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Electrophilic Aromatic Substitution. 5. A Kinetic Study of Friedel–Crafts Acylation in Nitromethane

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Noncompetitive kinetic studies were made of the $AlCl_3$-catalyzed reaction of 2,4-dichlorobenzoyl chloride with benzene and with toluene in nitromethane at 20 °C. The reaction appears to follow the kinetic expression: rate $= (k/[AlCl_3]_0)[ArH][\text{acid chloride}][AlCl_3]$. The $k_T/k_B = 472$ ● 84 and product isomer distributions $(8.4 \pm 0.3)\%$ ortho, $(0.43 \pm 0.02)\%$ meta, and $(91.2 \pm 0.3)\%$ para are in good agreement with the Brown selectivity relationship but unexpectedly indicate a weak rather than strong electrophile. This appears to be an artifact of the inverse rate order dependence upon initial $AlCl_3$ concentration.

Introduction

There is general agreement that the transition state for the attack of a weak electrophile on an aromatic substrate resembles a σ-complex or benzenium ion. The nature of the reaction pathway for the attack of a strong electrophile, on the other hand, is less certain. Highest energy states resembling either a σ- or a π-complex have been proposed by various groups.[2] In particular, the latter has been used to account for results obtained in studies of Friedel–Crafts reactions that seemingly deviate from substrate and positional selectivities predicted by the Brown selectivity relationship. The selectivity relationship predicts that substrate and positional selectivity both decrease as the reactivity of the electrophile increases.[2a] However, low substrate but high positional selectivites have been reported for strong electrophiles in several reactions.[2b]

The argument for a π-complex mechanism has been weakened by evidence that some of the anomolies arose from experimental difficulties such as mixing speeds[3] or the presence of small amounts of moisture.[4,5] Furthermore, several recent statistical analyses show that either some "deviant" results reasonably fit the Brown selectivity relationship,[6a] or that data correlation to π-complex stabilities is really no better than correlation to σ-complex stabilities.[6b] In particular, statistical regression analysis has shown that reported competitive acylation data and data for the similar sulfonylation reaction are in excellent agreement with the Brown selectivity relationship and therefore supportive of a σ-complex mechanism.[6c]

Even a stronger case would be presented if *noncompetitive* data for at least one such reaction involving a strong electrophile were obtained. Therefore, we decided to study the benzoylation reaction with our improved vacuum line techniques and thoroughly dried solvents. This approach in both ethylation and benzylation studies yielded reproducible results substantially different from those previously reported.[5,7]

We now report noncompetitive kinetic results for the $AlCl_3$-catalyzed reaction between the electrophile 2,4-dichlorobenzoyl chloride and benzene or toluene in nitromethane at 20 °C.

Experimental Section

Materials. Aromatic Hydrocarbons. Spectral grade benzene and toluene were used throughout. Drying and storage methods are described elsewhere.[5b]

Organic Halides. The 2,4-dichlorobenzoyl chloride (DCBC) obtained commercially was only 98% pure and contained more reactive isomers.[8] The purification procedure used was based upon that reported by Brown and Jensen.[9] A sample of DCBC was treated with small amounts of $AlCl_3$ and toluene (~3 mol % each) under vacuum with stirring and left overnight. Unreacted DCBC was separated by distillation under vacuum and then redistilled under vacuum in a spinning band Perkin-Elmer Microstill Model No. M-131T. The purified DCBC was kept in polyethylene-lined capped bottles under N_2 in the dry box.

The 2,4-dichloro-4′-methylbenzophenone (para product) was generously donated by Dr. L. Fontanella.[10b] The 2,4-dichloro-3′-methylbenzophenone and 2,4-dichlorobenzophenone were synthesized by a standard procedure.[10c] These materials were used to establish GC analytical calibration curves and to establish retention times.

