The Kinetics, Isotope Rate Effect, and Mechanism of Dehydrobromination of *cis*-1,2-Dibromoethylene with Triethylamine in Dimethylformamide[1]

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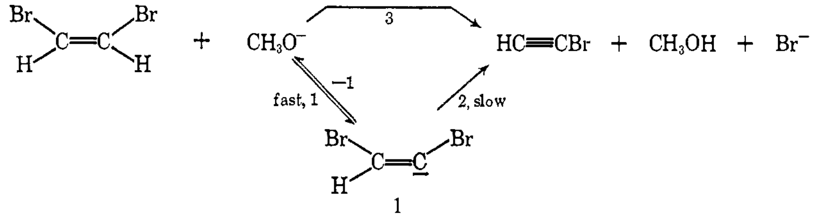
Abstract: The reaction between *cis*-dibromoethylene and triethylamine in dimethylformamide (DMF) is one of elimination rather than displacement. The probable first product is monobromoacetylene. The activation parameters for this second-order reaction are $\Delta H^{\ddagger} = 18.1$ kcal/mol and $\Delta S^{\ddagger} = -32$ eu. The isotope effect for elimination is $k_H/k_D = 1.00$, and there is neither rate retardation nor hydrogen exchange with *cis*-dibromoethylene, when triethylammonium or triethylammonium-*d* bromide is present during reaction. The reactivities of a few other compounds relative to *cis*-dibromoethylene with triethylamine in DMF were also estimated: $k(\mathrm{HCBr{=}CHN(CH_3)_3{}^+Br^-}) \simeq 2500\,(40°)$; $k(trans\text{-}\mathrm{C_2H_2Br_2}) \simeq 0.003\,(101.8°)$; $k(cis\text{-}\mathrm{C_2H_2Cl_2}) \simeq 0.0064\,(101°)$; $k(\mathrm{HC{\equiv}CBr}) \simeq 100\,(100°)$. To account for the observations on the *cis*-dibromoethylene, a novel $(\mathrm{E1cB})_{ip}$ or preequilibrium ion-pair mechanism is proposed, in which $(\mathrm{HCBr{=}CBr^-HN(C_2H_5)_3{}^+})$ is formed. Analogy for this elimination mechanism is found in the ion-pair processes of electrophilic substitution (S_E) reactions. The $(\mathrm{E1cB})_{ip}$ mechanism may provide a rationale for several "low" isotope effects, k_H/k_D. A reactivity scale, $sp^3 \sim sp > sp^2 > sp^{2.5}$, is also suggested for the S_N reactions of triethylamine with various organic halides.

Since a complete vibrational analysis was available for *cis*-dibromoethylene, it seemed to be an excellent model compound for the detailed study of isotope effects on a base-promoted dehydrobromination.[2,3] This objective was frustrated in our first study of dibromoethylene in methanolic methoxide, where evidence for the equilibration of a vinyl anion (**1**) with starting material was obtained.[2] Next we turned to the title system. We found no simple bimolecular elimination but again obtained evidence for the vinyl anion and an interesting elimination mechanism.

This mechanistic dichotomy shows up, for example, in the dehydrobromination of *cis*-*p*-nitro-β-bromostyrene and the substitution of bromide in *trans*-*p*-nitro-β-bromostyrene by methoxide ion.[6] Certainly, there is precedent for nucleophilic substitution at an ethylenic carbon in general[5-7] as well as the use of amines as nucleophiles at such centers.[7] Because of these and other mechanistic questions, a varied attack was necessary: isotope rate factors were measured; hydrogen-exchange experiments were carried out; rate data for reactions of possible intermediates (or their models) as well as structurally related molecules were obtained. With this background, we believe that we have accumulated strong evidence for a new E1cB elimination mechanism, one which has been elusive and may remain difficult to validate.[8,9]



