

- (4) L. Polgar and M. Bender, *J. Am. Chem. Soc.*, **88**, 3153–3154 (1966).
 (5) K. E. Neet and D. E. Koshland, Jr., *Proc. Natl. Acad. Sci. U.S.A.*, **56**, 1606–1611 (1966).
 (6) P. I. Clark and G. Lowe, *J. Chem. Soc., Chem. Commun.* 923–924 (1977).
 (7) N. O. Kaplan and M. M. Clotti, "Methods in Enzymology", Vol. 3, Academic Press, New York, N.Y., 1957, pp 253–255.
 (8) R. S. Hayward and S. B. Welss, *Proc. Natl. Acad. Sci. U.S.A.*, **55**, 1161–1168 (1966).
 (9) M. N. Lipsett and A. Peterkofsky, *Proc. Natl. Acad. Sci. U.S.A.*, **55**, 1169–1174 (1966).

Sue Kirkman, Richard Wolfenden*

Department of Biochemistry, University of North Carolina
 Chapel Hill, North Carolina 27514

Received May 22, 1978

A Kinetic Study of the Friedel–Crafts Benzylation Reaction in Excess Aromatic and in Nitromethane

Sir:

Recently reported benzylation results in excess aromatic hydrocarbon and in nitromethane indicate the reaction to be moderate in rate and free of undesirable isomerization and disproportionation side reactions.¹ Benzylation therefore is not subject to the sort of criticism raised concerning the validity of data for fast competitive reactions (nitration² and halogenation³), where mixing rates may be slow compared with the rate of reaction. Thus, the relatively slow benzylation reaction would seem to be an ideal system to test the Brown selectivity relationship in the ongoing debate regarding mechanisms of electrophilic aromatic substitution.⁴

Olah has reported noncompetitive as well as competitive kinetic data for this benzylation reaction.¹ However, the consistency between these results is open to question in that his noncompetitive k_T and k_B values were calculated from first-order plots which are curved (Figures 6 and 7 of ref 1) at early reaction times. Recently, we decided to reexamine the reaction at 30 °C between benzyl chloride and benzene or toluene in excess aromatic and in nitromethane using the mild catalyst TiCl_4 to minimize reaction speed as well as side reactions.

In excess aromatic these benzylation reactions proved to be exceedingly difficult to run in an homogeneous, reproducible fashion. Results depended *strongly* upon the amount of moisture present. Reaction mixtures prepared according to standard vacuum-line procedures with aromatic solvents dried to 0.0006 wt % water showed almost *immediate* precipitation in half the benzene runs and in all but one toluene run. Gas chromatographic data obtained from this toluene run gave a product isomer distribution of 39% ortho, 7% meta, and 54% para. At this point the obtained rate law, first order in benzyl chloride and second order in TiCl_4 , yielded a k_T/k_B of ~ 6 . The isomer percentages and rate constant ratio are in good agreement with values reported in the literature.¹

However, with improved vacuum-line methods to minimize water transfer, reaction mixtures could be prepared that showed no precipitation. Average toluene product isomer percentages obtained are essentially unchanged at $41 \pm 2\%$ ortho, $6 \pm 2\%$ meta, and $53 \pm 3\%$ para.⁵ The products must be formed under kinetically controlled, i.e., nonisomerizing, conditions because individual isomer percentages remain constant with time in any given experiment.

These isomer percentages are well within experimental error of those obtained from the reaction of benzyl chloride with toluene catalyzed by a wide variety of catalysts: InCl_3 ,⁶ FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$,⁷ ZnO , TiO_2 , ZrO_2 , and $\text{TiO}_2\text{-ZrO}_2$.⁸ This lack of sensitivity to the nature of the catalyst supports the possibility of the benzyl cation as a common electrophile in all these reactions.²

Even with improved techniques the rate law remained first

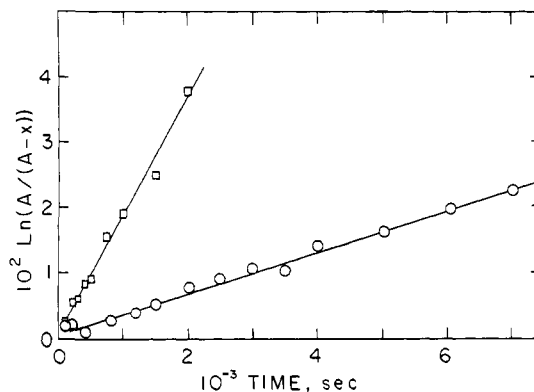


Figure 1. Typical first-order plots for the reaction of benzyl chloride with benzene or toluene in excess aromatic at 30 °C: A = initial concentration of benzyl chloride; \square refers to a toluene run with $[\text{TiCl}_4]_0 = 0.0174 \text{ M}$; \circ refers to a benzene run with $[\text{TiCl}_4]_0 = 0.0404 \text{ M}$.

order in benzyl chloride and second order in TiCl_4 , although the individual rates of reaction for both benzene and toluene showed marked deceleration. With the initial methods, we obtained $k_B = 1.04 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$. With our improved methods, the average value dropped by a factor of five to $k_B = 2.0 \times 10^{-3} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$. The k_T obtained = $3.9 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$. Typical pseudo-first-order plots are given in Figure 1.