Catalyst. Commercially available $AlCl_3$ often has a pale yellow color which indicates a significant amount of $FeCl_3$ impurity. For purification by sublimation, a glass-tube manifold, consisting of a series of four constrictions spaced about 2 ft apart leading to several attached reservoir tubes, was thoroughly flamed under high vacuum and then purged with dry N_2. The manifold was charged with $AlCl_3$ (~100 g) under a stream of dry N_2, sealed, and evacuated to 10^{-4}–10^{-5} torr. The $AlCl_3$ was sublimed from one chamber to the next using heating tapes (~100 °C) wrapped around the manifold but no closer than ~3 in. from each constriction. The less volatile $FeCl_3$ (bright yellow) tended to crystalize within the nonheated area. Each chamber was sealed off and removed (under vacuum) after all the $AlCl_3$ that would sublime had been transferred to the next chamber under the described conditions. The reservoir tubes containing perfectly white crystals were attached to a smaller glass-tube manifold to which were attached small break-tip ampoules into which the $AlCl_3$

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was transferred by vacuum sublimation for storage. A visual check was then made by melting the contents of each ampoule. Any sample giving a distinct yellow or grey-yellow solution was rejected. About 10 g of $AlCl_3$ of high purity was obtained with this multiple sublimation procedure.

GC Internal Standard. *m*-Nitrotoluene was selected for use as an internal standard for GC analysis because of its retention time and its inertness under the reaction conditions. A commercially obtained sample was dried by distillation from CaH_2 and stored under nitrogen in a foil wrapped glass bottle, fitted with a polyethylene-lined cap, in a dry box.

Solvent. The commercially available nitromethane used contained 95.29% nitromethane, 1.75% nitroethane, 2.77% 2-nitropropane, and 0.19% other impurities (excluding H_2O). (GC analysis: 20 ft, $^1/_8$ in. O.D. copper column, 5% diisodecylphthalate, 5% bentone 34 on Chromosorb W (60/80 mesh)). At first the kinetic data obtained at low $AlCl_3$ concentrations in dried solvent (vide infra) were inconsistent. Professor L. M. Stock[11] alerted us to the fact that the 2-nitropropane impurity alkylates aromatic hydrocarbons in the presence of $FeCl_3$. This may have been the cause of the problem because when the 2-nitropropane content was reduced to <0.03% by cryocrystallization (vide infra), consistent and reproducible kinetic data were obtained for all reactions, including $AlCl_3$ concentrations as low as 0.02 M. *Therefore, we suggest that kinetic data (and conclusions drawn) may be suspect in studies using strong catalysts and impure nitromethane, however dry.*

Cryocrystallization[12] was used for purification. A 50/50 mixture of CH_3NO_2 and diethyl ether was cooled to −60 °C in a dry ice/ethanol bath. The solid CH_3NO_2 was filtered off in a precooled medium frit, washed with cooled ether, and distilled several times to remove residual ether. The purified CH_3NO_2 was then dried by chemical and physical means. Where appropriate, contact with atmospheric moisture was avoided by use of drying tube (P_2O_5) attachments. First, about 250 mL nitromethane was stored over Drierite. Then, it was passed slowly overnight through a glass column (2.5 meters long,12 mm OD, fitted with a medium frit near a Teflon stopcock) packed with Linde Molecular sieves (Type 4A, 14/30 mesh). This partially dried material was stirred (Teflon stirring bar) for 20 min with crushed P_2O_5 pellets before being vacuum distilled at ambient temperature into a manifold (flamed out under vacuum) suitable for apportionment.[13] The ampoules used for storage are described elsewhere.[14] GC analysis (for conditions vide supra) of this purified, dried CH_3NO_2 showed 99.91 (±0.01)% nitromethane, 0.058 (±0.009)% nitroethane, and 0.033 (±0.002)% 2-nitropropane. GC water analysis, described elsewhere,[5b] revealed a water content of 0.005% (wt/wt).

Experimental Procedures. Noncompetitive reactions between $AlCl_3$, 2,4-dichlorobenzoyl chloride (DCBC), and either benzene or toluene in dried, purified nitromethane were carried out at 20.00 ± 0.05 °C in a reaction manifold system described in detail elsewhere.[5b] Upon addition of the $AlCl_3$ to solvent, a pale yellow color often appeared. The remaining components were injected into the solution in the order: *m*-nitrotoluene, aromatic hydrocarbon, and DCBC. The yellow color became progressively more pronounced upon addition of each component and the mixture darkened once the reaction started.[15] Neither phase separation nor precipitation were observed in any run. After injection of DCBC, aliquots were periodically withdrawn with clean, dry syringes and immediately quenched by injection into saturated NaCl solution contained in small bulbulous vials which were then corked and stored in a refrigerator.

