# Electrophilic Aromatic Substitution. 4. A Kinetic Study of the Friedel-Crafts Benzylation Reaction in Excess Aromatic

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Kinetic studies have been made of the titanium tetrachloride catalyzed reactions between benzyl chloride and benzene or toluene in an excess of the aromatic hydrocarbon at 30 °C. The reaction follows first-order dependence upon benzyl chloride and is second order with respect to catalyst. The results depend strongly on the amount of moisture present. Where moisture is minimized using new vacuum line procedures, the results obtained,  $k_T/k_B = 20 \ (\pm 12)$  and isomer product distribution 41  $(\pm 3)$ % ortho, 6  $(\pm 2)$ % meta, and 53  $(\pm 3)$ % para methyldiphenylmethane, are in good agreement with Brown's selectivity relationship. The reaction mechanism is discussed in terms of attack by a benzyl cation or an ion pair  $[C_6H_5CH_2^+ Ti_2Cl_9^-]$  on the aromatic.

#### Introduction

The ongoing debate regarding mechanisms of electrophilic aromatic substitution<sup>2</sup> has centered around data for fast competitive and noncompetitive reactions (nitration<sup>2</sup> and halogenation<sup>3</sup>), where reaction rates near or at the diffusion-controlled limit make mixing speeds an important factor. Mixing rates should be no problem for the inherently slower benzylation reaction. Therefore conclusions based on kinetic studies of the Friedel-Crafts benzylation reaction may be crucial to the debate.

Unfortunately no benzylation study has given a definitive answer. Brown and Grayson's early work,<sup>4</sup> involving the aluminum chloride catalyzed reaction of 3,4-dichlorobenzyl chloride with aromatics in nitrobenzene, is incomplete in that although the relative benzylation rate of toluene and benzene  $(k_T/k_B)$  was found to be 1.64 by noncompetitive studies, toluene product isomer distributions were not determined. Brown has also published kinetic data for the gallium bromide catalyzed reaction of benzyl bromide with benzene and toluene in excess aromatic.<sup>5</sup> These reactions proved to be exceedingly fast and showed considerable isomerization, so much so that even with a flow reactor, isomer distributions had to be extrapolated to zero time. As the authors themselves point out, the experimental difficulties encountered made this study a questionable one to test Brown's selectivity relationship.

Although the use of milder catalysts such as titanium tetrachloride and basic solvents such as nitromethane suppressed the side reactions, studies by Olah<sup>6</sup> and others,<sup>7</sup> involving benzylation with strong electrophiles, yielded data which did not fit Brown's selectivity relationship. However this is competitive rate data and therefore, at least to the extent these are fast reactions, is open to the same question raised re nitration and halogenation, i.e., are their  $k_T/k_B$  ratios an artifact of slow mixing rates? Olah has not been unresponsive to this question. In a more recent study,<sup>8</sup> he used noncompetitive methods to reevaluate the  $k_T/k_B$  ratio for benzylation. The results appear to substantiate his previous conclusions based on data obtained by competitive methods. Furthermore, the rates observed are moderate and therefore probably not affected by relatively slow mixing rates. However, from Figures 1 and 2 (Figures 6 and 7 of Olah's paper),<sup>8</sup> it appears that benzylation reactions either in excess aromatic or in nitromethane solvent are not straight forward. In both figures the "straight lines" miss the origin and show marked curvature for short reaction times.

This is exceedingly important because it is highly probable that the *true* rate constants are *not* found late, but rather early in the reaction, near zero time. From these figures, it is apparent that *zero time*  $k_T/k_B$  ratios may well be considerably larger than the ratios reported for longer times and further, might fit Brown's selectivity relationship.

Determination of zero time rate constants has proven essential in several related reports. In the kinetic study of the AlBr<sub>3</sub>-catalyzed methylation and ethylation of benzene and toluene in 1,2,4-trichlorobenzene,<sup>9</sup> the rate could be followed only over the early stages of reaction. In the later stages the rate dropped inordinately, perhaps, as suggested, by removal of the catalyst through stable  $\sigma$ -complex formation. Similarly in the GaCl<sub>3</sub>-catalyzed methylation of benzene and toluene in excess methyl chloride,<sup>10</sup> the zero time rate constants fit the selectivity relationship, but because of disproportionation (which could return appreciable amounts of toluene thus effectively lowering  $k_{\rm T}$ ) and/or inhibition through complexation of the catalyst (which would also lower  $k_{\rm T}$  relative to  $k_{\rm B}$ ), the  $k_{\rm T}/k_{\rm B}$  ratio dropped considerably as reactions progressed.