The relative rate value, $k_T/k_B = 20 \pm 12$ exhibits a high standard deviation, reflecting our lack of complete success in controlling the moisture problem. Considering the experimental scatter in the data, our results fit the Brown 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's⁹ least-squares slope of 1.31 ± 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.¹ 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 vary markedly through this series, thus implying different transition states, it now seems clear that for benzylation in excess aromatic *all* transition states resemble benzenium (σ complex) ions.

In nitromethane the benzylation reaction was readily followed at 30 °C. There were no difficulties with phase separation in this solvent. Solution homogeneity was maintained even after we purposefully injected small amounts of H_2O .¹⁰ However, minor amounts of H_2O did affect the reaction rate. Only after lowering the H_2O content of the solvent to 0.005 wt % did we obtain consistent results.

From a noncompetitive initial rate study the rate law was found to be rate = $k_4[\text{benzyl chloride}][\text{TiCl}_4]_0^3$.

There is an internal check possible for this unusual rate law because the rate expression can be written as rate = $k_{\text{app}}[\text{benzyl chloride}]$ where $k_{\text{app}} = k_{n+1}[\text{TiCl}_4]_0^n$. Values of rate constants corresponding to " n " = 2, 3, 4 were calculated and the best agreement found was for " n " = 3. The pseudo-first-order plots were linear and passed through the origin. From four benzene runs, $k_B = 2.14 \pm 0.11 \text{ M}^{-3} \text{ s}^{-1}$; from three toluene runs, $k_T = 2.19 \pm 0.59 \text{ M}^{-3} \text{ s}^{-1}$.

We should like to point out the significance of the zero-order dependence of the rate upon the aromatic hydrocarbon concentration for this reaction. It indicates that the rate-determining step is the formation of the electrophile—not the sub-

sequent attack on aromatic hydrocarbon. Therefore, the k_T/k_B determined noncompetitively does not reflect the relative reactivity of toluene over benzene, and thus can not be used to test the Brown selectivity relationship.

On the other hand, a k_T/k_B determined by competitive methods can be used.¹¹ Our preliminary results based upon three competitive runs indicate a $k_T/k_B = 2.5 \pm 0.1$, together with a toluene isomer product distribution of $45 \pm 2\%$ ortho, $6 \pm 1\%$ meta, and $49 \pm 2\%$ para. These values remained reasonably constant even after the addition of small amounts of H₂O. The isomer percentages are also in satisfactory agreement with values obtained by noncompetitive means: % ortho = 44 ± 3 , % meta = 7 ± 1 , and % para = 49 ± 3 .

It is noteworthy that the toluene product isomer percentages are essentially constant and consistent from run to run, whether competitive or noncompetitive, at longer times as well as short times, and regardless of H₂O concentration. These facts also support the proposal of a common electrophilic species reacting with the aromatic hydrocarbon substrates.

Our competitive results appear to be an exception to the Brown selectivity relationship. Whether this is a fundamental discrepancy or an experimental artifact remains to be seen. Further work, particularly that dealing with mixing control, is underway in our laboratory.

Acknowledgment. Financial assistance from the Research Corporation and the National Science Foundation Undergraduate Research Participation Program is gratefully acknowledged. We also thank Professor L. M. Stock for a helpful discussion.

References and Notes

- (1) G. A. Olah, S. Kobayashi, and M. Tashiro, *J. Am. Chem. Soc.*, **94**, 7448 (1972).
- (2) For a recent review article, see L. M. Stock, *Prog. Phys. Org. Chem.*, **12**, 21 (1976).
- (3) For example, S. Y. Caille and R. J. P. Corriu, *Chem. Commun.*, 1251 (1967).
- (4) G. A. Olah, *Acc. Chem. Res.*, **4**, 240 (1971).
- (5) Throughout this paper data uncertainty is expressed as \pm standard deviation.
- (6) O. Tsuge and M. Tashiro, *Bull. Chem. Soc. Jpn.*, **40**, 125 (1967).
- (7) K. Arata and I. Toyoshima, *Chem. Lett.*, 929 (1974).
- (8) K. Arata, N. Azumi, and H. Sawamura, *Bull. Chem. Soc. Jpn.*, **48**, 2944 (1975).
- (9) L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963).
- (10) Olah added a small amount of water to each run in an attempt to standardize the effect of moisture in his non-vacuum-line procedures.¹
- (11) J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity", Cambridge University Press, New York, N.Y., 1971, p 46; C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, 905 (1938); L. P. Hammett, "Physical Organic Chemistry", 2nd ed, McGraw-Hill Co., New York, N.Y., 1970, p 91.
- (12) Teaching-Research Postdoctoral Fellow, 1974-1976. Supported by Research Corporation.

