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.

Acknowledgment. Financial support was provided by the Research Corporation and the National Science Foundation (Grant CHE-7707604 and 7915122 and the Undergraduate Research Participation Program). We also wish to thank Dr. L. Fontanella and Avery International Research Center[10a] for their help.

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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(1) (a) National Science Foundation Postdoctoral Fellow 1977–1979. (b) L.A. Pierce College, Woodland Hills, CA 91371.

(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.

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Table I. Rate Constants and Initial Rates for the Aluminum Chloride Catalyzed Reaction of 1,1-Dichloromethyl Methyl Ether with Benzene and Toluene in Nitromethane at -27 °C

reactants,[a] M				initial rate $\times 10^6$M s^{-1}	initial rate $\times 10^3$ / $[DCME]_0[AlCl_3]_0$	initial rate $\times 10^2$ / $[DCME]_0[AlCl_3]_0[C_6H_6]_0$	$10^2 k_{2,app}/[AlCl_3]_0$, M^{-2} s^{-1}	max % reactn[b]
$[C_6H_6]$	$[C_6H_5CH_3]$	[DCME]	$[AlCl_3]$					
0.5530		0.1953	0.0321	73 ± 11[c]	11.6	2.11	1.2 ± 0.2[c]	13
0.1005		0.0538	0.0762	6.8 ± 0.9	1.66	1.65	1.6 ± 0.3	10
0.1057		0.1086	0.0683	11 ± 1	1.48	1.40	1.3 ± 0.1	8
0.2869		0.0623	0.0882	13 ± 2	2.37	0.825	0.83 ± 0.07	25
				av	4.3 (±4.9)[d]	1.5 ± 0.5[d]	1.2 ± 0.3[d]	
	0.2758[e]	0.1033	0.0365				141 ± 45[c]	71

[a] Internal standard, bicyclohexyl. [b] Based on DCME or benzene as limiting reagent. [c] 95% confidence limit. [d] Standard deviation. [e] Toluene product isomer percentages: ortho 41.4 ± 0.1, meta 0.95 ± 0.06, and para 57.7 ± 0.1 (±standard deviation).

Table II. Results of the Aluminum Chloride Catalyzed Competitive Formylation of Benzene and Toluene in Nitromethane at -27 °C

reactants,[a] M				product isomer %			k_T/k_B
$[C_6H_6]$	$[C_6H_5CH_3]$	[DCME]	$[AlCl_3]$	ortho	meta	para	
0.4326	0.4341	0.4348	0.0389	42.3 ± 0.7	0.5 ± 0.3	57.2 ± 0.7	203 ± 20
0.2729	0.0200	0.0592	0.0785	46.4 ± 0.9		53.6 ± 0.9	196 ± 7

[a] Internal standard, bicyclohexyl.

chloromethyl methyl ether ((dichloromethoxy)methane, 4885-02-3), of purity greater than 99% (GC analysis with SE 30 column) was used without further purification. Small amounts of pure benzaldehyde and the tolualdehydes were used to determine GC response calibrations.

Kinetic Procedure. The general kinetic procedure and computerized data evaluation were given previously.[5] Reagents were added in the usual order: to a solution of titanium tetrachloride in nitromethane we injected bicyclohexyl or *o*-dichlorobenzene and then aromatic(s) and initiated the reaction by injecting DCME. Samples were removed by using syringes precooled in -27 °C *n*-heptane.

Because the internal standard bicyclohexyl rather slowly dissolved in nitromethane, particularly at -27 °C, it was necessary to use small amounts and to await total dissolution before starting the reaction. To avoid this problem we switched to the internal standard *o*-dichlorobenzene for all $TiCl_4$-catalyzed reactions.