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 or 5700A dual flame-ionization instrument. Good separation of the three isomeric products from the toluene runs were obtained with a 9 ft, $^1/_8$ in. O.D. stainless steel column (10% HI EFF 4BP (butanediol succinate) on Gas Chrom Q (60/80 mesh)). It is noteworthy that the use of copper tubing promoted primary and secondary product formation in samples of benzoylchloride and toluene and yielded low isomer percentages, especially for the para isomer. The use of stainless steel circumvented these problems. Characteristic retention times are given below for an N_2 carrier gas flow rate of 20 mL/min and for the following temperatures: injection port 300 °C; oven, 200° C; detector, 300 °C.

compd	retention times, min
benzene	0.5
toluene	0.5
nitromethane	1.0
m-nitrotoluene	2.5
2,4-dichlorobenzophenone	35.0
2,4-dichloro-2′-methylbenzophenone (ortho)	36.0
2,4-dichloro-3′-methylbenzophenone (meta)	45.0
2,3-dichloro-4′-methylbenzophenone (para)	54.0

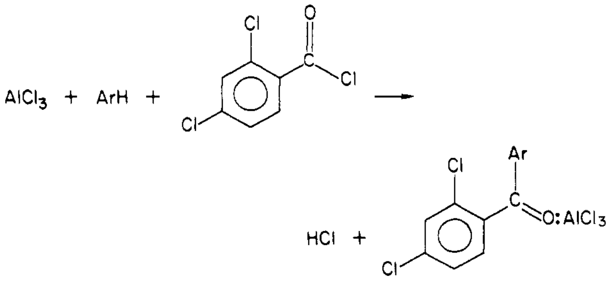
These retention times became shorter the longer the column was used probably because DCBC attacks the packing material. The product from benzene and the ortho isomer from toluene appeared with similar retention times and therefore precluded competitive runs.

Calibration curves correlating peak area ratios and mole ratios of products to internal standard were prepared by using weighed samples of each. The areas were determined by cutting out and weighing Xerographic copies of the peaks.

Data Reduction. Calculations were carried out on a NOVA mini computer from programs prepared in this lab. Initial 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 by using GLC techniques and used to calculate initial rates. Graphs of various first-order, second-order, and third-order correlations of reactant concentrations to the product concentrations produced plotted against time were prepared and inspected for consistency and linearity. All initial rates and rate constants were calculated as slopes by using the least squares method along with the 95% confidence limits and linear correlation coefficients.

Results and Discussion

Aluminum trichloride strongly complexes with product benzophenones[16] in benzoylation reactions of benzene or toluene and therefore functions more as a reactant than as a catalyst. The overall reaction for our study can be written as



(1)

where ArH = aromatic hydrocarbon. The reaction is readily followed at 20 °C in nitromethane with the toluene

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[11] Private communication, 1977; $AlCl_3$ also catalyzes this reaction: Bonvino, V.; Casini, G.; Ferappi, M.; Cingolani, G. M.; Peitroni, B. R. *Tetrahedron* **1981**, *37*, 615.

[12] Parrett, F. W.; Sun, M. S. *J. Chem. Educ.* **1977**, *54*, 448.

[13] It is noteworthy that a gradual darkening of the P_2O_5–CH_3NO_2 mixture occurred at longer stirring times with impure but *not* with the purified CH_3NO_2. In either case, GC analysis of the distillate from this mixture did not detect any unusual impurities when contact time was minimal, i.e., less than 30 min at ambient temperature.

[14] See Figure 3—insert; ref 5b.

[15] Carefully prepared mixtures of $CH_3NO_2/AlCl_3$ are colorless. Addition of benzene or toluene produces yellow colors, darker for toluene. These observations are generally reported (see, for example, Brown, H. C.; Grayson, M. *J. Am. Chem. Soc.* **1953**, *75*, 6285) and are taken as support for the formation of a ternary complex (see ref 17a) in CH_3NO_2.

[16] Gore, P. H.; Hoskins, J. A. *J. Chem. Soc. C* **1970**, 517.