Recently, we decided to re-examine the benzylation reaction in excess aromatic.<sup>11</sup> We felt it was crucial to obtain noncompetitive kinetic data for short reaction times and we picked the milder catalyst TiCl<sub>4</sub> to minimize reaction speed as well as side reactions. Thus our initial approach was to run the reaction much as Olah did, but using es-

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 <sup>(2)</sup> For recent review articles, see: (a) Stock, L. M. Prog. Phys. Org.
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<sup>(9)</sup> Jungk, H.; Smoot, C. R.; Brown, H. C. J. Am. Chem. Soc. 1956, 78, 2185.

<sup>(10)</sup> DeHaan, F. P.; Brown, H. C. J. Am. Chem. Soc. 1969, 91, 4844, 4850.

<sup>(11)</sup> Preliminary communication: DeHaan, F. P.; Covey, W. D.; Anisman, M. S.; Ezelle, R. L.; Margetan, J. E.; Miller, K. D.; Pace, S. A.; Pilmer, S. L.; Sollenberger, M. J.; Wolf, D. S. J. Am. Chem. Soc. 1978, 100, 5944.



Figure 1. Pseudo-first-order plot of TiCl<sub>4</sub>-catalyzed benzylation of toluene and benzene at 30 °C. Reprinted with permission from: Olah, G. A.; Kobayashi, S.; Tashiro, M. J. Am. Chem. Soc. 1972, 94, 7448. Copyright 1972, American Chemical Society.



Figure 2. Pseudo-first-order plot of benzylation of toluene and benzene with antimony pentachloride catalyst in nitromethane solution at 30 °C. Reprinted with permission from: Olah, G. A.; Kobayashi, S.; Tashiro, M. J. Am. Chem. Soc. 1972, 94, 7448. Copyright 1972, American Chemical Society.

### tablished vacuum line procedures.

A similar kinetic study was made of the benzylation reaction in the polar solvent  $CH_3NO_2$ . These results are reported elsewhere.<sup>11,12</sup>

## **Experimental Section**

**Materials.** All reagents (benzene, toluene, benzyl chloride, and TiCl<sub>4</sub>) were obtained in spectral grade quality from commercial sources with better than 99.6% purity by our chromatographic analysis. Except where noted, dehydration was effected by distillation under vacuum from CaH<sub>2</sub>. The amount of moisture in the solvent benzene and toluene was then determined to be  $\leq 0.0006$  weight % (by Poropak Q column-thermal conductivity GC analysis<sup>13</sup>). The benzene, toluene, and TiCl<sub>4</sub> were stored in individual breaktip ampoules of appropriate size. Most glassware was constructed in this laboratory and was dried thoroughly under high vacuum by flame before use.

Titanium tetrachloride (99.95% pure from Research Organic/Inorganic Chemical Corp.) was purchased in breaktip ampoules which could be glassblown to the vacuum line. The TiCl<sub>4</sub> was distilled twice under vacuum at ambient temperatures and then proportioned in small ampoules. The internal standard for chromatographic analysis, bicyclohexyl (Aldrich Chemical), was stored in a dry box under N<sub>2</sub> and used without further purification.

Small samples of (4-methylphenyl)phenylmethane and (3methylphenyl)phenylmethane were synthesized for use in the GC



Figure 3. Apparatus for the benzylation reactions. Insertalternate solvent addition system.

product mixture analysis. The synthesis involved preparation and purification of the intermediate methylbenzophenone using the appropriate toluoyl chloride via Friedel–Crafts acylation. Subsequent reduction of the ketone was accomplished through modification of the Wolff–Kishner reaction.<sup>14</sup> GC analysis of the vacuum distilled products indicated a purity >99%.

