

filled with steam to a height above the solvent level. The magnet was repeatedly raised to the top with an external magnet and dropped. Its fall to the bottom from a mark 24 cm up was timed. Terminal velocity was clearly reached well above the mark. Densities were measured at 100 °C in 5-mL volumetric flasks.

n-Octane: 1.6, 1.4, 1.6, 1.4, 1.6, 1.6, 1.6, 1.6, 1.6, s; average 1.56 ± 0.067; density 0.643.

Isooctane: 1.6, 1.4, 1.4, 1.6, 1.4, 1.4, 1.6, 1.4, 1.4 s; average 1.46 ± 0.084 s; density 0.631.

Octacosane: 8.0, 8.0, 8.0, 8.0, 8.0, 8.0, 8.0, 8.0, 8.0, 8.2 s; average 8.02 ± 0.02 s; density 0.755.

Nujol: 19.6, 19.6, 20.0, 19.8, 19.8, 20.0, 20.0, 19.4, 19.8, 19.8 s; average 19.78 ± 0.148 s; density 0.831.

Nujol-polyethylene: 81.8, 81.8, 81.8, 81.8, 82.0, 81.8, 81.8, 81.6, 81.8, 81.6 s; average 81.78 ± 0.070 s; density 0.835.

Glyme: 1.6, 1.4, 1.4, 1.6, 1.4, 1.6, 1.6, 1.4, 1.6, 1.4 s; average 1.50 ± 0.10 s; density 0.812.

Diglyme: 2.0, 2.0, 2.0, 2.0, 2.2, 1.8, 2.0, 1.8, 2.0, 2.0 s; average 1.98 ± 0.072 s; density 0.891.

Triglyme: 2.4, 2.4, 2.4, 2.4, 2.6, 2.4, 2.4, 2.4, 2.6, 2.4 s; average 2.44 ± 0.064 s; density 0.937.

Tetraglyme: 3.2, 3.2, 3.2, 3.2, 3.2, 3.2, 3.2, 3.0, 3.2 s; average 3.18 ± 0.036 s; density 0.966.

For the four glymes, falling times and densities were also determined at 25 °C, giving exactly the same relative viscosities.

The magnet used weighed 0.2176 g and occupied 0.068 ± 0.001 mL, density 3.20. The relative viscosities were calculated from eq 6 in which η = viscosity, D = density of the magnet, d = density

$$\frac{\eta}{\eta_s} = \frac{(D-d)t}{(D-d_s)t_s} \quad (6)$$

of the liquid, and t = falling time.³⁴

Registry No. 1, 1746-13-0; 4, 56948-77-7.

(34) F. Daniels, J. H. Mathews, and J. W. Williams, "Experimental Physical Chemistry", 3rd ed., McGraw-Hill, New York, 1941, p 326.

Investigation of Valency of Carbocationic Intermediates by use of Potential Energy Diagrams

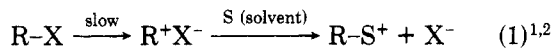
Steven G. Shafer and J. Milton Harris*

Department of Chemistry, The University of Alabama in Huntsville, Huntsville, Alabama 35899

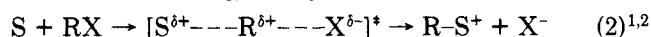
Received September 26, 1980

More O'Ferrall-type potential energy diagrams are constructed for the Doering-Zeiss mechanism for nucleophilic aliphatic substitution and for the conventional mechanism in which rate-determining ionization proceeds without nucleophilic solvent assistance. These diagrams, used in conjunction with α -deuterium isotope effects and m values for benzhydryl chloride solvolyses, give predictions of structural variations in transition states that are consistent with either a Doering-Zeiss reaction mechanism or with a conventional ion-pair mechanism. The important point is that the generally ignored Doering-Zeiss mechanism is a viable alternative that should be added to the already complex mechanistic situation for solvolysis reactions.

Some 25 years ago Doering and Zeiss presented an interesting elaboration of Hughes' and Ingold's classical S_N1 (without nucleophilic assistance, eq 1)^{1,2} and S_N2 (with nucleophilic assistance, eq 2)^{1,2} mechanisms for nucleo-

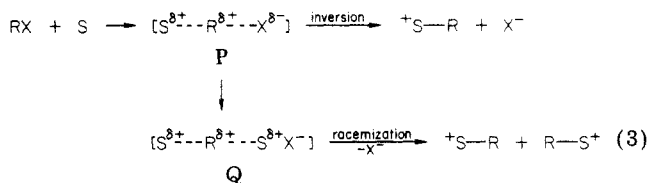


S_N1 or k_c mechanism



S_N2 or k_s mechanism

philic aliphatic substitution.³ According to Doering and Zeiss, a few substrates can react by rate-determining ionization without nucleophilic solvent assistance (i.e., according to eq 1), but most substrates, including many tertiaries, react with nucleophilic solvent assistance as shown in eq 3. According to this scheme, species P may be a transition state, as it is in a simple S_N2 reaction, or it may be an intermediate.