Table I. Initial Reagent Concentrations and Calculated Initial Rates[a] for Acylation of Benzene and Toluene Catalyzed by $AlCl_3$ in Nitromethane at 20 °C

	reactants, M					
run[a]	$[\text{aromatic}]_0$	$[\text{acyl halide}]_0$[b]	$[AlCl_3]_0$	rate ± 95% CL[a]	r[c]	no. pt[d]
1 (B)	0.0317	0.0319	0.0310	$(2.0 \pm 0.7) \times 10^{-7}$	0.8692	14
2 (B)	0.0297	0.0607	0.0316	$(3.5 \pm 0.5) \times 10^{-7}$	0.9553	20
3 (B)	0.1350	0.1513	0.0615	$(5.6 \pm 0.4) \times 10^{-6}$	0.9918	17
4 (B)	0.0331	0.0330	0.0657	$(3.0 \pm 0.2) \times 10^{-7}$	0.9850	23
5 (B)	0.2682	0.2507	0.0867	$(1.9 \pm 0.5) \times 10^{-5}$	0.9876	5
6 (B)	0.2542	0.2451	0.1123	$(1.5 \pm 0.2) \times 10^{-5}$	0.9899	9
7 (B)	0.1887	0.1761	0.1540	$(9.2 \pm 1.0) \times 10^{-6}$	0.9891	12
8 (T)	0.0328	0.0323	0.0177	$(7.2 \pm 0.4) \times 10^{-5}$	0.9559	3
9 (T)	0.0336	0.0325	0.0312	$(6.7 \pm 1.5) \times 10^{-5}$	0.9874	6
10 (T)	0.0347	0.0332	0.0322	$(7.4 \pm 2.4) \times 10^{-5}$	0.9944	4
11 (T)	0.0487	0.0521	0.0365	$(1.5 \pm 1.1) \times 10^{-4}$	0.9985	3

[a] Rates are slopes, calculated by least-squares method, from product concentration vs. time (s) data. The 95% confidence limit is included. B = benzene. T = toluene. [b] 2,4-Dichlorobenzoyl chloride. [c] r = linear correlation coefficient. [d] Number of points, generally for <12% reaction based upon total product concentration.

reaction occurring at a 10-fold faster rate than the benzene reaction at the concentration levels used.

Experimental reagent concentrations are presented in Table I. The smaller concentrations used for the toluene runs insured reasonable sampling times but were one tenth those used by other workers in related systems.[17,18] Further, the limited ranges for both benzene and toluene runs made determination of the reactant concentration orders from intitial rate data difficult.

There was marked curvature to slower rates at longer reaction times in every plot of product concentration vs. time, generally appearing sooner in benzene runs (at ~ 20% total reaction) than in toluene runs (at ~40% total reaction). This behavior may have arisen from the experimental techniques: syringe needles were poked through a rubber septum to withdraw aliquots for quenching and GC analysis. Air leakage through enlarged needle holes in the septum at longer times, or insertion of the heat-dried but air re-equilibrated needles themselves may have allowed H_2O intrusion and concomitant $AlCl_3$ destruction. Regardless of the percentage total reaction at which it occurred, the curvature appeared regularly after about 20 data points, i.e., after about 20 needle insertions.

The initial rates given in Table I were calculated with the least-squares method as initial slopes (generally, <10% total reaction) of the product concentration vs. time date. That the values are reasonably well determined can be seen from the ±95% confidence limits and the linear correlation coefficients. The larger error limits for the toluene runs may reflect the fewer number of points available for calculation rather than scatter in the data.

The results suggest a rate law first order in acid chloride and in aromatic hydrocation but zero order in metal chloride. This can be explained if the rate law in fact resembles eq 2. Near the beginning of the reaction, metal

$$d[\text{product}]/dt = (k_3/[AlCl_3]_0)[\text{acid chloride}][AlCl_3][\text{aromatic}] \quad (2)$$

chloride concentrations are close in value to the initial concentration. These two terms in eq 2 would then cancel yielding an expression for the initial rate that would apparently depend only upon acid chloride and aromatic hydrocarbon concentrations. It is noteworthy that rate laws involving an inverse dependence upon initial metal halide concentration have been reported for the benzoylation reaction catalyzed by several different metal halides.[19]

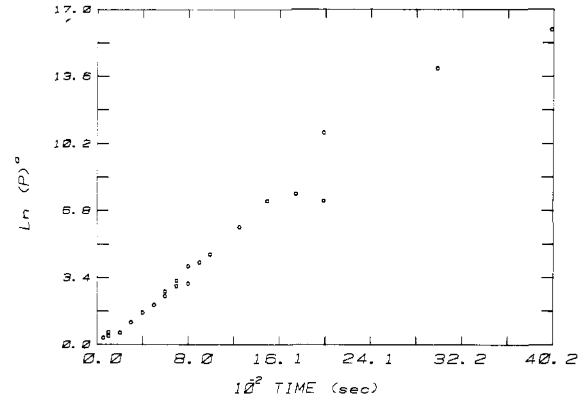

Figure 1. Third-order plot for the reaction of 2,4-dichlorobenzoyl chloride and benzene (run 3) with $AlCl_3$ catalyst in nitromethane at 20 °C. Double points indicate duplicate GC analysis.

