysis of each toluene run. The percentages as well as the meta/para and ortho/para ratios remained essentially constant throughout the course of a reaction and from run to run. Calculated overall averages for all toluene runs are % ortho = 47 ± 2, % meta = 6 ± 1, and % para = 47 ± 2 (±standard deviation).

A series of competitive runs were also carried out to determine k_T/k_B reagent concentrations and values obtained for k_T/k_B, as well as toluene product isomer percentages, are presented in Table II. Four different stirring techniques were used in this competitive study phase of the project in order to determine whether these reactions were kinetically controlled, i.e., that the rate of stirring was greater than the rate of reaction.

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[8] It is known that $AlCl_3$ coordinates to nitromethane. We refer to $AlCl_3$ concentration for convenience rather than to the more correct $AlCl_3$:CH_3NO_2 concentration.

Table III. Competitive Results for the $AlCl_3$-Catalyzed Reaction of (*p*-Chlorophenyl)methanesulfonyl Chloride (PCBSC) with Benzene and Toluene in Nitromethane at 20 °C[a]

time, s	% reactn[b]	k_T/k_B	% ortho	% meta	% para
500	70	2.2	46.8	8.8	44.3
1000	87	2.1	46.6	9.0	44.4
12000	62[d]	2.5	47.2	8.9	43.9
c	29[d]	1.8	48.3	9.2	42.4
	av	2.2 ± 0.3[e]	47.2 ± 0.8[e]	9.0 ± 0.2[e]	43.8 ± 0.9[e]

[a] Concentration data: [PCBSC] = 5.41×10^{-2} M; [$AlCl_3$] = 0.116 M; [benzene] = 0.104 M; [toluene] = 0.137 M. [b] Based upon apparent primary product evolution. [c] Sample taken after 24 h. [d] The observed reduction in percentage reaction at longer times may arise from slow primary product disproportionation. [e] Standard deviation.

In the first reaction, stirring was discontinued shortly after dissolution of all reagents. In the second, stirring was carried out in the usual manner with a water driven paddle.[4b] In the third, stirring was effected by placing the reaction manifold into a thermostated L & R Maxomatic Ultrasonic Cleaner. The ultrasonic cleaner emits high frequency sound waves through a liquid medium which vibrates the solution on a microscopic level. The principle being that if small microscopic micelles of mixed aromatic hydrocarbons exist in solution, the vibrations should disperse them. Finally, in the fourth, A Brinkmann wave generator was used to mix the solution. The generator has a high speed rotor inside a stationary cage. The effect is to emulsify the solution by creation of currents which draw the mixture into the cage where the rotor chops and grinds the solution in a manner similar to that of a garbage disposal.

Despite the variety of different mixing methods employed, the k_T/k_B ratios do not differ significantly. This seems to indicate that mixing is not a problem for this reaction.

Finally, one competitive run was made using (*p*-chlorophenyl)methanesulfonyl chloride (PCBSC) in place of BSC. Reagent concentrations and pertinent results are presented in Table III.

Discussion

From the noncompetitive initial rate study, the rate law was found to be first order in the concentrations of phenylmethanesulfonyl chloride (BSC) and $AlCl_3$, and zero order in the aromatic hydrocarbon concentration. As an internal check, the rate expression was taken to be rate = k_{app}[BSC] where $k_{app} = k_{n+1}[AlCl_3]_0{}^n$; and values of rate constants corresponding to "n" = $^1/_2$, 1, $^3/_2$ were calculated along with the standard deviation of each mean. The least deviation found was for $n = 1$.