(1) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed; Cornell University Press: Ithaca, New York, 1969.

(2) Schleyer, P. v. R.; Fry, J. L.; Lam, L. K. M.; Lancelot, C. J. *J. Am. Chem. Soc.* 1970, 92, 2542.

(3) Doering, W. v. E.; Zeiss, H. H. *J. Am. Chem. Soc.* 1953, 75, 4733.

Thus, Doering and Zeiss have introduced a third type of substitution pathway, which is proposed as occurring for substrates with intermediate ability to stabilize a carbocation and which involves nucleophilic solvent assistance to yield a pentavalent carbocationic intermediate. This mechanism was postulated to explain the excess inversion of configuration observed in reactions of tertiary derivatives previously thought to react without nucleophilic solvent assistance. Reference to eq 3 shows that the balance between inversion and racemization can be explained by assuming varying proportions of intermediates P and Q.

In the intervening years the Doering-Zeiss mechanism has been generally ignored, although the concept of a pentavalent intermediate has been invoked to explain the solvolysis of derivatives (e.g., secondaries) clearly reacting by a k_s mechanism.⁴⁻⁸ In only a few instances has it been suggested that nucleophilic assistance in simple tertiary substrates leads to an intermediate such as I.⁹ Bordwell

(4) Winstein, S.; Darwish, D.; Holness, N. H. *J. Am. Chem. Soc.* 1956, 78, 2915.

(5) Martin, J. C.; Basalay, R. J. *J. Am. Chem. Soc.* 1973, 99, 2972.

(6) Hayami, J.-I.; Tanaka, N.; Hihara, N.; Kawai, A. *Tetrahedron Lett.* 1973, 385.

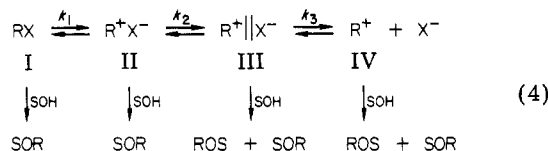
(7) (a) Harris, J. M. *Prog. Phys. Org. Chem.* 1974, 11, 89. (b) Friedberger, M. P.; Thornton, E. R. *J. Am. Chem. Soc.* 1976, 98, 2861.

(8) (a) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* 1977, 99, 4219. (b) Radom, L. "Modern Theoretical Chemistry"; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 4, Chapter 8. (c) Dannenberg, J. J. *J. Am. Chem. Soc.* 1976, 98, 6261.

(9) (a) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1976, 98, 7658. (b) Bentley, T. W.; Bowen, C. T. *J. Chem. Soc.* 1978, 557.

and Grob have described such a possibility for specially constructed molecules.¹⁰

The Doering-Zeiss explanation has not often been applied to reaction of tertiary and related substrates, probably because of the indisputable kinetic evidence that such substrates react with nonsolvent nucleophiles (such as azide) after rate-determining unimolecular formation of an intermediate. If bimolecular displacement of the leaving group by a powerful nucleophile such as azide is not energetically competitive, then it can be reasoned that neither would a similar reaction with the much more weakly nucleophilic solvent be favored.¹¹ An alternative, generally accepted explanation for the confusing stereochemical results of Doering and Zeiss is provided by assuming that nucleophilic attack occurs after rate-determining, unimolecular formation of trivalent ion-pair intermediates (eq 4).^{6,12} Also, operation of the Doering-Zeiss



mechanism for S_N1-type substrates appears to be ruled out by recent measures of nucleophilic solvent involvement^{6,13,14} which indicate that nucleophilic solvent assistance is important for primary and simple secondary (e.g., isopropyl) derivatives, vanishingly small for sterically congested secondary derivatives (e.g., 2-adamantyl),¹⁵ and absent for tertiary and resonance-stabilized secondary (e.g., benzhydryl) derivatives.^{16,17} However, recent work from our laboratory is interesting in this regard. In this work we found both *tert*-butyl chloride and *tert*-butyl bromide to react more slowly than expected in the weakly nucleophilic solvent aqueous trifluoroethanol.^{14b} We explained this result by assuming that destruction of the *tert*-butyl cation becomes rate limiting in the absence of a good nucleophile or base. Alternatively, it could have been concluded on the basis of this experiment alone that the *tert*-butyl derivatives were receiving nucleophilic solvent assistance (a *k_s* mechanism) and were reacting slowly in aqueous trifluoroethanols because of the weakness of this assistance in this solvent;¹⁰ precisely the same reactivity pattern is observed for known *k_s* substrates such as the simple secondary derivatives. This *k_s* mechanism was considered unlikely in the reaction of the *tert*-butyl derivatives for the reasons presented above; actually, however, there was