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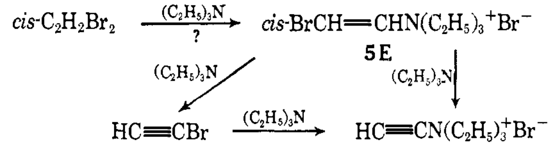

(2)

Breslow has made the valid point that even if the vinyl anion were detected in systems such as ours, it need be no more than a blind alley intermediate irrelevant to the elimination process.[4] At the same time, we recognized that the significant processes in our system might not even be elimination, but substitution.[5]

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[1] (a) Acknowledgment is made to the Research Corporation, the Public Health Service, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (b) This work was taken from the Ph.D. theses of W. K. K. (1967) and W. G. L. (1961), in which detailed kinetic data, relevant plots, and calculations may be found. (c) Author to whom inquiries should be addressed.

[2] S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

[3] J. M. Dowling, P. G. Puranik, A. G. Meister, and S. I. Miller, *J. Chem. Phys.*, **26**, 233 (1957).

[4] R. Breslow, *Tetrahedron Letters*, 399 (1964).

[5] S. I. Miller and P. K. Yonan, *J. Am. Chem. Soc.*, **79**, 5931 (1957); S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968).

[6] G. Marchese, G. Modena, and F. Naso, *Tetrahedron*, **24**, 663 1968).

[7] S. Ghersetti, G. Lugli, G. Melloni, G. Modena, P. E. Todesco, and P. Vivarelli, *J. Chem. Soc.*, 2227 (1965).

[8] (a) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Company, Amsterdam, 1963, Chapter 4; (b) G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **4**, 49 (1965); (c) J. F. Bunnett, *ibid.*, **1**, 225 (1962).

[9] D. J. McLennan, *Quart. Rev.* (London), **21**, 490 (1967). Numerous citations on the carbanion mechanism of olefin-forming eliminations are given here. After our paper was submitted we learned of

Experimental Section[1b]

Infrared spectra (ir) were determined on Beckman (IR8) or Perkin-Elmer Models 21, 137, and 121 spectrophotometers. Proton magnetic resonance (pmr) spectra were taken on a Varian A-60 spectrometer. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Perkin-Elmer Model 154 and Aerograph Model 90-P3 gas chromatographs were used to check the purity of solvents and reagents.

Materials. A commercial grade of dimethylformamide (DMF) was purified by a standard method.[10,11] After standing over sodium hydroxide or barium oxide, the solvent was filtered and fractionally distilled. The middle fraction, bp 62° (30 torr), $n^{25}\mathrm{D}$ 1.4270 (lit.[11] 63° (30 torr), $n^{25}\mathrm{D}$ 1.4269), was used for the kinetic runs. From ir spectra, we could easily detect 0.1% water and by vapor phase chromatography (vpc), we could easily detect 0.05–0.1% dimethylamine, when these impurities were added to pure DMF.

Deuterium oxide (99.8%), triethylammonium bromide (mp 254–255°), triethylammonium chloride (mp 258–259°), and compressed trimethylamine gas were used as purchased. Halide analyses of the salts were satisfactory. *cis*-Dichloroethylene was obtained by fractional distillation of the 1,2-dichloroethylenes and had bp 60.2–60.3° (752 torr) (lit.[12] 59.65–59.80° (765 torr)).

Triethylamine was heated at reflux over sodium for 24 hr, then fractionally distilled under nitrogen. The middle fraction had bp 88.6–89.0° (750 torr), $n^{26.2}\mathrm{D}$ 1.3952. Infrared spectra indicated that no water was present; separate tests showed that we could detect 0.1% of added water.