Pseudo-first-order plots were linear up to 20% reaction (based upon product) and passed through the origin. The benzene runs, see Table I, yielded an average $k_B = 3.14\ (\pm 0.85) \times 10^{-2}\ M^{-1}\ s^{-1}$ and the toluene runs yielded an average $k_T = 5.12\ (\pm 0.2) \times 10^{-2}\ M^{-1}\ s^{-1}$. These rate constants are statistically significantly different and suggest a $k_T/k_B = 1.6 \pm 0.5$. However, this ratio does not reflect the relative reactivity of toluene over benzene because the rate law indicates the rate-determining step to be the formation of the electrophile—not the subsequent attack by the electrophile on aromatic hydrocarbon. This is the significance of the zero order in aromatic hydrocarbon concentration in the rate expression.

The relative reactivity ratio, k_T/k_B, in this case can be determined by competitive methods.[9] Therefore, a series of competitive runs were carried out by using different stirring techniques in an attempt to determine whether these reactions were kinetically controlled, that is, whether the rate of reaction is slower than the rate of stirring. Further, widely differing ratios of aromatic hydrocarbons were used in an effort to detect the formation of microscopic "micelles" of toluene/benzene in nitromethane. Such micelles would contain a mixture of toluene/benzene related to the initial ratio of these aromatic hydrocarbons. Should the electrophiles attack a micelle, they might preferentially react with toluene, say, but when the toluene supply is exhausted, the electrophiles would than attack the benzene hence resulting in a higher than usual benzene selectivity. If this were the case, changing the initial ratio of aromatic hydrocarbon would lead to variant k_T/k_B ratios.

Neither variation in aromatic hydrocarbon ratios nor variation in stirring methods yielded significant changes in either relative reactivity ratio, k_T/k_B, or the isomer product percentages. These results suggest that the reaction is indeed kinetically controlled and that micelle formation is not a problem.

Negative evidence of this sort does not eliminate the possibility of some sort of mixing control. However, these reactions are relatively slow, so mixing control should not be a problem unless there is phase separation. Along with our negative evidence this appears unlikely based upon the critical consolute temperatures calculated for mixtures of toluene and nitromethane (6 °C) and benzene and nitromethane (−59 °C).[10] At our reaction temperature, 20 °C, and concentration range [CH_3NO_2] $\simeq$ 16 M, [aromatic] $\simeq$ 0.5 M or less, micelle formation is very unlikely.

The competitive study yielded a $k_T/k_B = 2.1 \pm 0.1$, together with a toluene product isomer product distribution of 47 ± 1 % ortho, 6.0 ± 0.7 % meta, 47 ± 2 % para. These isomer percentages are also in satisfactory agreement with values obtained by noncompetitive means: % ortho = 47 ± 2, % meta = 6 ± 1, % para = 47 ± 2.

Our competitive results appear to be another exception to the Brown selectivity relationship. We have already reported initial results for the benzylation of toluene/benzene at 30 °C by benzyl chloride with $TiCl_4$ as catalyst.[4a] It is curious that this latter reaction, carried out in excess aromatic hydrocarbon, yields results consistent with the Brown selectivity relationship, but when carried out in nitromethane yields results much like those reported herein, namely, results discordant with the Brown selectivity relationship. It appears therefore that solvation or some other special solvent interaction accompanies the introduction of nitromethane as the reaction medium. Further theoretical discussion is deferred to a later report.[11]

Two possible mechanisms have been proposed for catalyzed desulfonylative benzylation.[2] The one involves stepwise formation of the benzyl cation, or benzyl cation/tetrachloroaluminate(III) ion pair, with loss of SO_2 before reaction with aromatic hydrocarbon. The other involves displacement by the aromatic hydrocarbon of the sulfonyl chloride–catalyst part of a polarized phenyl-

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methanesulfonyl chloride–catalyst complex initially formed, with subsequent formation of SO_2 and other products.

The rate law reported herein, zero order in aromatic hydrocarbon concentration, appears to rule out this second proposed mechanism in that this S_N2-like mechanism predicts rate law dependence upon this concentration.