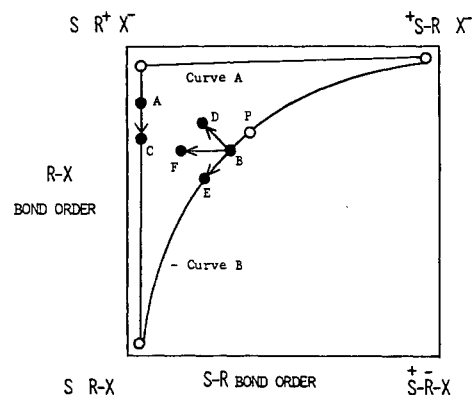
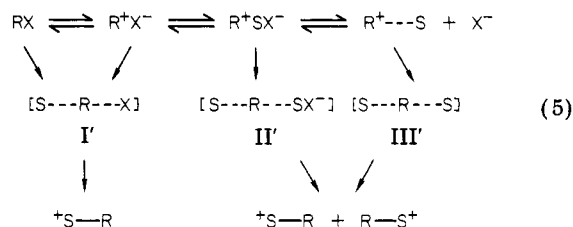


Figure 1. More O'Ferrall plots for an S_N1 mechanism (eq 1, curve A) and for the Doering-Zeiss mechanism (eq 3, curve B); the P to Q pathway is not shown. Minima and maxima are represented by open and closed circles, respectively.

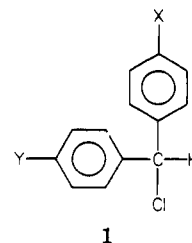
no good basis for distinguishing between the two mechanistic possibilities. Recently in a similar study, Bentley and co-workers^{9b} have concluded that *tert*-butyl derivatives do solvolyze with nucleophilic solvent assistance and further that nucleophilically solvated, ion-pair intermediates are formed.

It should be noted that the Doering-Zeiss and ion-pair mechanisms can be merged by including the possible formation of pentavalent intermediates in the ion-pair scheme (eq 5).¹² In this scheme I'-III' can be intermediates or transition states, and S represents solvent.



Experimental Test

Thus, there is little experimental evidence relating to the Doering-Zeiss mechanism, and it appears in most instances to have been ignored for less-than-concrete reasons. The purpose of the present work is to examine the Doering-Zeiss hypothesis by searching for evidence of nucleophilic involvement in the formation of a solvolytic intermediate. We have chosen to study the reaction of substituted benzhydryl derivatives **1** because there is ev-



(9) (a) Frisone, G. J.; Thornton, E. R. *J. Am. Chem. Soc.* **1968**, *90*, 1211. (b) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *Ibid.* **1979**, *101*, 2486. (c) Burton, G. W.; Sims, L. B.; Wilson, J. C.; Fry, A. *Ibid.* **1977**, *99*, 3371.

(10) (a) Bordwell, F. G.; et al. *J. Am. Chem. Soc.* **1975**, *97*, 118, 123, 127, 132. (b) Grob, C. A.; Seckinger, K.; Tam, S. W.; Traber, R. *Tetrahedron Lett.* **1973**, 3051.

(11) Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4821.

(12) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley: New York, 1974; Chapter 3.

(13) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

(14) (a) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137. (b) Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *Ibid.* **1978**, *100*, 8147.

(15) For discussion of other crowded secondaries see: Smith, M. R.; Harris, J. M. *J. Org. Chem.* **1978**, *43*, 3588. Harris, J. M.; Mount, D. L.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 3139.

(16) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540.

(17) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977.

(18) For leading references see: (a) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295; (b) Jencks, D. A.; Jencks, W. P. *Ibid.* **1977**, *99*, 7948.

to answer is this: do benzhydryl derivatives solvolyze to yield an intermediate according to eq 4, (i.e., without nucleophilic solvent assistance) or according to eq 3 (i.e., with nucleophilic solvent assistance)? Part of the answer can be obtained by use of More O'Ferrall-type potential energy plots.¹⁸

The reaction coordinate for the classical S_N1 mechanism (eq 1), or for a corresponding segment of eq 4 which might be rate determining, is as shown in curve A of Figure 1, and that for the Doering-Zeiss mechanism (eq 3 with P being an intermediate) is as shown in curve B of Figure 1. The important point regarding the Doering-Zeiss mechanism is that there is S-R bond formation in transition state B, and thus the reaction coordinate must be diagonally arranged between reactants and products at point B.

The upper left corner (S R⁺ Cl⁻) of this potential energy surface can be stabilized by placing electron-donating substituents on the benzhydryl system at positions X and Y in 1. This change in the potential energy surface produces quite different results for the transition states A and B on curves A and B. According to the modified¹⁸ rules of Thornton,¹⁹ the primary effect of stabilizing the upper left corner will be to move transition state A to point C (parallel movement away from the stabilization)¹⁸ and transition state B to point D (perpendicular movement toward the stabilization); continued perpendicular motion would change curve B to curve A. Therefore, if benzhydryl chloride undergoes solvolysis by the S_N1 mechanism (i.e., curve A is followed), then substituting electron-donating groups on the benzhydryl system should result in an earlier transition state that is more crowded and that has less charge development.²⁰ In contrast, if the reaction is in accord with the Doering-Zeiss mechanism (curve B), the substitution should shift the transition state so that it has more R-Cl bond cleavage and less S-R bond formation; such a transition state is well described as being "looser".