The properties of *cis*-dibromoethylene-d_2 have been recorded[2] and those of the *cis*- and *trans*-dibromoethylenes are similar to those given previously.[12–14] These compounds were obtained by fractional distillation in absolute alcohol. The *trans*-alcohol azeotrope had bp 75.1–75.3° (750 torr), and the *cis*-alcohol azeotrope had bp 78.2–78.5° (750 torr). When the dibromoethylene was needed, these ethanolic solutions were drowned in ice water; the oil was separated and dried over calcium chloride. Pure *cis* isomer could be stored in a refrigerator for at least a month; the pure *trans* form isomerized on standing overnight under the same conditions.[12] The purity of these isomers was checked by their ir spectra[3] and vpc retention times.[14]

Triethylammonium Deuterium Bromide. Phosphorus tribromide was purified by distillation, bp 36° (2 torr). The liquid (30 ml) was placed in a 200-ml, three-necked flask, fitted with a dropping funnel, nitrogen gas inlet, and outlet. Deuterium oxide (12 ml) was added dropwise to the phosphorus tribromide. The deuterium bromide formed was swept out of the flask in a stream of nitrogen through a cooled trap (−78°) into a cooled flask, fitted with a calcium chloride outlet and containing triethylamine (150 ml). The salt formed instantly. The white solid was filtered under nitrogen, washed twice with absolute ether, dried under reduced pressure, and sublimed at *ca.* 240° (1 torr) to give a solid, mp 254–255°. An ir spectrum showed that the solid contained *ca.* 50% of the deuterated compound. It is not clear why or at what stage the deuterium was diluted with protium.

Anal. Calcd for $(C_2H_5)_3N \cdot DBr$: Br, 43.69. Found: Br, 43.94.

Monobromoacetylene. This substance is hazardous: on contact with air, it burns and may explode; it may be handled in solvents. 1,2-Dibromoethylene was treated with sodium ethoxide in ethanol under nitrogen in a flask fitted with a cold finger condenser. Monobromoacetylene was swept out of the mixture in a gentle stream of nitrogen through a line equipped with a large calcium chloride tube and two traps at −78°. The impure bromoacetylene (lit.[15] bp 2°), which had collected in the traps, was brought to 0–5° and allowed to distil into a receiver containing DMF at −78°. The calcium chloride removed most of the ethanol, and the trap-to-trap distillation left dibromoethylene (bp 110°) behind. The bromoacetylene–DMF solution was used for kinetic studies immediately.

(2-Bromovinyl)trimethylammonium Bromide (Bromoneurine Bromide) (5M). This compound was prepared in a four-step sequence (eq 3). Satisfactory bromide analyses were obtained for

$$\mathrm{BrCH_2CH_2Br} \xrightarrow{(\mathrm{CH_3})_3\mathrm{N}} \underset{\mathbf{2}}{\mathrm{BrCH_2CH_2N(CH_3)_3{}^+Br^-}} \xrightarrow{\mathrm{KOH}}$$

$$\underset{\mathbf{3}}{\mathrm{H_2C{=}CHN(CH_3)_3{}^+Br^-}} \xrightarrow{\mathrm{Br_2}} \underset{\mathbf{4}}{\mathrm{BrCH_2CHBrN(CH_3)_3{}^+Br^-}} \xrightarrow{\mathrm{KOH}}$$

$$\underset{\mathbf{5M}}{\mathrm{BrCH{=}CHN(CH_3)_3{}^+Br^-}} \quad (3)$$

all compounds, **2–5**. Following published procedures, we obtained an 88% yield of **2** and an 85% yield of **3**.[16,17] Bromine addition to a solution of **3** in chloroform gave **4** in 57% yield, an apparent improvement over Bode's method.[18] In the final step, we obtained 40% of **5M**, mp 144–145° (lit.[18] 145°). A pmr spectrum of **5M** in deuterium oxide (99.8%) showed three doublets, with peak heights in the ratio 1:1:9, at −1.963 (CHBr), −1.52 (CHN), and 1.00 (CH_3) in which the negative and positive signs are down- and upfield shifts, respectively, from water (τ 4.8). The pmr coupling constant, J = 7 cps, for the vinyl hydrogens,[19] and the absence of the typical strong *trans* absorption at *ca.* 940 cm^{-1} in the ir spectrum,[20] are indicative of a *cis* structure.