Analysis. All aliquots were quenched in a saturated NaCl solution. The resulting upper oily layer was gas chromatographed on a Hewlett-Packard 5710A dual flame-ionization instrument fitted with a $^1/_8$ in. 20 ft column packed with 10% diethylene glycol succinate on 80/100 mesh Chromosorb W-AW. Instrument temperatures were oven 150 °C, injection port 200 °C, detector 250 °C. With a He carrier gas flow rate of 30 mL/min retention times were *o*-dichlorobenzene 4 min, benzaldehyde 9.2 min, *o*- and *m*-tolualdehyde 12.2 min, and *p*-tolualdehyde 13.2 min. The three tolualdehydes were separated with a 25 m OV 101 glass capillary column and temperatures were oven 50 °C, injection port 200 °C, detector 250 °C. Typical retention times were *o*-tolualdehyde 51.2 min, *m*-tolualdehyde 52.3 min, and *p*-tolualdehyde 58.1 min.

Results

We have now completed a re-examination of the kinetics of this reaction, again with interesting (and suprising) results. Initially we attempted to follow the benzene and toluene formylation reactions individually. At the temperature used by Olah et al., 25 °C, the aluminum chloride catalyzed toluene reaction was essentially finished within 30 s and went to about 25% completion. The benzene reaction stopped in a few minutes at 5% reaction. When DCME was added to a solution of $AlCl_3$ in nitromethane at 25 °C, a large quantity of HCl gas was evolved.

At -27 °C gas evolution had slowed to the point that assuming a 1:1 DCME:HCl ratio, 1% DCME decomposition had occurred at 300 s and 15% at 6000 s. Because a reasonably high HCl solubility is expected in the polar solvent nitromethane, these decomposition estimates are likely on the low side. However, we decided to attempt kinetic runs at this temperature. These are reported in Tables I and II.

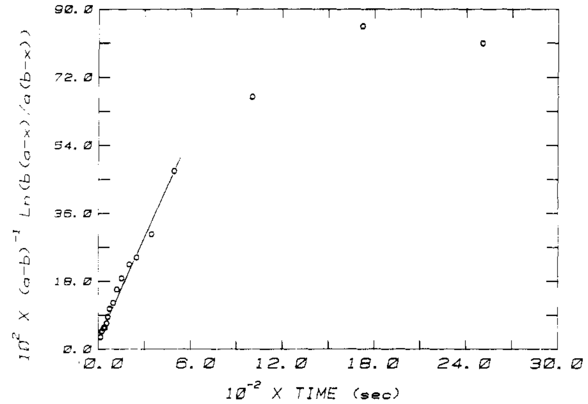

Figure 1. Typical second-order plot of the aluminum chloride catalyzed reaction of 1,1-dichloromethyl methyl ether and benzene (benzene run 3, Table I) in nitromethane at -27 °C.

In order to minimize DCME decomposition this reagent was always added last. As usual our $AlCl_3$-nitromethane solution was colorless and remained so when internal standard bicyclohexyl was added. It turned faint yellow with the addition of benzene (yellow with toluene) and pale pink upon DCME injection. The pink color deepened during reaction and eventually the solution turned dark brown after several days.

The benzene initial rate data is strongly indicative of a third-order rate law, first order in the initial concentration of each reagent, Table I. The yields of benzaldehyde were too low to establish whether aluminum chloride was a true catalyst or a reactant. However, with the faster toluene reaction (Table I) *all* data points had product tolualdehyde concentration well above that of $[AlCl_3]$. Thus complexation between $AlCl_3$ and product aldehydes is not occurring, $AlCl_3$ is a true catalyst and the rate law is

$$\frac{d[\text{product}]}{dt} = k_3[AlCl_3]_0[DCME][\text{aromatic}]$$

where $k_3 = k_{2,app}/[AlCl_3]_0$.

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[5] DeHaan, F. P.; Covey, W. D.; Delker, G. L.; Baker, N. J.; Feigon, J. F.; Ono, D.; Miller, K. D.; Stelter, E. D. *J. Org. Chem.*, preceding paper in this issue.