These distinct predictions can be examined experimentally by determining kinetic α -deuterium isotope effects (α -*d*) and responses to altered solvent ionizing power (the Winstein-Grunwald *m* value)²¹ as a function of variation of X and Y in 1. As Shiner has clearly demonstrated,²² the magnitude of the α -*d* is a sensitive function of differences in crowding between reactant and transition state, such that the larger the decrease in crowding the larger the isotope effect. In that an increase in crowding results from the earlier S_N1 transition state (Figure 1, curve A), it should also lead to a reduction in the α -*d*; if the Doering-Zeiss mechanism obtains, an increase in α -*d* should result from substitution of electron-donating substituents since this produces a looser transition state (Figure 1, curve B). The *m* value has been shown to vary from near unity (for the reaction of neutral substrates via transition states having extensive charge development) to small fractional values (for reaction via transition states having little charge development).²³ Also, dispersal of charge because of nucleophilic-solvent and neighboring-group involvement has been demonstrated to lower the *m* value.²³ Thus for the S_N1 mechanism, substitution of electron-donating substituents on the benzhydryl chloride

Table I. *m* Values and α -Deuterium Isotope Effects for the Solvolysis of Substituted Benzhydryl Chlorides, XC₆H₄CHClC₆H₄Y^a

X	Y	<i>m</i>	α - <i>d</i> ^b
H	CH ₃	0.860 ± 0.014	
H	H	0.813 ± 0.004	1.16 ± 0.01
H	Cl	0.781 ± 0.003	1.14 ± 0.01
Cl	Cl	0.765 ± 0.006	1.11 ± 0.01

^a Errors are standard deviations of the mean (experimental Section). ^b α -Deuterium isotope effect determined in 80% ethanol.

Table II. Solvolysis Rates for Substituted Benzhydryl Chlorides, XC₆H₄CHClC₆H₄Y, at 25 °C^a

		10 ⁴ <i>k</i> , s ⁻¹			
X	Y	<i>k</i> _H (90E)	<i>k</i> _H (80E)	<i>k</i> _D (80E)	<i>k</i> _H (70E)
H	CH ₃	6.69 ± 0.07 ^b	29.5 ± 0.07 ^b		
H	H	5.10 ± 0.02	20.8 ± 0.1	17.9 ± 0.1	
H	Cl	1.91 ± 0.01	7.35 ± 0.02	6.47 ± 0.04	
Cl	Cl		2.89 ± 0.02	2.59 ± 0.03	8.30 ± 0.07

^a The symbols 90E, 80E, and 70E represent the percentage (volume/volume) of ethanol in water. Error limits are given as standard deviation of the mean. The symbols *k*_H and *k*_D represent rate constants for substrates containing α -protium or α -deuterium, respectively. ^b At 0 °C.

should lead to a lower *m* value, while for the Doering-Zeiss mechanism this substitution should lead to a higher *m* value.

The experimentally determined *m* values and the α -*d*'s for the aqueous ethanolysis of four substituted benzhydryl chlorides, 1, are presented in Table I, and the data from which these parameters were derived are presented in Table II. These particular substrates were chosen because their reaction rates could be accurately determined at 25 °C. Substrates reacting faster than benzhydryl or slower than dichlorobenzhydryl did not give kinetics of sufficient accuracy to be useful in the isotope-effect studies because of the relatively small substituent-induced changes in isotope effects. These same small changes made temperature extrapolations undesirable.

Reference to Table I shows that the α -*d*'s and *m* values increase as electron donation to the cationic center is enhanced. This result is that predicted for the Doering-Zeiss mechanism and is consistent with the aqueous solvolysis of benzhydryl chlorides proceeding with nucleophilic solvent assistance. Alternative explanations are considered below.

As noted above, there is extensive evidence that the solvolysis of benzhydryl derivatives proceeds via rate-limiting formation of an intermediate.^{1,24} For example, the addition of lyate ion has no measurable effect on the ethanolysis²⁵ or methanolysis²⁶ of benzhydryl chloride. Similarly, in the reaction of *p,p'*-dimethylbenzhydryl chloride with aqueous sodium azide,²⁷ no relationship is observed between the product ratio and the azide kinetic effect; if this were a simple bimolecular displacement reaction, the effects of an added nucleophile on product ratios and on the rates of reaction would be directly related.¹¹ Also, the reactions of benzhydryl chloride and

(19) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915.