$$a \ln P = \frac{1}{(a-b)(b-c)(c-a)} \ln \left(\frac{a-x}{a}\right)^{b-c} \left(\frac{b-x}{b}\right)^{c-a} \left(\frac{c-x}{c}\right)^{a-b}$$

Support for unit order in metal chloride concentration is not found in our initial rate data but may be inferred from studies of similar systems. Brown and Jensen[9] reported a second-order rate law when this reaction is carried out in excess benzoyl chloride. For this system $AlCl_3$ exists completely in a 1:1 complex with the benzoyl chloride solvent. Thus, the rate law is first order in aromatic hydrocarbon and in the benzoyl chloride:$AlCl_3$ complex. Furthermore, for the reaction carried out in nitrobenzene solvent, Brown and Young reported a third-order rate law for benzene runs but a rate law with total order of 7/2 for toluene runs. The metal chloride in their system, and in our system, preferentially forms a 1:1 complex with the solvent rather than with the acid chloride.[20] Thus, the rate law, at least for benzene runs, is first order in aromatic hydrocarbon, in benzoyl chloride, and in $AlCl_3$ as the solvent:$AlCl_3$ complex. From these reports it seemed reasonable to presume unit order in $AlCl_3$ as the solvent:$AlCl_3$ complex, for our system.

Third-order, as well as second-order, rate constants[21] were calculated by the least-squares method as slopes of the appropriate function of product concentration vs. time. Generally, third-order calculations yielded more consistent results than did second order. A typical third-order plot

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[17] Brown, H. C.; Young, H. L. *J. Org. Chem.* **1957**, *22*, 719 and 724.

[18] Olah, G. A.; Kobayashi, S. *J. Am. Chem. Soc.* **1971**, *93*, 6964.

[19] Jensen, F. R.; Brown, H. C. *J. Am. Chem. Soc.* **1958**, *80*, 3039.

[20] (a) Vandyke, R. E.; Crawford, H. E. *J. Am. Chem. Soc.* **1951**, *73*, 2018. (b) Hoornaert, G.; Slootmakers, P. J. *Bull. Soc. Chim. Belg.* **1969**, *78*, 257.

[21] The second-order rate laws tried were rate = k_2[acid chloride][ArH] and rate = k_2[ArH][$AlCl_3$:acid chloride].

Table II. Calculated Rate Constants[a] for the Acylation[b] of Benzene and Toluene Catalyzed by $AlCl_3$ in Nitromethane at 20 °C

run[a]	k_3 ± 95% CL[a]	r[c]	% reactn[d]	k_{3c}[e]
1 (B)	$(5.4 \pm 0.3) \times 10^{-3}$	0.9933	13	$(1.7 \pm 0.1) \times 10^{-4}$
2 (B)	$(5.2 \pm 0.5) \times 10^{-3}$	0.9922	20	$(1.6 \pm 0.2) \times 10^{-4}$
3 (B)	$(5.0 \pm 0.4) \times 10^{-3}$	0.9918	12	$(3.1 \pm 0.3) \times 10^{-4}$
4 (B)	$(4.7 \pm 0.6) \times 10^{-3}$	0.9671	7	$(3.1 \pm 0.2) \times 10^{-4}$
5 (B)	$(3.2 \pm 0.3) \times 10^{-3}$	0.9939	19	$(2.8 \pm 0.2) \times 10^{-4}$
6 (B)	$(2.5 \pm 0.2) \times 10^{-3}$	0.9974	19	$(2.8 \pm 0.2) \times 10^{-4}$
7 (B)	$(2.1 \pm 0.1) \times 10^{-3}$	0.9932	12	$(3.2 \pm 0.2) \times 10^{-4}$
8 (T)	4.2 ± 0.4	0.9859	36	$(7.4 \pm 1.1) \times 10^{-2}$
9 (T)	2.8 ± 0.2	0.9910	42	$(8.7 \pm 0.9) \times 10^{-2}$
10 (T)	2.4 ± 0.1	0.9933	39	$(7.7 \pm 0.6) \times 10^{-2}$
11 (T)	2.4 ± 0.2	0.9981	52	$(8.8 \pm 1.0) \times 10^{-2}$

[a] B = benzene. T = toluene. The constants tabulated are third-order constants, k_3, along with the 95% confidence limits. [b] 2,4-Dichlorobenzoyl chloride. [c] r = linear correlation coefficient. [d] % reaction = the percent reaction. [e] $k_{3c} = k_3[AlCl_3]_0$; along with 95% confidence limits.