Table III. Initial Rate Data for Titanium Tetrachloride Catalyzed Formylation of Toluene with 1,1-Dichloromethyl Methyl Ether in Nitromethane at –27 °C

toluene run no.	initial rate $\times 10^5$ M s^{-1}	$\frac{\text{initial rate} \times 10^3}{[\text{DCME}]_0[\text{TiCl}_4]_0}$	$\frac{\text{initial rate} \times 10^2}{[\text{DCME}]_0[\text{TiCl}_4]_0[\text{C}_6\text{H}_6]_0}$	no. pt	r[a]
1	1.3 ± 0.8[b]	4.5	2.2	5	0.953
2	2.1 ± 0.6	3.2	2.4	6	0.977
3	1.8 ± 0.3	3.4	1.9	8	0.989
4	4.2 ± 0.8	1.9	1.8	8	0.983
5	1.4 ± 0.1	7.3	2.4	7	0.996
6	0.28 ± 0.02	1.4	1.4	8	0.997
	av	4 ● 2[c]	2.0 ± 0.4[c]		

[a] Linear correction coefficient. [b] 95% confidence limits. [c] Standard deviation.

Table IV. Rate Constants for the Titanium Tetrachloride Catalyzed Formylation of Benzene and Toluene with 1,1-Dichloromethyl Methyl Ether in Nitromethane at –27 °C

reactants,[a] M				$10^4 k_{2,\text{app}}/[\text{TiCl}_4]_0$, M^{-2} s^{-1}	max % reactn[b]
$[C_6H_6]$	$[C_6H_5CH_3]$	[DCME]	$[TiCl_4]$		
0.2105		0.0476	0.0452	1.63 ± 0.8	2.3
0.4752		0.0572	0.0236	0.59 ± 0.01	4.1
0.05158		0.1146	0.0371	0.67 ± 0.05	8.4
0.2046		0.0995	0.1044	2.8 ± 0.4	6.3
			av	1.4 ± 1.0[c]	
	0.2065	0.0556	0.0520	190 ± 30	44
	0.1338	0.0615	0.1080	250 ± 80	58
	0.1750	0.0994	0.0538	180 ± 20	18
	0.1054	0.1004	0.0220	200 ± 30	10
	0.3035	0.0975	0.0196	240 ± 10	19
	0.1024	0.1019	0.0193	140 ± 10	7
			av	200 ± 40[c]	

[a] Internal standard, *o*-dichlorobenzene. [b] Based on DCME as limiting reagent. [c] Standard deviation.

Table V. Results of the Titanium Tetrachloride Catalyzed Competitive Formylation of Benzene and Toluene in Nitromethane at –27 °C

reactants,[a] M				product isomer %			
$[C_6H_6]$	$[C_6H_5CH_3]$	[DCME]	$[TiCl_4]$	ortho	meta	para	k_T/k_B
0.2499	0.0290	0.0356	0.0387	42.4 ± 0.8	1.2 ± 0.3	56.4 ± 1.1	164 ± 3

[a] Internal standard, *o*-dichlorobenzene.

Because all of the second-order kinetic plots are curved in the latter stages, Figure 1, only the early linear portion is reported. From the average k_3 for benzene data, 1.2 (±0.3) × 10^{-2} M^{-2} s^{-1}, the toluene product isomer percentages, ortho 41.4 ± 0.1, meta 0.95 ± 0.06, para 57.7 ± 0.1, and k_3 value 141 ± 45 M^{-2} s^{-1}, k_T/k_B is calculated to be 120 ± 70 and the Brown slope 1.25. Thus although the data are limited it appears this reaction fits the selectivity relationship.

Although the results shown in Table I are meaningful, we had indicators that some side reaction, possibly involving DCME decomposition, was still occurring. In all cases, benzene product yields are modest. In two runs (not reported in Table I) little (1.7% maximum) or no product was observed. For this reason we decided to limit further study to the competitive approach, taking data only for short reaction times—less than 450 s. The results are given in Table II and yield a Brown slope of 1.20, again a reasonable fit with the selectivity relationship.

To circumvent the problem of DCME decomposition, we switched to the milder catalyst $TiCl_4$. For the system DCME–$TiCl_4$ in nitromethane at –27 °C, no gas evolution was noticeable.