(20) For a discussion of the effects of substituents on the transition state for benzhydryl solvolyses see: O'Brien, M.; More O'Ferrall, R. A. *J. Chem. Soc.* **1978**, 1045.

(21) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.

(22) (a) Shiner, V. J., Jr. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: New York, 1970, Chapter 2. (b) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980.

(23) See ref 13 and 14a for discussion and leading references.

(24) Streitwieser, S., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962.

(25) Ward, A. M. *J. Chem. Soc.* **1927**, 2285.

(26) Benfey, O. T.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1952**, 2494.

(27) Reference 1, p 467.

bromide with a solution of sodium azide in aqueous acetone were found to produce the same mixture of azide and alcohol products; the absence of a leaving group effect on the product mixture indicates that products are formed, in this reaction, from a carbocationic intermediate which is dissociated from the leaving anion.²⁷ This interpretation is supported by the observation of a common-ion rate depression for these same hydrolyses,^{12,28} although common-ion rate depression does not occur in the present reactions in aqueous ethanol (see Experimental Section); this change upon going to aqueous ethanol is not surprising since this solvent is known to minimize return processes.¹² The exact nature of the intermediates formed in benzhydryl solvolyses has been investigated in great detail, particularly by Goering and co-workers,²⁹⁻³¹ and it appears that, in addition to the free carbocation, tight and solvent-separated ion pairs are involved. The stereochemical outcome of benzhydryl solvolyses appears to be a complex function of ion-pair return which, in turn, is controlled by the substituents on the aryl rings, the leaving group, and the solvent.²⁸⁻³⁰

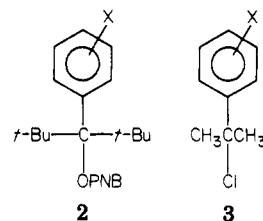
In summary, then, the present results have shown that the aqueous ethanolysis of benzhydryl chlorides may proceed with nucleophilic solvent assistance (see below), and the work of others has shown that the rate-determining step for these reactions must yield carbocationic intermediates which react with added nonsolvent nucleophiles only after the rate-determining step. These combined results are consistent with a Doering-Zeiss reaction mechanism. The observation that solvent is nucleophilically involved but added nucleophiles are not can be rationalized by assuming that the presence of solvent nucleophile in the solvation shell of the chloride confers an advantage on the solvent. If this argument is correct, the act of desolvating an anionic nucleophile such as azide and of removing a solvent molecule from the solvent shell of the reacting alkyl derivative can be energetically prohibitive. The present interpretation is also consistent with the extensive evidence for formation of ion-pair intermediates in benzhydryl solvolyses if it is assumed that P and Q are in fact the tight and solvent-separated ion pairs of earlier studies.

One point which is not clear from these results is whether or not the shifting of intermediate P to a transition state will always be accompanied by the kinetic involvement of *nonsolvent* nucleophiles. Thus in the present instance, nucleophilic solvent assistance is indicated by use of More O'Ferrall plots, and the existence of an intermediate is indicated, in large part, by the absence of kinetic effects of nonsolvent molecules. However, in the case of simply secondary derivatives such as 2-propyl tosylate, both nucleophilic solvent assistance and nucleophilic assistance by nonsolvent nucleophiles have been demonstrated,^{11,13,14} and the reaction is commonly (although not always)^{22,32} assumed to proceed via a simple S_N2 mechanism in which species I is a transition state.⁸ The question, which we cannot answer, is when this shift of species I from transition state to intermediate occurs.

Alternative Mechanisms

Our results for benzhydryl solvolyses are also consistent with a mechanism involving nucleophilic solvent attack on

the ring rather than on the central carbon; however, an experiment performed by Lomas and Dubois³³ demonstrates the invalidity of this alternative. These workers determined the *m* values for the aqueous acetolysis of aryl di-*tert*-butylcarbinyl *p*-nitrobenzoates (2; OPNB = *p*-



nitrobenzoate) and found that the *m* values were reduced as X became more electron-donating. This trend is the opposite of that which we observed for the benzhydryl compounds and also the opposite of that observed for cumyl chlorides (3).³⁴ An obvious explanation is that backside nucleophilic solvent participation (and its concomitant, perpendicular, transition-state movement for electron donation, Figure 1) is possible for benzhydryl and cumyl derivatives but not for the very hindered 2. This opposite result for compound 2 excludes the possibility that solvent nucleophilic involvement takes place at the aryl ring of the benzhydryl derivatives. Such a possibility could explain the benzhydryl results, but it would also require that a similar effect be observed for compound 2 since its aryl ring is still accessible to nucleophilic solvent interaction.