Table III. Product Isomer Distribution[a] for Acylation[b] of Toluene in Nitromethane at 20 °C

run[a]	% ortho	% meta	% para	10^3(m/p)
8 (T)	8.8 ± 0.4	0.43 ± 0.08	90.8 ± 0.4	4.8 ± 0.9
9 (T)	8.5 ± 0.3	0.44 ± 0.14	91.1 ± 0.4	4.9 ± 1.5
10 (T)	8.2 ± 0.2	0.39 ± 0.05	91.4 ± 0.3	4.4 ± 0.7
11 (T)	8.1 ± 0.3	0.41 ± 0.05	91.5 ± 0.3	4.8 ± 0.6
av	8.4 ± 0.3	0.42 ± 0.02	91.2 ± 0.3	4.7 ± 0.2

[a] The standard deviations are included. T = toluene. [b] 2,4-Dichlorobenzoyl chloride.

is presented in Figure 1. In our calculations we used points from the beginning of the reaction up to just before the curvature was apparent. The slopes obtained are given as k_3 in Table II along with the 95% confidence limits and linear correlation coefficients which together indicate that the values are well determined. These k_3 values are an inverse function of the initial $AlCl_3$ concentration as can be seen in Figure 2 wherein the pertinent data has been plotted. This trend was generally observed for reactions in relatively nonpolar solvents.[22] Several studies investigating the effect of solvent polarity have not come up with a satisfactory explanation for these trends.[23]

Third-order rate constants corrected for initial $AlCl_3$ concentration, k_{3c}, are included in Table II and show a smaller range of variation than the uncorrected k_3 values. However, the variation that remains still represents a minor difficulty in k_T/k_B comparisons which can be circumvented by comparing rate constants at the same concentration. We chose to use averaged k_3 values obtained for initial $AlCl_3$ concentrations of 0.03 M. These values, $k_T = 2.5 \pm 0.2$ M^{-2} s^{-1} (average for runs 9, 10, and 11, together with standard deviation) and $k_B = 5.3 \pm 0.1 \times 10^{-3}$ M^{-2} s^{-1} (average for runs 2 and 3, together with standard deviation), yield $k_T/k_B = 472 \pm 84$, in good agreement with our previously reported result for this initial $AlCl_3$ concentration.[6c]

The isomer percentage distribution is presented in Table III. The low ortho and meta percentages are in harmony with previous reports of similar reactions[17,18] and suggest a large steric requirement in the reaction process and a high positional selectivity, respectively. Using the meta and para percentages along with the k_T/k_B ratio, we calculate a $b = 1.29$ which is in good agreement with Brown selectivity relationship for which $b = 1.31 \pm 0.2$.[2a]

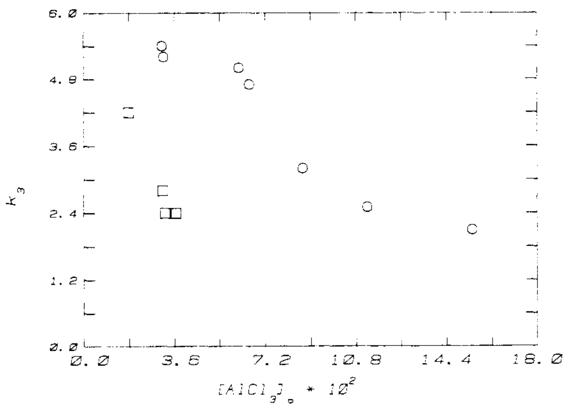

Figure 2. Inverse dependence of third-order rate constants upon initial $AlCl_3$ concentration (toluene (□) k_3, benzene (○) 10^3k_3)