At this temperature toluene formylation proceeds at a convenient pace but the benzene reaction is slow and the product yield is low. However at 0 °C yields were considerably lower, probably again due to DCME decomposition. Therefore all reactions were studied at –27 °C.

As is the case of $AlCl_3$, the titanium tetrachloride formylation reactions slowed perceptibly in the later stages with toluene and even further with benzene. Product benzaldehyde and tolualdehyde concentrations would reach a maximum and then decline afterwards. The reactions, particularly toluene, exhibited satisfactory kinetics in the early stages of reaction and this portion was used for the kinetic study.

Under these circumstances, the initial rates method was used to determine the rate law, Table III. The data is most consistent with a third-order equation, first in each component. The mode of titanium tetrachloride action is unresolved, but since the stronger, Lewis acid, aluminum trichloride, is a catalyst in this reaction it is reasonable to assume this to be the case with $TiCl_4$ as well. Thus $k_{2,\text{app}}/[\text{TiCl}_4]_0$ values are reported in Table IV, with calculated averages for benzene 14 (±10) × 10^{-5} M^{-2} s^{-1} and toluene 2.0 (±0.4) × 10^{-2} M^{-2} s^{-1}.

Although there is a large standard deviation in the k_3 for benzene (reflecting our difficulty in studying this very slow reaction), the calculated value of k_T/k_B of 143 for these noncompetitive results is in agreement with the competitively obtained value of 164, Table V.

For this competitive run product isomer distributions were determined via glass capillary gas chromatography. The average results (±standard deviation) are ortho 42.4 ± 0.8%, meta 1.2 ± 0.3%, and para 56.4 ± 1.1%.

For noncompetitively studied toluene reactions, product isomer distributions were determined with a 20 ft diethylene glycol succinate column. At oven temperatures of 150 °C *o*- and *m*-tolualdehyde eluted as one peak. Tolualdehyde product percentages were constant with time

Table VI. Summary of Competitive Friedel–Crafts Formylation of Benzene and Toluene

formylating agent	catalyst	solvent	temp, °C	k_T/k_B	% tolualdehydes ortho	meta	para	b^a	ref
CO	HF–SbF_5	SO_2ClF	−95	1.6	45.2	2.7	52.1	0.44	4
HCOF	BF_3	excess aromatics	25	34.6	43.3	3.5	53.2	1.38	4
HCN–HCl	$AlCl_3$	excess aromatics	25	49.1	39.9	3.7	56.4	1.50	4
$Zn(CN)_2$–HCl	$AlCl_3$	CH_3NO_2	25	92.8	38.7	3.5	57.8	1.65	4
$Zn(CN)_2$–HCl	$AlCl_3$	excess aromatics	50	128	34.3	1.8	63.9	1.45	4
Cl_2CHOCH_3	$AlCl_3$	CH_3NO_2	25	119	35.8	3.8	60.4	1.75	4
Cl_2CHOCH_3	$AlCl_3$	CH_3NO_2	−27	200	42.3	0.5	57.2	1.20	this work
Cl_2CHOCH_3	$TiCl_4$	CH_3NO_2	−27	164	42.4	1.2	56.4	1.39	this work
CO + HCl	$AlCl_3Cu_2Cl_2$	excess aromatics	25	155	8.6	2.7	88.7	1.60	4
CO + HCl	$AlCl_3$	excess aromatics	0	319	6.6	0.8	92.6	1.37	4
CO + HF	BF_3	excess aromatics	0	860	3.5	0.5	96.0	1.43	4

[a] Calculated slope for Brown selectivity relationship.

and from run to run; the averages were ortho and meta, 44 ± 2% and para 56 ± 2%.