Halide Analyses. The concentration of halide ion was estimated with standard silver nitrate. The solutions were diluted with water and acidified with glacial acetic acid. Where possible, titrations to the eosin or phenosafranine indicator end point for bromide and the dichlorofluorescein indicator end point for chloride were used.[21a] For the kinetic studies, in which the bromide concentrations were low and the reaction mixtures colored, electrometric titrations had to be used.[21b] In the potentiometric determinations, a Beckman pH meter (Model G), a silver electrode, a salt bridge (saturated ammonium nitrate and 3% agar), and a calomel electrode were used. For amperometric determinations, a Sargent Ampot, a platinum electrode rotated by a Sargent synchronous motor, a salt bridge as described above, and a calomel electrode were used. All of these titrimetric procedures on 5.00 ml of sodium bromide (0.05183 *M*) with silver nitrate (0.02410 *M*) had a precision within 0.3%.

Dibromoethylene–Triethylamine Products. *cis*-Dibromoethylene in ether, acetone, or toluene was treated with an excess of triethylamine. The product mixture was treated with excess ether, after the reaction was complete. The precipitated solid, usually dark, was extensively washed with ether, dried, and heated at 250° under vacuum (1 torr). The sublimable salt was triethylammonium bromide. The dark residue was taken up in chloroform and reprecipitated with ether; after several such cycles, the white nonsublimable salt was identified as tetraethylammonium bromide. The mole ratio of the first to the second salt was *ca.* 1.5. Although their elemental analyses were not wholly satisfactory, the comparison of the ir spectra of these salts with authentic samples, taken in potassium bromide pellets, left no doubt as to the identity of the major constituent of these solids. Bands expected for an ethynyl group, as in $HC{\equiv}CN(C_2H_5)_3{}^+Br^-$, were not apparent.

Anal. Calcd for $(C_2H_5)_3NHBr$: C, 39.57; H, 8.86; Br, 43.88. Found for sublimable salt: C, 40.61; H, 8.90; Br, 44.25, 44.70.

Anal. Calcd for $(C_2H_5)_4NBr$: C, 46.97; H, 9.54; Br, 38.07. Found for nonsublimable salt: C, 44.68; H, 8.86; Br, 38.77, 38.90.

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three interesting variants of the E1cB mechanism: (a) Z. Rappoport, *Tetrahedron Letters*, 3601 (1968), illustrates the limiting case of elimination from a relatively strong acid. (b) T. I. Crowell, R. T. Kemp, R. E. Lutz, and A. A. Wall, *J. Am. Chem. Soc.*, **90**, 4638 (1968), gives an $(\mathrm{E1cB})_{\mathrm{ip}}$ example with $k_H/k_D \simeq 1.0$, with general base catalysis and no proton exchange with the medium. (c) R. A. More O'Ferrall and S. Slae, private communication on simultaneous elimination and hydrogen exchange in the system 9-(hydroxymethyl)fluorene.

(10) A. B. Thomas and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 1843 (1957).

(11) "A Review of Catalytic and Synthetic Applications for DMF/DMAC" and Supplement, and "DMF," a product information bulletin, prepared and published by E. I. du Pont de Nemours and Company, Inc., Wilmington, Del. 19898.

(12) S. I. Miller and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 629 (1952).

(13) W. G. Lee and S. I. Miller, *ibid.*, **82**, 2463 (1960).

(14) W. K. Kwok and S. I. Miller, *Can. J. Chem.*, **45**, 1161 (1967).

(15) I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, 1953.

(16) W. C. Davies, E. B. Evans, and F. L. Hulbert, *J. Chem. Soc.*, 412 (1939).