What is surprising here is the marked substrate and positional selectivities of 2,4-dichlorobenzoyl chloride. This compound was chosen partly because of its ready commercial availability but more importantly because it was expected to be a relatively strong electrophile by virtue of the strong inductive electron-withdrawing effect exerted by the chlorines upon the aromatic ring to which they are attached. Indeed, Slootmakers[8] has reported 2,4-dichlorobenzoyl chloride to be 69.6 times as reactive as benzoyl chloride in the $AlCl_3$-catalyzed acylation of toluene in *o*-dichlorobenzene solvent at −3 °C. In systematically varying the ring substituents in benzoyl chloride, Olah found k_T/k_B values ranging from 16 to 233.[18] As expected, his highest ratios occurred for electron-donating groups: *p*-CH_3, *p*-F, 2,4,6 - trimethyl, and *p*-OCH_3. Brown and co-workers[17,24] found ratios of about 150 for benzoyl chloride in good agreement with Olah. Thus, our k_T/k_B ratio of 472 and the product isomer percentages are characteristic of a very weak electrophile instead of a relatively strong one as expected.

We offer an explanation for this surprising result. Both Olah and Brown used initial $AlCl_3$ concentreations ~0.4 M, whereas our values are ~0.03 M. Recall that k_3 decreases with increasing initial $AlCl_3$ concentration. The k_T/k_B ratio may be smaller for our system were it to be evaluated for initial $AlCl_3$ concentrations comparable to those used by Olah and Brown. To illustrate our point, we extrapolated our k_3 vs. initial $AlCl_3$ concentration data for both benzene and toluene and obtained k_T/k_B values of 440, 285, and 181 for $[AlCl_3]_0$ values of 0.11, 0.15, and 0.40, respectively. We realize that these values are not to be taken literally, but the trend does support our proposal.

With regard to the product isomer percentages, if they should remain the same at higher initial $AlCl_3$ concentrations, the possibly lower k_T/k_B ratios obtained would still be statistically in agreement with the Brown selectivity relationship. Using the percentages along with k_T/k_B = 181 obtained by extrapolation, we calculate a $b = 1.14$ which is still within the 95% confidence limits of $b = 1.3 \pm 0.2$. Further, the percentages may in fact not be unusual. Slootmakers[22b,23b] has reported absolute rates and isomer percentages for a number of meta- and para-substituted benzoyl chlorides reacting with toluene and $AlCl_3$ (~0.2 M) in *o*-dichlorobenzene at 25 °C. The absolute rates are in the order expected, with electron-withdrawing groups showing fast rates: *p*-NO_2 > *m*-NO_2 ~ *m*-Cl > *m*-OCH_3 > H > *m*-CH_3 ~ *m*-*t*-Bu > *p*-ipr > *p*-OCH_3. Yet, the reported isomer distributions are essentially identical over the same series. Similar results were reported by Slootmakers[25] for the same reactions carried out in chlorobenzene. It is noteworthy that the Hammett relationship

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[22] (a) For polar solvent effect, see ref 17a and 19. (b) For nonpolar solvent effect, see, for example: Slootmakers, P. J.; Roosen, R.; Verhulst, J. *Bull. Soc. Chim. Belg.* **1962**, *71*, 446.

[23] (a) Jensen, F. R.; Marino, G.; Brown, H. C. *J. Am. Chem. Soc.* **1959**, *81*, 3303. (b) Hoornaert, G.; Slootmakers, P. J. *Bull. Soc. Chem. Belg.* **1969**, *78*, 257 and 295.

failed to correlate the relative reactivities of meta-, para-, and disubstituted benzoyl chlorides in reactions with toluene and AlCl$_3$ in either chlorobenzene or o-dichlorobenzene solvents,[23b,25] but that it successfully correlated relative rates for the reaction of monoalkylbenzenes with AlCl$_3$ and benzoyl chloride in nitromethane solvent at 25 °C.[24]

Finally, we suggest that part of the difficulty in sorting out the kinetic behavior observed for acylations, especially in nitro hydrocarbons, may be an artifact of experimental procedure and data reduction. On the one hand, complexes such as catalyst:solvent, catalyst:benzoyl chloride, catalyst:benzophenone product, and catalyst:solvent:aromatic hydrocarbon are known to exist.[26] In the literature discussions can be found regarding the ionic or nonionic character of the reacting species.[27] Surely, these complexes and species must be in some state of interconversion with one another throughout the course of the reaction.[28] On the other hand, reaction rates determined by rate of benzoyl chloride loss or of product (HCl, ketones) evolution are related directly to reagent concentration in the usual manner by expressions such as

$$[\text{catalyst}]_t = [\text{catalyst}]_0 - [\text{product}]_t \qquad (3)$$

It seems to us that use of this expression simply is not valid, especially for the catalyst, in light of the plethora of complexes possibly existent. Until more is known about the identity of the complexes actually present *and about the interconversion rates or equilibria between these complexes*, mechanistic assignments or discussions seem fruitless.