General Procedure for Kinetics Studies. A manifold, see Figure 3, was assembled with side arms containing glass enclosed magnetic breaker bars and breaktip ampoules of solvent and catalyst, with a reaction chamber fitted with a small breaktip and containing a small teflon coated stirring bar, and connected to a high-vacuum line. The manifold was dried under high vacuum with a flame, sealed off at constriction A and removed from the vacuum line. In turn each breaktip ampoule was broken open with a magnetic breaker. After the released reagents were condensed into the reaction chamber by means of an applied  $N_{2(1)}$ bath, the amount of catalyst and solvent transferred was determined by weighing the respective broken, empty ampoule after removing it from the line by sealing (constriction B and C). After the last transfer, the manifold was reattached to the vacuum line at D via an arm containing an in-line breaktip and a magnetic breaker bar. After flaming the region D to E, the breaktip at E was broken to allow pressurization with dry  $N_2$  to about 650 torr. The system was sealed off at F and removed to a circulating water bath held at  $30.00 \pm 0.05$  °C. The breaktip atop the reaction chamber was covered by a rubber septum and then broken open with a plugged stiff syringe needle inserted through the septum. At this point the reaction vessel was prepared to receive the remaining chemicals. Rapid stirring was effected by means of a water-driven magnetic paddle immersed in the bath just below, but not touching, the reaction chamber.

Samples of dried benzyl chloride and commercial bicyclohexyl were kept in a dry box under  $N_2$  in separate, paper-wrapped,

<sup>(12)</sup> DeHaan, F. P.; Delker, G. L.; Covey, W. D.; Anisman, M. S.; Brehm, E. C.; Cowan, R. L.; Ferrara, D. M.; Fong, C. H.; Irani, C. D.; Miller, K. D.; Roberts, M. P.; Suh, Y. J.; Williams, E. L., manuscript in preparation.

<sup>(13)</sup> Hogan, J. M.; Engel, R. A.; Stevenson, H. F. Anal. Chem. 1970, 42, 249.

poly-lined screw-cap bottles. A gas-tight syringe of appropriate size was rinsed twice with small aliquots before being filled with a predetermined amount of the chemical. The syringe was weighed outside the dry box on a B5 Mettler Balance, before and after injection of the chemical into the reaction mixture via the septum. A small cork was stuck on the end of the syringe to minimize evaporation. After the last chemical was injected into the reaction mixture, aliquots were periodically removed with clean, dry syringes, injected into small glass vials containing water for quenching the reaction, and stored in a refrigerator.

**Gas-Liquid Chromatographic Analysis.** The aliquots of reaction product mixtures were treated with NaCl<sub>(s)</sub> to effect reasonable separation of aqueous and oily phases.<sup>15</sup> The oily phase was then sampled and analyzed by gas-liquid chromatography on a Hewlett-Packard 5710A dual flame-ionization instrument. Good separation of the three isomeric products from the toluene runs was obtained with a 20 ft  $^{1}/_{8}$  in. OD copper column (5% diisodecylphthalate and 5% bentone 34 on Chromosorb W (60/80 mesh)) and nitrogen as carrier gas. Characteristic retention times are given below for an oven temperature of 150 °C and for a carrier gas flow of 16.6 mL/min.

compd	retention time, min
benzene	2.0
toluene	2.4
nitromethane	3.4
benzyl chloride	5.8
bicyclohexyl	8.8
diphenylmethane	56.4
(2-methylphenyl)phenylmethane	72.6
(3-methylphenyl)phenylmethane	89.2
4-methylphenyl)phenylmethane	95.9

The areas were determined by cutting out and weighing Xeroxed copies of the peaks. Calibration curves correlating peak area ratios and mol ratios for comparison of product peaks with the bicyclohexyl standard compound were prepared by using samples of the commercially available bicyclohexyl and diphenylmethane and of synthesized (3-methylphenyl)phenylmethane and (4-methylphenyl)phenylmethane.

Data Reduction and Evaluation. Calculations were carried out on a NOVA Minicomputer with programs prepared in this lab. Initial concentrations were calculated after correction for moles in the gas phase at 30 °C. Product concentrations and pseudo-first-order parameters  $\ln (A/A - x)$  values plotted against time were prepared and inspected for linearity. The slopes (first 5% reaction or less for initial rates) were calculated along with the 95% confidence limits and linear correlation coefficients.