The interpretation of *m* values in terms of structural variations in the transition state is significant in another context. Several groups have examined the solvolyses of crowded substrates such as 2 and have concluded that many of the mechanistic properties of such systems result from the steric inability of the aryl group to rotate to the proper conformation relative to the developing cationic center.³⁵⁻³⁷ However, as the present results indicate and as O'Brien and More O'Ferrall²⁰ and Lomas³⁸ have pointed out, ρ values and *m* values can also be affected by transition-state variation, and these effects must be taken into account before factors such as hindered aryl rotation can be identified.

Another experiment in apparent contradiction to our conclusion requires discussion. Farinacci and Hammett³⁹ have noted that the amounts of alcohol and ether products from the aqueous ethanolysis of benzhydryl chloride are not in accord with the Olson-Halford equation,^{1,24} which relates the kinetic and product effects of solvent variation on S_N2 reactions. The usual interpretation of this lack of accord is that nucleophilic attack occurs after the rate-determining step²⁴ and not as part of the rate-determining step as we have concluded. However, product formation according to the Doering-Zeiss mechanism proceeds via two pathways (reaction of P and Q, eq 3) which become involved *after* rate-determining, nucleophilically assisted formation of the first intermediate, and thus product formation would not be expected to be controlled by the rate-determining step. The Olson-Halford equation can be used to distinguish between simple S_N1 and S_N2

(33) Lomas, J. S.; Dubois, J. E. *J. Org. Chem.* 1975, 40, 3303.

(34) Okamoto, Y.; Brown, H. C. *J. Am. Chem. Soc.* 1958, 80, 4972.

(35) Tanida, H.; Matsumura, H., *J. Am. Chem. Soc.* 1973, 95, 1586.

(36) McManus, S. P.; Harris, J. M. *J. Org. Chem.* 1977, 42, 1422.

(37) Peters, E. N. *J. Org. Chem.* 1977, 42, 1419.

(38) Lomas, J. S. *Tetrahedron Lett.* 1978, 1783.

(39) Farinacci, N. T.; Hammett, L. P. *J. Am. Chem. Soc.* 1937, 59, 2542.

(28) Reference 24, p 52.

(29) Goering, H. L.; Hopf, H. *J. Am. Chem. Soc.* 1971, 93, 1224.

(30) Winstein, S. W.; Ledwith, A.; Hojo, M. *Tetrahedron Lett.* 1961, 341.

(31) Reference 12, 284.

(32) Sneen, R. A.; Larsen, J. W. *J. Am. Chem. Soc.* 1969, 91, 362.

mechanisms, but it cannot be used to distinguish between the S_N1 and the Doering-Zeiss mechanisms or between simple S_N1 and ion-pair mechanisms.

The greatest challenge to the Doering-Zeiss interpretation of the present results comes from alternative interpretations in terms of the Winstein ion-pair scheme, eq 4. There are two ways in which this scheme can be used to explain an increase in α - d 's resulting from the substitution of electron-donating substituents. The first of these explanations assumes that the rate-determining step changes from k_1 to k_2 or attack on an ion pair as a consequence of substituent variation (the "Shiner interpretation" of α - d 's).^{22a} The second assumes that the rate-determining step remains the same but that the amount of return (e.g., k_{-1}/k_{-2}) varies (the "Murr partitioning isotope effect").⁴⁰ According to Shiner, the magnitude of the α - d for a solvolysis reaction can vary from a low of near unity for nucleophilic attack on a neutral substrate to steadily increasing values as the rate-determining step shifts to k_1 and then to k_2 , with the maximum α - d of 1.22 (for sulfonates) observed for k_2 being rate-determining. Intermediate values are also observed for rate-determining attack on the ion pairs. Just such a trend to more dissociated species would be expected to result in the benzhydryl series as the aryl substituents become more electron-releasing. Similarly, Murr has shown that electron-donating substituents may cause an increase in α - d by increasing partitioning of ion pairs to ion-pair return (i.e., an increase in k_{-1}/k_2 or k_{-2}/k_3).⁴⁰

Although the relationship of the two ion-pair mechanisms to variation in m values is not clear, rationales consistent with the observed trends (Table I) can be proposed. For example, in the case of the Shiner mechanism, electron donation gives a shift toward more highly ionized intermediates, presumably via more highly dissociated transition states that would be more responsive to an increase in solvent ionizing power. In the case of the Murr mechanism, one could theorize that if the species containing the more electron-donating substituents are in fact giving more ion-pair return (thus explaining the trend in α - d 's), then changing to a more highly ionizing solvent might remove more of the ion-pair return from those substrates in which ion-pair return was more important; thus larger m values would be observed for the species containing the more electron-donating substituents.

At present the only evidence pertinent to choosing between the ion-pair and the Doering-Zeiss mechanisms is circumstantial and derives from consideration of the observation of Lomas and Dubois³³ that the m values for 2 decrease as reactivity increases. This trend is the opposite of that expected from the ion-pair mechanisms as presented above. Examining the Shiner mechanism first, it is difficult to see why substitution of electron-donating substituents would cause opposite trends in variation of the rate-determining step for 1 and 2. Regarding the Murr mechanism, it is again difficult to rationalize opposing trends in ion-pair partitioning for compounds 1 and 2, although it is possible that ion pair return is totally absent for 2 (but not for 1) so that m values for this substrate are controlled by Hammond-type parallel motion of the transition states.