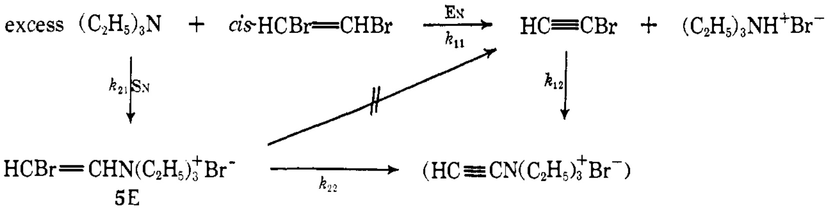
(17) R. R. Renshaw and J. C. Ware, *J. Am. Chem. Soc.*, **47**, 2989 (1925).

(18) J. Bode, *Ann.*, **267**, 278 (1892).

(19) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1964, p 85.

(20) G. Huett and S. I. Miller, *J. Am. Chem. Soc.*, **83**, 408 (1961).

(21) (a) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis, II," 2nd ed, Interscience Publishers, New York, N. Y., 1947, p 239; (b) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, New York, N. Y., 1958, Chapters VI, XII.



(4)

Approximately 95% of the expected bromide ion was isolated in the two salts. But after repeated experiments of the type described above and examination of the several filtrates and residues, we were still unable to determine the fate of the ethynyl group. Finally, we kept a solution of bromoacetylene (*ca.* 2 g), triethylamine (10 ml), and ether (20 ml) in a sealed ampoule at 85° for 24 hr. The dark brown solution was distilled under reduced pressure to remove the ether and triethylamine. The dark oily residue was distilled at *ca.* 0.3 torr in a smaller apparatus to give a colorless liquid, $n^{24.8}\text{D}$ 1.4311. Apart from a trace of triethylamine, the ir and pmr spectra were identical with those taken on an authentic sample of N,N-diethylacetamide, $n^{25.5}\text{D}$ 1.4360; $\nu_{C=O}$ 1630 cm^{-1}; τ 8.05 (CH_3CO), 8.89 (CH_3), and 6.70 (CH_2). These observations account adequately, if not in detail, for our products.

Attempted Deuterium Exchange of *cis*-Dibromoethylene. An ampoule containing triethylammonium deuterium bromide (6 g, 0.033 mol), *cis*-dibromoethylene (3 g, 0.0161 mol), triethylamine (10 ml, 0.07 mol), and DMF (15 ml) was kept at 100° for 6 hr, or *ca.* 10% elimination. The resulting mixture of dark brown solution and solid quaternary salt was cooled, poured into 100 ml of ammonium chloride solution (10 g, 0.19 mol), and extracted with carbon tetrachloride (three 20-ml portions). The extract was dried with calcium chloride and its ir spectrum taken. Only *cis*-dibromoethylene was in evidence; none of the bands expected from deuteration was present.[3] If the rates of elimination and exchange were equal, the starting material would contain *ca.* 5% deuterium. Since this is readily detectable in dibromoethylene by our method,[2,3] we conclude that $k_{\text{elim}} > k_{\text{ex}}$.

Kinetic Studies. Initially, we hoped we could study the system sodium methoxide-*cis*-dibromoethylene without the complications of hydrogen exchange in an "aprotic" solvent. But the sodium methoxide had negligible solubility in dioxane, dimethyl sulfoxide, trimethylpentane, or DMF. Switching to the base triethylamine, we found DMF to be the "fastest" solvent.

The reactions were carried out in DMF with a large excess of triethylamine. A typical run was prepared by adding triethylamine (100.0 ml) to an aliquot of stock organic halide in a volumetric flask (250 ml). The solution was made up to the required volume and the ambient temperature recorded. Aliquots (10 ml) were now distributed in Pyrex ampoules, which were capped temporarily, cooled (−78°), and later sealed. These were placed in suitable constant temperature baths, removed at fixed intervals, cooled quickly, and stored in a refrigerator. For analysis, the ampoules were opened, and the contents washed into 5 ml of acetic acid with several portions of methanol. Because the solutions were often brown, amperometric or potentiometric titrations were used.