The first proposed mechanism involves loss of SO_2 before reaction of the evolved electrophile with aromatic hydrocarbon. We attempted to measure the rate of SO_2 evolution by following increases in gas volume as a function of time in a benzene run. The rate, $k_2 = 1.9 \times 10^{-2}$ M^{-1} s^{-1}, is within experimental error of "k_B" (see Table I) measured noncompetitively. This supports the proposal that SO_2 is released during formation of the electrophile.

Although there is little evidence for ionization of sulfonyl chlorides,[12] one study of the thermal decomposition of phenylmethanesulfonyl chloride has been interpreted in terms of benzyl cation formation.[13] To explain the little variation in product isomer distribution with changes in catalyst, the benzyl cation has been suggested as the common electrophile in the benzylation of toluene using benzyl chloride in excess aromatic hydrocarbon.[4b] It appears the same is valid for this reaction carried out in nitromethane, nitrobenzene, or sulfolane.[11] The results we obtained by using phenylmethanesulfonyl chloride are similar to those obtained using benzyl chloride.[6] Furthermore, competitive results, see Table III, obtained using (*p*-chlorophenyl)methanesulfonyl chloride are similar to those obtained using *p*-chlorobenzyl chloride.[14] We therefore conclude that there is a common electrophile for catalyzed benzylation carried out with either benzyl chlorides or phenylmethanesulfonyl chlorides and suggest that the common electrophile is the benzyl cation.

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Registry No. BSC, 1939-99-7; PCBSC, 6966-45-6; $AlCl_3$, 7446-70-0; benzene, 71-43-2; toluene, 108-88-3; *o*-benzyltoluene, 713-36-0; *m*-benzyltoluene, 620-47-3; *p*-benzyltoluene, 620-83-7; *o*-(*p*-chlorobenzyl)toluene, 55676-88-5; *m*-(*p*-chlorobenzyl)toluene, 91410-28-5; *p*-(*p*-chlorobenzyl)toluene, 30203-87-3.

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Evidence for Concerted Transfer of Hydrogen from Tetralin to Coal Based on Kinetic Isotope Effects

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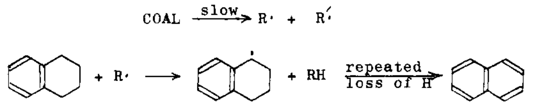
The H/D kinetic isotope effects for the reaction of subbituminous coal with tetralin-d_{12}, tetralin-*1,1,4,4*-d_4, and tetralin-*2,2,3,3*-d_4 are respectively 3.7, 2.0, and 2.0. This pattern is consistent with concerted transfer of a pair of hydrogen atoms from the 1- and 2-positions. It does not result from exchange of hydrogen in unreacted tetralin and is difficult to explain as an anomalous secondary effect. The H/D kinetic isotope effects for 1,2-dihydronaphthalene-d_{10} and -*1,1,3*-d_3 are 2.7 and 1.1. The latter appears to be a typical secondary effect. The rate-determining step is thought to be transfer of a single hydrogen from the 2-position, probably as hydride ion. The activation volume for 1,2-dihydronaphthalene is −23 mL/mol. This result is consistent with the proposed mechanism or almost any other bimolecular mechanism.

In recent years much effort has gone into the study of the chemical details of the reaction of coal with hydrogen donor solvents such as 1,2,3,4-tetrahydronaphthalene (tetralin). Most investigators adopt the hypothesis of Curran, Struck, and Gorin[1] that the coal molecule homolyzes and the free radicals abstract hydrogen atoms from the donor as shown in Scheme I. Several studies[2–8] have involved the use of model compounds of such constitution that they homolyze at reasonable rates at temperatures near 400 °C and conform to the types of structure which could occur in coal. A special type of model compound having a three-atom bridge between aromatic rings can react by a radical chain mechanism[9–11] with a faster rate than substrates which simply homolyze to benzylic or aryloxy radicals. It is uncertain how abundant such structures would be in coal. A problem with all of the free radical model compounds is that they are less reactive than coal even though ideal examples are chosen. Our sample of coal has the same half-life for conversion of tetralin to

Scheme I



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