In contrast to reaction in aqueous acetone, the reaction of 1 in aqueous ethanol proceeds without a common-ion rate depression (see Experimental Section). The importance of the return steps from tight and solvent-separated ion pairs has not been evaluated in the present work but

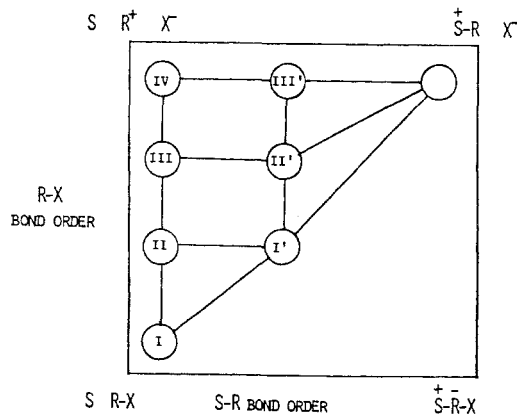


Figure 2. Composite potential energy diagram for the ion-pair scheme given in eq 4.

is the subject of future work.

Although solvolysis reactions are frequently used to introduce the study of organic reaction mechanisms, these reactions are quite complex. As the previous discussion illustrates, the prime contributor to this complexity is the involvement of ion pairs. Further illustration of this point is provided by consideration of the fact that a More O'Ferrall plot is necessary for reaction of each ion pair. Thus three figures similar to Figure 1 are needed, with the lower-left reactant corner of the figure being occupied by solvent and RX, R^+X^- , or $R^+||X^-$; a fourth figure is required for the simple reaction path of free cation IV. A composite of these four diagrams is presented in Figure 2. To further complicate matters, it is necessary also to consider the interconversion and destruction of the nucleophilically solvated intermediates I'-III' (eq 5) and, further, the possibility of elimination from each of the possible intermediates.

With all of these mechanistic possibilities and a corresponding set of potential energy diagrams, it would seem that it is possible to explain practically any experimental result. For example, consider what might happen if electron-donating substituents were substituted on the aryl rings of benzhydryl chloride 1, assuming that the Doering-Zeiss mechanism is the proper description of this reaction. Eventually curve B of Figure 1 would shift into curve A. Thus the α - d 's would be expected (as explained above) to first increase with increasing electron donation as long as the reaction coordinate was described by curve B and then decrease with increasing electron donation when the reaction coordinate fits curve A. At the same time, however, electron donation could cause a shift in the rate-determining step from formation of II to formation of III (eq 5), for example. Shiner has proposed that rate-determining interconversion of II and III would produce the maximum α - d (approximately 1.15 for chlorides).^{22a} This proposal seems reasonable since the maximum extent of hydrogen out-of-plane bending would appear to have been reached upon formation of II. Also, there would seem to be little change in crowding around the central carbon for steps II to III or III to IV or for interconversion of intermediates I'-III'.

The result of this consideration would be that one could explain substituent variation causing first an increase and then a decrease in α - d as the result a shift from curve B to curve A or Figure 1; similar possibilities are, of course, present in Figure 2. Alternatively, if the substituent changes were to cause an increase in α - d 's which reach a maximum and then remain unchanged despite dramatic changes in rates, one could then propose that the constancy resulted because the rate-determining step had changed

(40) Murr, D. L.; Donnelly, M. F. *J. Am. Chem. Soc.* 1970, 92, 6686, 6688.

to interconversion of II to III (or a similar process from Figure 2 or eq 5). Shiner has observed just such a trend in α -d's for the solvolysis of 1-phenylethyl chlorides.^{22a} Although it is unsettling to realize that one can explain practically any trend in mechanistic parameters, it is important to note that this is the case.

Experimental Section

Rates were determined conductimetrically and solvents prepared as described previously.¹⁷ The nondeuterated chlorides were available commercially and were distilled before use. The deuterated chlorides were prepared by reducing the appropriate ketone with lithium aluminum deuteride and then reacting the resulting alcohol with hydrogen chloride.