Franklin P. DeHaan,* William D. Covey¹²
 Mark S. Anisman, Robert L. Ezelle, Joanna E. Margetan
 Kurt D. Miller, Steven A. Pace, Sharon L. Pilmer
 Michael J. Sollenberger, Daryl S. Wolf
 Department of Chemistry, Occidental College
 Los Angeles, California 90041
 Received May 1, 1978

Kinetics of the Silane and Silylene Decompositions under Shock Tube Conditions

Sir:

We have studied the silane decomposition in a single pulse shock tube at temperatures between 1200 and 1300 K, and can conclude from our results (Tables I-III) that at shock temperatures the initiation reaction for the silane decomposition is the H₂ molecular elimination reaction (1) and not the bond fission process (2). These were the initiation reactions first

Table I. Hydrogen Products from Decompositions of Silane (1250 K)

	% reactants in argon			hydrogen product ratios, H ₂ :HD:D ₂
	SiH ₄	SiD ₄	toluene	
1	1.00	1.00	0.00	2.94:2.50:1.00
2		0.50	1.00	0.29:1.00
3		0.10	1.00	0.94:1.00
4		0.01	1.00	0.91:1.00

Table II. Rate Constants for SiH₄ Loss at 1250 K^{a,b}

% SiH ₄ in argon	ln [(SiH ₄) ₀ / (SiH ₄)]	$k \times 10^{-4} \text{ s}^{-1}$
1.00	1.36	1.13
0.10	1.66	1.38
0.01	1.46	1.22

^a Residence times at shock temperatures were $T \approx 120 \pm 5 \mu\text{s}$.

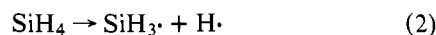
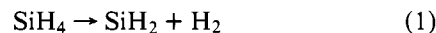
^b Silane concentrations before and after the shock were measured by mass spectroscopy relative to xenon as an internal standard at a concentration 3.13 times that of the SiH₄.

Table III. Preliminary Kinetic Data for Dissociation Reaction 1

no. of runs	$\tau, \mu\text{s}$	T, K	$k \times 10^{-4} \text{ s}^{-1a}$
3	140 \pm 5	1204	0.285 \pm 0.032
5	120 \pm 5	1250	1.056 \pm 0.071
5	100 \pm 5	1304	1.857 \pm 0.153

^a Errors shown are $\pm \sigma$ (1 standard deviation).

proposed as possibilities by Purnell and Walsh¹ on the basis of their thorough and pioneering study of the silane pyrolysis at temperatures between 653 and 703 K.



The first entry of Table I shows the hydrogen isotope product ratios generated in the copyrolysis of equimolar mixtures of SiH₄ and SiD₄ at 1250 K. Clearly hydrogen atom processes are as evident at shock temperatures as they were in lower temperature static studies.² Under single pulse shock conditions, with the possible exception of some very fast H-atom reactions, only homogeneous and unimolecular reactions are possible. The rate constant data of Table II support this expectation. Thus there is no apparent variation in the rate constants of dissociation with silane concentration. Hence there is no chain dissociation of silane in either the shock period or in the subsequent cool-down period. The rate constants observed then apply to the initial silane dissociation process. Further, since the observed rate constants are five orders of magnitude larger than the rate constant value expected for reaction 2 at 1250 K,³ it is clear that the initiation reaction of the silane pyrolysis must be reaction 1.

In a start toward obtaining the Arrhenius parameters of reaction 1, a total of 13 pyrolyses covering the 1200-1300 K temperature range were made. Results (shown in Table III) are tentative and not particularly reliable since the temperatures noted were calibrated from the extent of cyclohexene dissociation in separate studies under similar shock conditions (i.e., an external method). The usual Arrhenius least-square analysis of the rate constant data give parameters of $A_1 = 10^{13.7 \pm 0.3} \text{ s}^{-1}$ and $E_1 = 56.1 \pm 1.7 \text{ kcal/mol}$. However, transition-state considerations indicate that this A factor is certainly too low for the high pressure limiting reaction.⁴ Strausz and Neudorfl⁵ have recently studied the static system ($T \approx 700 \text{ K}$) pyrolysis kinetics of CH₃SiH₃ and (CH₃)₂SiH₂ in