A conventional (batch) method could be used to study the kinetics of **5M**. This and triethylamine solutions were placed in separate compartments of a divided flask. After equilibration had been reached in a constant-temperature bath, the flask was inverted, its contents throughly mixed, and the flask replaced in the bath. Aliquots were taken at fixed intervals and analyzed in the usual manner.

During the runs, the variation in the temperature of the constant-temperature baths was generally <0.1°. Our thermometers were calibrated against a standard platinum resistance thermometer. The rate constants were corrected for solvent expansion by assuming that the density of the solvent was the weighted mean of DMF and triethylamine densities at the given temperature.[11,22]

The reactions of the *cis*- and *trans*-dibromoethylenes and *cis*-dichloroethylene with triethylamine produced two halide ions in two steps. Since the second step was relatively fast and the triethylamine was in large excess, we could use the pseudo-first-order rate expression in its integrated form, to process the data. Here, a = initial concentration of organic halide in moles/liter, $[X^-]$ = concentration of halide produced, b = initial concentration of triethylamine, t = time, and

$$d[X^-]/dt = 2k'(a - [X^-]/2) \tag{5}$$

$$\ln a - \ln (a - [X^-]/2) = k't \tag{6}$$

$$k = k'/b = k_{\text{obsd}}\ M^{-1}\ \text{sec}^{-1} \tag{7}$$

Normally, it was convenient to work with k', and this quantity is retained in several tables and figures.

To illustrate our dibromoethylene data, we give two plots of $k't$ (actually the left-hand side of eq 6) *vs.* t in Figures 1 and 2. Generally, six to eight points were taken for each run. The final rate constant at 130.87° is based on 25 points of four runs, in which the concentration of *cis*-dibromoethylene was varied from 0.01 to 0.1 M. Results for two temperatures are given in Table I and final averaged values are given in Table II.

Table I. The Reaction between *cis*-Dibromoethylene and Triethylamine (2.86 M) in DMF in the Presence of Salts[a]

Temp, °C ± 0.05°	*cis*-$C_2H_2Br_2$, $M \times 10^2$	$(C_2H_5)_3N\cdot$ HCl, $M \times 10^2$	$(C_2H_5)_3N\cdot$ HBr, $M \times 10^2$	k_1, min^{-1}
98.2	1.175			3.37×10^{-4}
	0.787	2.156		3.28
	0.565	1.849		3.23
	2.265		1.781	3.27
	1.699		1.757	3.23
	1.132		2.256	3.15
			k_{av} =	3.26 ± 0.05
123.6	1.175			1.70×10^{-3}
	0.787	2.156		1.79
	0.565	1.849		1.70
	2.265		1.781	1.68
	1.699		1.757	1.71
	1.132		2.256	1.68
			k_{av} =	1.71 ± 0.03

[a] This pseudo-first-order constant has been corrected for solvent expansion: 1.090 at 98.2°, 1.130 at 123.6°

Table II. Rate Data for the Reactions of Normal and Deuterated *cis*-Dibromoethylene with Triethylamine (2.86 M) in Dimethylformamide[a,b]

Temp, °C	No. of runs	$k_H' \times 10^6$, sec^{-1}	No. of runs	$k_D' \times 10^6$, sec^{-1}
90.10 ± 0.08	5	3.23 ± 0.13	4	3.23 ± 0.1
98.20 ± 0.05	6	5.43 ± 0.10[c]		
113.86 ± 0.10	3	15.4 ± 0.6		
114.46 ± 0.10			4	16.7 ± 0.7
115.86 ± 0.10	1	17.8 ± 0.7		
123.60 ± 0.05	6	28.5 ± 0.5[c]		
130.87 ± 0.10	4	44.1 ± 1.6	4	46.0 ± 1.6
E_a, kcal/mol		18.9 ± 0.5		19.0 ± 0.5
$\Delta H^{\ddagger}$, kcal/mol		18.1 ± 0.5		18.2 ± 0.5
$\Delta S^{\ddagger}$, eu		−32 ± 2		−33 ± 2

[a] Average deviations are listed. [b] The pseudo-first-order rate constants have been corrected for solvent expansion. They may be converted to second-order rate constants by dividing by 2.86. See eq 6 and 7. [c] From Table I.