### Results

Although the titanium tetrachloride catalyzed benzylation reaction

$$C_6H_5CH_2Cl + ArH \xrightarrow{TiCl_4} C_6H_5CH_2Ar + HCl$$
 (1)

#### ArH = benzene or toluene

in excess aromatic was readily followed at 30 °C (even with the faster toluene reactions six or more samples could be removed before one percent reaction), phase separations were common. In most instances a flocculent precipitate appeared when the titanium tetrachloride-aromatic mixture was first thawed, i.e., before the addition of benzyl chloride. Since titanium tetrachloride should be very soluble in benzene or toluene, the logical precipitate would be the  $\sigma$ -complex, formed from HCl produced by the reaction of titanium tetrachloride with minute amounts of water. Of our first eight benzene runs, four proceeded without phase separation. However, only one of eight toluene reactions was completely free of precipitation.



Figure 4. Typical first-order plots for the reaction of benzyl chloride with benzene or toluene in excess aromatic at 30 °C. A = initial concentration of benzyl chloride.  $\Box$  refers to toluene run 4 with  $[TiCl_4]_0 = 0.0174$  M. O refers to benzene run 3 with  $[TiCl_4]_0 = 0.0404$  M.

Table I. Experimental Data for the Titanium Tetrachloride Catalyzed Reaction of Benzyl Chloride with Toluene in Excess Toluene at 30 °C

run	[BzCl] <sub>0</sub>	[TiCl <sub>4</sub> ] <sub>0</sub>	[bicyclo- hexyl]	10 <sup>5</sup> [slope <sup>a</sup> ± 95% C.L.]	r
1	0.4321	0.0358	0.0118	6.2 ± 1.5	0.973
2	0.4145	0.0150	0.0111	$0.74 \pm 0.22$	0.931
3	0.2214	0.0067	0.0127	$0.167 \pm 0.057$	0.972
4	0.3065	0.0174	0.0097	$1.72 \pm 0.15$	0.994
5	0.3436	0.0124	0.0574	$0.320 \pm 0.077$	0.959

<sup>a</sup> First-order plot.

Table II. Experimental Data for the Titanium Tetrachloride Catalyzed Reaction of Benzyl Chloride with Benzene in Excess Benzene at 30 °C

run	[BzCl] <sub>0</sub>	[TiCl <sub>4</sub> ] <sub>0</sub>	[bicyclo- hexyl]	10 <sup>6</sup> [slope <sup>a</sup> ± 95% C.L.]	r
1	0.3617	0.0202	0.0233	$0.451 \pm 0.036$	0.988
2	0.3947	0.0323	0.0293	$1.17 \pm 0.22$	0.966
3	0.5530	0.0404	0.0376	$5.64 \pm 0.41$	0.994
4	0.4700	0.1181	0.0216	$32.31 \pm 0.98$	0.999

<sup>a</sup> First-order plot.

Where was the water coming from? Although extreme care was taken in drying the solvents with calcium hydride and in flaming out the system, one area was not flamed—in fact could not be flamed—and this was the outer wall of the ampoule containing the solvent (Figure 3). Upon switching to an alternate mode of adding solvents (Figure 3—insert) in which all the outside wall were flamed,<sup>16</sup> all runs were completely homogeneous. These results are now reported.

The titanium tetrachloride catalyzed benzylation reaction in excess aromatic clearly follows pseudo-first-order kinetics

$$rate = k_{app}[C_6H_5CH_2Cl]$$
(2)

Typical ln (A/(A - x)) vs. time plots  $(A = [C_6H_5CH_2Cl]_0)$  are presented in Figure 4. It is noteworthy that the graphs are linear and generally pass through the origin within experimental error.

The experimental data are presented in Tables I and II. Each slope is well determined as can be seen from the 95% confidence limits and the linear correlation coefficient.

<sup>(16)</sup> Even though all outside walls were thoroughly flamed with the nonampoule method of adding solvent, the walls of the catalyst ampoule and the glass enclosed breaker bars could not be heated to the "flame-out" temperature. Although the amount of water still present on their wall surfaces after flaming must be very small, it might explain the scatter in our data even with the nonampoule method of adding solvent.

Table III. Product Isomer Distribution for a Typical Titanium Tetrachloride Catalyzed Reaction of Benzyl Chloride with Toluene in Excess Toluene at 30 °C. Data Given Is for Toluene Run 4, Alternate Points

		product isomer distribution			
time, s	% reactn	% ortho	% meta	% para	
25	0.24	43.9	5.2	50. <del>9</del>	
109	0.31	42.5	4.5	53.0	
302	0.63	39.5	5.5	55.0	
502	0.92	37.5	7.8	54.7	
1001	1.88	39.1	4.2	56.8	
2003	3.73	36.8	4.5	58.6	
	ava	$40.3 \pm 1.4$	$5.1 \pm 1.2$	54.6 ± 1.5	

<sup>a</sup> All points.