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Registry No. DCBC, 89-75-8; benzene, 71-43-2; toluene, 108-88-3; 2,4-dichloro-2'-methylbenzophenone, 42600-30-6; 2,4-dichloro-3'-methylbenzophenone, 91385-23-8; 2,4-dichloro-4'-methylbenzophenone, 5953-02-6.

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[24] Brown, H. C.; Bolto, B. A.; Jensen, F. R. *J. Org. Chem.* **1958**, *23*, 414.

[25] Slootmakers, P. J.; Rasschert, A.; Janssens, W. *Bull. Soc. Chim. Belg.* **1966**, *75*, 199.

[26] Indeed, AlCl$_3$ would seem to coordinate to any basic oxygen-bearing species, including the internal GC standard *m*-nitrotoluene, to form 1:1 and perhaps even 2:1 complexes.

[27] For reviews, see: Jensen, F. R.; Goldman, G. In "Friedel-Crafts and Related Reactions"; Olah, G. A., Ed.; Wiley-Interscience: New York-London, 1964; Vol. III, Part 2, pp 1003-1032. Taylor, R. In "Reactions of Aromatic Compounds"; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: London-New York, 1972; Vol XIII. Pross, A. In "Advances in Physical Organic Chemistry"; Gold, V., Bethel, D., Eds., Academic Press: London-San Francisco, 1977; Vol. XIV, p 69.

[28] In ref 19, Brown stated that the reaction did not come to a complete halt for the reaction of AlCl$_3$ and excess benzene carried out in benzoyl chloride as solvent at 49.9 °C. This demonstrates the error in assuming AlCl$_3$ can be treated solely as a reactant.

Electrophilic Aromatic Substitution. 6. A Kinetic Study of the Formylation of Aromatics with 1,1-Dichloromethyl Methyl Ether in Nitromethane

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The reaction between 1,1-dichloromethyl methyl ether (DCME), benzene or toluene, and aluminum chloride or titanium tetrachloride was studied in nitromethane solvent at −27 °C with vacuum line techniques and gas chromatography. For either aromatic the rate law was first order in aromatic, in DCME, and in metal halide as catalyst. With both metal halides, k_T/k_B ratios and product isomer percentages are consistent with Brown's selectivity relationship. Aluminum chloride catalyzed decomposition of DCME was observed at higher temperatures. The side reaction probably invalidates earlier literature results.

Introduction

In our continuing attempt to assist in the resolution of the controversy[2] concerning the mechanism(s) of electrophilic aromatic substitution, we are examining a number of reactions for which the substrate selectivity value k_T/k_B and positional selectivity values (as measured by percent ortho, meta, and para toluene products) yield a slope, *b*, from the Brown selectivity relationship[3] $\log p_f = b \log S_f$ outside the established error limits.

Of the many formylation reactions examined by Olah,[4] only two give slope values well outside the 95% confidence limits (1.31 ± 0.20 determined by Brown and Stock.[3] One of these is the aluminum trichloride catalyzed formylation reaction using 1,1-dichloromethyl methyl ether (DCME) in nitromethane. Therefore a kinetic investigation of this reaction, called Gross' formylation, was undertaken.

Experimental Section

Materials. Our methods of analysis, purification, drying, and storage of nitromethane, benzene, toluene, aluminum chloride, titanium tetrachloride, and internal standards *o*-dichlorobenzene and bicyclohexyl were described previously.[5] MCB, 1,1-di-

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[2] For Example: (a) Olah, G. A. *Acc. Chem. Res.*, **1971**, *4*, 240-248. (b) Santiago, C.; Houk, K. N.; Perrin, C.L. *J. Am. Chem. Soc.* **1979**, *101*, 1337-1340.

[3] Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35-154. Brown, H. C.; Stock, L. M. *J. Am. Chem. Soc.* **1962**, *84*, 3298-3306.

[4] Olah, G. A.; Pelizza, F.; Kobayashi, S.; Olah, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 296-297.