The reaction of *cis*-dibromoethylene with triethylamine yields 2 equiv of bromide. Since two consecutive pseudo-first-order reactions are involved, we could use an appropriate computer program

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(22) E. W. Washburn, Ed., "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1933, p 243.

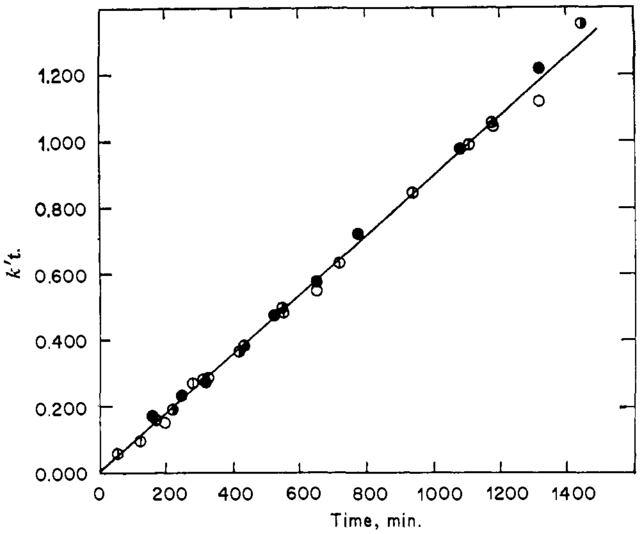

Figure 1. Rate data for the reaction of *cis*-$C_2D_2Br_2$ and triethylamine (2.86 *M*) in DMF at 114.46°. Four runs are included (Table II). These data are not corrected for solvent expansion.

to evaluate the rate constants k_{11} and k_{12}.[23] Rough limits of k_{11} and k_{12} were estimated by us, and the computer varied k_{11} and k_{12} within these limits, until values were found for which the deviations of the calculated [Br⁻] from the observed [Br⁻] were minimized. Because the computer output of k_{12} (not k_{11}) is extremely sensitive to the estimate of the ratio, k_{11}/k_{12}, fed in, we prefer to use k_{12} obtained from the bromoacetylene runs. The results of such computations are given in Table III.

Table III. Computer Output for the Two Successive Steps in the Reaction of *cis*-Dibromoethylene and Triethylamine (2.86 *M*) in DMF at 98.2°[a]

cis-$C_2H_2Br_2$, $M \times 10^3$	$(C_2H_5)_3N \cdot HCl$, $M \times 10^3$	$k_{11} \times 10^3$, min^{-1}	$k_{12} \times 10$, min^{-1}
11.75	0	0.309	0.448
7.87	21.56	0.309	0.238
5.65	18.49	0.334	0.260
	Mean	0.317 ± 0.01	0.31 ± 0.09

[a] The rate constants were obtained as computer output; we prefer the rate constants calculated elsewhere, *i.e.*, $k_{11} = 0.326 \times 10^{-3}$ and $k_{12} = 0.031$ (see text). To correct for solvent expansion, these values would be increased by the factor 1.09.

Activation parameters were obtained from an Arrhenius plot (Figure 3) and the standard expressions

$$\Delta H^{\ddagger} = E_a - RT$$

$$\Delta S^{\ddagger} = 2.303R[\log k - \log (kT/h)] + \Delta H^{\ddagger}/T$$

The reactions of bromoacetylene and bromoneurine bromide (5) with triethylamine produced one halide ion. To obtain the rate constants, we integrated the standard pseudo-first-order rate expression

$$d[Br^-]/dt = k'(a - [Br^-]) \qquad (8)$$

The four kinetic studies of compounds other than *cis*-dibromoethylene were not meant to stand up on their own and usually were terminated, as soon as sufficient data were obtained to make comparisons with the title system possible. These rate data are summarized in Table IV.