Table IV. Rate Constants for the Titanium Tetrachloride Catalyzed Benzylation of Toluene in Excess Toluene at 30 °C

		rate constants $\times 10^3$		
run	[TiCl <sub>4</sub> ] <sub>0</sub>	$k_2^a$	k3 <sup>b</sup>	k4 <sup>c</sup>
1	0.0358	1.74	$48.9 \pm 4.8^{d}$	$1.37 \times 10^{3}$
2	0.0150	0.49	$32.8 \pm 4.4$	2.18
3	0.0067	0.25	$37.4 \pm 6.2$	5. <b>6</b> 0
4	0.0174	0.99	56.8 ± 2.6	3.26
5	0.0124	0.26	$20.9 \pm 2.4$	1.69

av  $k_3 = 39(\pm 14^d) \times 10^{-3} L^2 \text{ mol}^{-2} \text{ s}^{-1}$ 

 ${}^{a}k_{2} = k_{app}/[\text{TiCl}_{4}]_{0} \text{Lmol}^{-1} \text{s}^{-1}$ .  ${}^{b}k_{3} = k_{app}/[\text{TiCl}_{4}]_{0}^{2} \text{L}^{2} \text{mol}^{-2} \text{s}^{-1}$ .  ${}^{c}k_{4} = k_{app}/[\text{TiCl}_{4}]_{0}^{3} \text{L}^{3} \text{mol}^{-3} \text{s}^{-1}$ .  ${}^{d} \pm \text{actual standard deviation}$ . Based on the uncertainty of the slope in each run the expected experimental standard deviation is  $\pm 4$ .

Product isomerization and disproportionation are commonplace in Friedel–Crafts alkylation reactions, particularly in weakly basic solvents such as excess aromatics, where  $\sigma$ -complexes are relative stable. In particular, active catalysts such as aluminum and gallium halides are known to isomerize and disproportionate the benzylation reaction product methyldiphenylmethanes in excess benzene.<sup>5,8</sup> However under identical conditions, Olah observed neither side reaction with the milder catalyst titanium tetrachloride.<sup>8</sup>

Our kinetic results support this observation of Olah. From Table III it is apparent that the products are being obtained under kinetically controlled, i.e., nonisomerizing, conditions. Product toluene isomer percentages did not vary with time or from run to run. For all toluene runs the average percentages are ortho  $41 \pm 3$ , meta  $6 \pm 2$ , and para  $53 \pm 3$ .

Under our reaction conditions neither secondary benzylation of the products or polymerization of benzyl chloride were observed. This was true out to 23% reaction, the extent of any of our analyses.

The order with respect to catalyst concentration was determined by comparison of calculated slopes from the pseudo-first-order plots

$$k_{\rm app} = k [\text{catalyst}]_0^n$$

and the corresponding catalyst concentration. As shown in Tables IV and V the order that yielded the most consistent results for the benzene data and for the toluene data was an order of "2". Thus the overall rate law in excess aromatic is

rate = 
$$k_3$$
[TiCl<sub>4</sub>]<sub>0</sub><sup>2</sup>[C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl] (3)

and from the rate constants the  $k_{\rm T}/k_{\rm B}$  ratio is found to be 20 ± 12. The scatter in the data is greater than the expected experimental uncertainty (±3). The scatter reflects the effect of varying minute amounts of moisture (still

Table V. Rate Constants for the Titanium Tetrachloride Catalyzed Benzylation of Benzene in Excess Benzene at 30 °C

		ra	3	
run	[TiCl <sub>4</sub> ] <sub>0</sub>	$k_2^a$	k <sub>8</sub> <sup>b</sup>	k4c
1	0.0202	0.0223	$1.11 \pm 0.05^d$	54.7
2	0.0323	0.0360	$1.12 \pm 0.10$	34.6
3	0.0404	0.140	$3.46 \pm 0.13$	86
4	0.1181	0.272	$2.29 \pm 0.35$	19.3