Discussion

The Friedel–Crafts substitution of aromatic hydrocarbons by 1,1-dichloromethyl methyl ether (or the so-called "Gross' formylation") was first reported in 1960 by A. Rieche, H. Gross, and E. Hoft.[6] They reported that many aromatic hydrocarbons, including benzene and toluene, react with α-halo ethers, including DCME, in the presence of Friedel–Crafts catalysts ($AlCl_3$, $TiCl_4$, and $SnCl_4$ were mentioned) to produce the isomeric aromatic ether substitution products. These aromatic ethers, they report, are unstable and decompose when heated and/or hydrolyze in water to the corresponding aromatic aldehydes. Using DCME and the solvents dichloromethane and carbon disulfide they reported a 37% yield with benzene ($AlCl_3$ catalyzed) and an 80% yield with toluene ($TiCl_4$ catalyzed) as well as a para isomer percentage of at least 60% (the rest being predominately ortho). No kinetic data were presented and it was stated that isomer percentages were not further investigated. These values are apparently for reactions run near 0 °C.

More recently Lewin and co-workers[7] found yields were improved in the $SnCl_4$-catalyzed reaction between aromatics and DCME by adding the aromatic slowly to a solution of DCME–catalyst and by using excess DCME. This procedure helped minimize further reaction of the intermediate (postulated as either the chlorobenzyl carbonium ion ArC^+HCl or the methoxybenzyl carbonium ion ArC^+HOCH_3) with aromatic to produce Ar_2CH_2 and possibly Ar_3CH. In all likelihood our low yields are due to similar secondary reactions made unavoidable because we could not, in a kinetic run, add aromatic slowly over 1 h. Indeed, higher temperature glass capillary gas chromatographic analysis of random samples of runs shows a small peak with retention time corresponding to diphenylmethane.

The complication of these secondary reactions apparently is avoidable at early reaction times. The data are reproducible and support a rate law first order in DCME, first order in aromatic, and first order in metal halide as catalyst.

Olah and co-workers reported k_T/k_B values and product isomer percentages for a series of formylation reactions including the aluminum chloride catalyzed substitution of benzene and toluene using DCME. For this reaction run competitively at 25 °C in nitromethane, the reported values are k_T/k_B of 119 and isomer percentages 35.8 *o*-tolualdehyde, 3.8 and *m*-tolualdehyde and 60.4 *p*-tolualdehyde. From these values a Brown slope of 1.75 is calculated, well outside the 95% confidence limits of 1.31 ± 0.20. However as we have shown, extensive DCME decomposition occurs in the presence of aluminum chloride at this temperature. Therefore these results may not be a valid test of the selectivity relationship.

Alternatively one could argue that since substrate selectivity normally decreases with increasing temperature, the differences in the k_T/k_B values reported here for −27 °C and those of Olah at 25 °C may be expected. The major difference in our results then becomes the *m*-tolualdehyde percentage. since tolualdehydes oxidize fairly readily and might do so in the presence of nitromethane in the 200 °C GC injection port, selective oxidation might affect the observed product ratios. We tested and eliminated this possibility by dividing a known, typical mixture of the three tolualdehydes and *o*-dichlorobenzene in two, mixing one half with a typical excess of nitromethane and the other with a comparable amount of cyclohexane, and comparing their GC chromatograms. The peak area ratio of each tolualdehyde to internal standard did not change with solvent. Thus these data show clearly that the difference between apparently anomalous results and normal results could be nothing more than a few percent of the meta product.

In summary, our results at −27 °C with aluminum chloride and titanium tetrachloride yield slope values of 1.20 and 1.39, respectively. Thus it seems clear that Gross' formylation also fits within the family of reactions which follow the selectivity relationship. Furthermore all the other formylation reactions studied by Olah, with the exception of the HF–SbF_5-catalyzed formylation with CO in sulfuryl chloride fluoride at −95 °C appear to fit Brown's theory (Table VI).

Acknowledgment. This work was supported by the National Science Foundation (Grants CHE-7707604 and PRM-7911225 and the Undergraduate Research Participation Program).

Registry No. Cl_2CHOMe, 4885-02-3; $AlCl_3$, 7446-70-0; $TiCl_4$, 7550-45-0; benzene, 71-43-2; toluene, 108-88-3.

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