The error limits reported in Tables I and II are standard deviations of the mean (i.e., standard deviation divided by the square root of the number of determinations; eq 6). The standard

$$s_m = s/n^{1/2} \quad (6)$$

deviations of the mean for functions such as the α -d and the m values are dependent on errors from two sources (e.g., k_H and k_D) as given by eq 7 and 8 which reduce to eq 9 and 10, respectively, for the α -d and the m values.⁴¹

$$Q = f(a, b, c, \dots) \quad (7)$$

$$s_{mQ}^2 = \left(\frac{\partial Q}{\partial a}\right)^2 s_{ma}^2 + \left(\frac{\partial Q}{\partial b}\right)^2 s_{mb}^2 + \dots \quad (8)$$

$$s_{m,\alpha-d}^2 = \frac{s_{mH}^2 k_H}{k_D^2} + \frac{s_{mD}^2 k_H^2}{k_D^3} \quad (9)$$

$$s_{mm}^2 = \left(\frac{1}{2.303Yk_2}\right)^2 s_{m2}^2 + \left(\frac{1}{2.303Yk_1}\right)^2 s_{m1}^2 \quad (10)$$

A common-ion rate depression is indicated by a reduction in the instantaneous rate constant as the reaction proceeds. For the reactions reported in this work, depression in the rate constants was not observed. Rather, only a very slight random scatter was observed for the measured rate constants as a function of percent reaction.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 1 (X = H; Y = CH₃), 779-14-6; 1 (X = H; Y = H), 90-99-3; 1 (X = H; Y = Cl), 134-83-8; 1 (X = Cl; Y = Cl), 782-08-1.

(41) Young, H. D. "Statistical Treatment of Experimental Data"; McGraw-Hill: New York, 1962; p 98.

Notes

Bromination of Deactivated Aromatics Using Potassium Bromate

J. J. Harrison,* J. P. Pellegrini, and C. M. Selwitz

Gulf Research & Development Company, Pittsburgh, Pennsylvania 15230

Received November 19, 1980

The bromination of aromatic rings containing electron-withdrawing groups has long been an area of concern.¹⁻⁷ Currently, methods used for brominating deactivated aromatics such as nitrobenzene (1), include high-temperature ion-catalyzed brominations,¹ brominations involving acid-catalyzed reactions of hypobromous acid,²⁻⁴ bromination using dibromoisocyanuric acid,^{5,6} and other methods.⁷ Because of our interest in synthesizing *m*-bromonitrobenzene (2), which is the precursor to (3-aminophenyl)acetylene,⁸ we have investigated the reaction of potassium bromate in sulfuric acid with nitrobenzene. Potassium bromate in sulfuric acid is a convenient and powerful brominating agent capable of brominating aromatic rings containing deactivating groups.

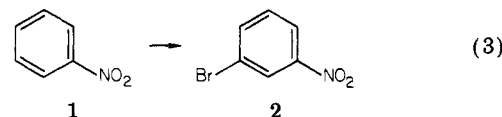
Kraft⁹ first reported in 1875 that potassium bromate in sulfuric acid brominated benzene to bromobenzene. Derbyshire and Waters⁴ brominated benzoic acid using

molecular bromine with potassium bromate as a catalyst. They postulated that bromate functioned by removing bromide ions from the equilibrium (eq 1 and 2) to generate



hypobromous acids which is a powerful brominating agent in acid solution.¹⁰ Japanese workers¹¹ reported that potassium bromate brominated benzene in acetic acid in the presence of a catalytic amount of sulfuric acid. Under these conditions, however, nitrobenzene was not brominated. Recently Orban and Körös have reported the bromination of aniline and phenol derivatives using bromate uncatalyzed by metals.^{12,13}

Initially, we investigated the bromination of nitrobenzene using the conditions of Derbyshire and Waters.⁴ We discovered initially that the bromination reaction (eq 3) was insensitive to the amount of molecular bromine or the amount of potassium bromide used and depended solely on the amount of potassium bromate used.



On scale-up, a yield of 88% 3-bromonitrobenzene was obtained after reacting equal molar amounts of potassium bromate and nitrobenzene in 68% sulfuric acid solution

(1) J. R. Johnson and C. G. Gauerke, "Organic Syntheses", Wiley, New York, Collect Vol. 1, 1956, p 123.

(2) S. J. Branch and B. Jones, *J. Chem. Soc.*, 2317 (1954).

(3) P. B. D. De La Mare and I. C. Hilton, *J. Chem. Soc.*, 997 (1962).

(4) D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 573 (1950).

(5) W. Gottardi, *Monatsh. Chem.*, 99, 815 (1968).

(6) W. Gottardi, *Monatsh. Chem.*, 100, 42 (1969).

(7) J. Huthmacher and F. Effenberger, *Synthesis*, 693 (1978).

(8) A. Onopchenko, E. T. Sabourin, and C. M. Selwitz, *J. Org. Chem.*, 44, 1233 (1979).

(9) F. Kraft, *Chem. Ber.*, 8, 1045 (1875).

(10) H. M. Gilow and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1321 (1973).

(11) Y. Furuya, A. Morita, and I. Urasaki, *Bull. Chem. Soc. Jpn.*, 41, 997 (1968).

(12) M. Orban and E. Körös, *J. Phys. Chem.*, 82, 1672 (1978).

(13) M. Orban, E. Körös, and R. M. Noyes, *J. Phys. Chem.* 83, 3056 (1979).