 ${}^{a}k_{2} = k_{app}/[\text{TiCl}_{4}]_{0} \text{L} \text{mol}^{-1} \text{s}^{-1}$ .  ${}^{b}k_{3} = k_{app}/[\text{TiCl}_{4}]_{0}^{2} \text{L}^{2} \text{mol}^{-2} \text{s}^{-1}$ .  ${}^{c}k_{4} = k_{app}/[\text{TiCl}_{4}]_{0}^{3} \text{L}^{3} \text{mol}^{-3} \text{s}^{-1}$ .  ${}^{d} \pm \text{actual standard deviation}$ . Based on the uncertainty of the slope in each run the expected experimental standard deviation is  $\pm 0.2$ .

present in spite of our efforts<sup>16</sup>).

## Discussion

Olah and co-workers have published extensive studies of the kinetics of the Friedel–Crafts benzylation reaction in excess aromatic<sup>8</sup> and in the more polar solvent nitromethane<sup>6,8,17</sup> (discussed elsewhere<sup>12</sup>). In the case of excess aromatic as solvent they have (properly) used the mild catalyst titanium tetrachloride to minimize isomerization and disproportionation of the products.

Their systematic study of substituent effects on the (electrophile) benzyl chloride through a series of competitive reactions<sup>8</sup> seems to provide clear support for Olah's suggestion that "in electrophilic aromatic substitutions the position of the transition state is not a fixed one but can change with ease from an 'early' one resembling starting aromatics thus being of  $\pi$ -complex (benzonium ion) nature, to one of 'late' character, i.e., resembling intermediate benzenium ion or  $\sigma$ -complex."<sup>18</sup> Olah's data showed the benzylation reaction with benzyl chloride or with substituted benzyl chlorides with electron-withdrawing substituents to be one of low substrate selectivity (low  $k_{\rm T}/k_{\rm B}$ ratios) and relatively high positional selectivity (low meta product percentage), at odds with Brown's selectivity relationship but consistent with Olah's postulated transition state for strong electrophiles, "a transition state of highest energy (which) leads to formation of an oriented  $\pi$ -complex in the substrate selectivity determining step, followed by the formation of  $\sigma$ -complexes for the ortho, para, and meta positions which differ substantially in energy."<sup>8</sup>

Furthermore, Olah has noncompetitive kinetic data for the titanium tetrachloride catalyzed reaction of benzyl chloride with benzene or toluene in excess aromatic which is in good agreement with all his noncompetitive experiments. These results *are* crutical because they show the  $TiCl_4$ -catalyzed reaction to take place at modest speed and under kinetically controlled (rather than diffusion or thermodynamically controlled) conditions. Thus Olah's benzylation studies appear to strongly support his variable transition-state theory.

While we have no difficulty accepting the idea that the transition state does vary in electrophilic aromatic substitution (in fact are driven to it by the change in relative importance of bond making vis a vis bond breaking in the transition state as shown by differing kinetic isotope effects for different reactions<sup>19</sup>), our data reported here clearly show no evidence for Olah's  $\pi$ -complex mechanism for strong electrophiles in the benzylation reaction in excess

<sup>(17)</sup> Olah, G. A.; Kuhn, S. J.; Flood, S. H. J. Am. Chem. Soc. 1962, 84, 1695.

<sup>(18)</sup> Olah, G. A.; Kobayashi, S.; Nishimura, J. J. Am. Chem. Soc. 1973, 95, 564.

<sup>(19)</sup> For some review articles see footnote 28 of ref 2b.

aromatic. On the contrary, the data fits the selectivity relationship<sup>20</sup> (vide infra).

As is typical of Friedel–Crafts alkylation reactions, these benzylation reactions proved to be exceedingly difficult to run in homogeneous, reproducible fashion. Results depend strongly upon the amount of moisture present.<sup>21</sup> With the original ampoule method of transferring solvent (which adds very small, unknown amounts of moisture to the reaction) the average rate constant for the four benzene runs which showed no phase separation was  $k_3 = 1.04 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ . With our improved method which minimized water transfer<sup>16</sup> (Figure 3—insert) the average value dropped by a factor of five to  $k_3 = 2.0 \times 10^{-3} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ .

For toluene runs the effect is less certain since the original ampoule method of solvent transfer produced a precipitate in all but one toluene run. However data from these original runs (one toluene and four benzene) gave  $k_{\rm T}/k_{\rm B}$  of ~6 product isomer distribution similar to those in Table IV. Thus, to this point our data agreed with that reported by Olah.

However, the agreement is not complete. Olah added a small amount of water to each run in an attempt to standardize the effect of moisture in his nonvacuum line procedures.<sup>8</sup> When we injected similar amounts with a syringe we observed almost *immediate* precipitation in all toluene runs and often with benzene runs (as well as a marked acceleration of the rate in both cases). The same results were observed when similar amounts of water were injected into "dry" benzene or toluene runs. Olah stated his reactions were homogeneous even with added water.<sup>8</sup>

Further, the reactions are second order with respect to initial titanium tetrachloride concentration. (Olah assumed a first-order TiCl<sub>4</sub> rate dependence but since in his case all reagent concentrations were identical, this incorrect assumption should have little or no bearing on his  $k_{\rm T}/k_{\rm B}$ value.) Second-order catalyst dependence has also been observed in gallium bromide catalyzed alkylation in excess aromatic,<sup>22</sup> in the reaction of ethyl bromide with benzene or toluene in hexane,<sup>23</sup> and in the gallium chloride catalyzed methylation reaction in excess methyl chloride.<sup>10</sup> While mechanistic details must await the determination of the solute species in the aromatic–TiCl<sub>4</sub>–benzyl chloride system, the kinetics point to a rate-determining step involving the aromatic and a benzyl cation or a 1:2 benzyl chloride:catalyst ion pair (eq 4).

Alternatively the reaction could involve a polarized addition compound  $C_6H_5CH_2^{\delta+}-Cl:^{\delta-}Ti_2Cl_8$ .<sup>10,22</sup> This is less likely since the reaction of benzyl chloride with toluene shows remarkably litle variation in product isomer distribution wih changes in catalyst:  $InCl_3$ ,<sup>7a</sup> FeSO<sub>4</sub>, Fe<sub>2</sub>(S-O<sub>4</sub>)<sub>3</sub>,<sup>24</sup> ZnO, TiO<sub>2</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>-ZrO<sub>2</sub><sup>25</sup> all give product



isomer percentages within experimental error of Olah's and ours, thus supporting the possibility of the benzyl cation as a common electrophile.

Because over 60 reactions have already been shown to correlate with the Brown selectivity relationship, 19,26 it was of interest to see if the titanium tetrachloride catalyzed benzylation reaction in excess aromatic would fit this relationship. In spite of all efforts to avoid the presence of even exceedingly small amounts of moisture, the relative rate value,  $k_{\rm T}/k_{\rm B} = 20 \pm 12$  exhibits a high standard deviation, reflecting our lack of complete success in controlling the moisture problem. Considering the experimental scatter in the data, the results fit the selectivity relationship as well as could be expected. From the calculated partial rate factors  $o_f = 25$ ,  $m_f = 4$ ,  $p_f = 64$  and the selectivity factor  $S_f = 1.25$ , the slope b of the linear free energy equation  $\log p_f = bS_f$  is calculated to be 1.4 in good agreement with Stock and Brown's<sup>19</sup> least-squares slope of  $1.31 \pm 0.10$  (standard deviation).

This is most significant. Olah has already shown the benzylation reaction in excess aromatic to fit the selectivity relationship when the aromatic was attacked by weak electrophiles, e.g., benzyl chloride molecules containing electron-donating substituents.<sup>8</sup> We now find a similar fit to the selectivity relationship with a strong electrophile, the benzyl cation itself. Thus although  $k_T/k_B$  values and product isomer percentages very markedly through this series, thus implying different transition states, it now seems clear that for benzylation in excess aromatic all transition states resemble benzenium ( $\sigma$ -complex) ions.

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**Registry No.** TiCl<sub>4</sub>, 7550-45-0; benzyl chloride, 100-44-7; benzene, 71-43-2; toluene, 108-88-3; (2-methylphenyl)phenylmethane, 713-36-0; (3-methylphenyl)phenylmethane, 620-47-3; (4-methylphenyl)phenylmethane, 620-83-7.

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(21) See van den Berg and Westerink [van den Berg, H.; Westerink, R. M. Ind. Eng. Chem. Fundam. 1976, 15, 164] for a quantitative study

of the role of small amounts of water in the FeCl<sub>3</sub>-catalyzed chlorination reaction.

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