There were two problem systems. The rate constants for *cis*-dichloroethylene–triethylamine drifted downward with time (20%) in each run. Therefore the rate constant was that taken from the extrapolated value at zero time. Many runs on *trans*-dibromoethylene–triethylamine were discarded, since the rate constants decreased drastically in a given run. Although the initial constants were of the same order of magnitude as those of the *cis* isomer, we could estimate the rate constant roughly from the slope of plots of bromide formations *vs.* time at high conversions. With a *trans* sample of *ca.* 95% purity we obtained somewhat more satisfactory constants, by using eq 6 and neglecting the first points.

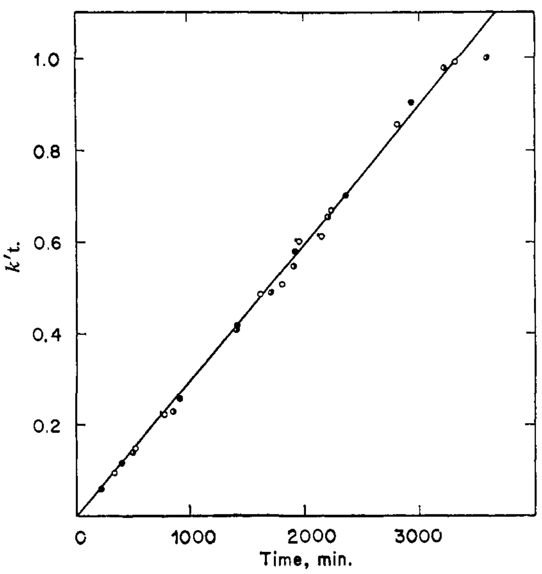

Figure 2. Rate data for the reaction of *cis*-$C_2H_2Br_2$ and triethylamine (2.86 *M*) in DMF at 98.2°, in the presence of added triethylammonium bromide. Three runs are included (Table II). These data are not corrected for solvent expansion.

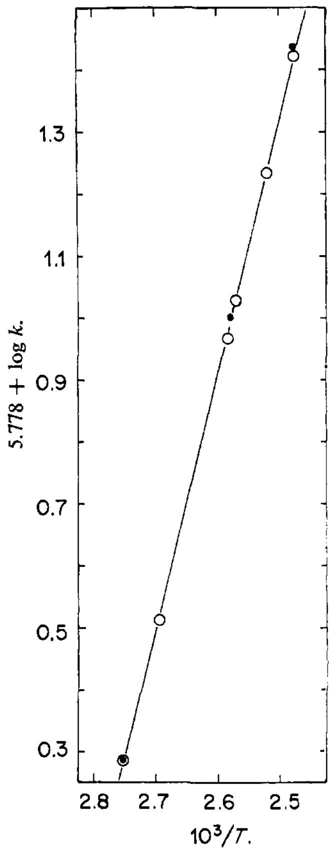

Figure 3. Arrhenius plot for the reaction of *cis*-dibromoethylene (○) or *cis*-dibromoethylene-d_2 (●) with triethylamine in DMF. The units of *k* are sec⁻¹.

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[23] K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, pp 567–569. This program was modified for us by Mr. E. R. Stedronsky.

Table IV. Elimination Rate Data and Comparisons[a]

System	Solvent	Temp, °C	k, M^{-1} sec^{-1}	$k(\mathrm{RX})/k(\mathrm{C_2H_2Br_2})$
cis-$C_2H_2Br_2$–$(C_2H_5)_3N$	DMF	100	2.02×10^{-6}	1.00
$HC{\equiv}CBr$–$(C_2H_5)_3N$	DMF	100.22	2.0×10^{-4} [b]	$\sim 1 \times 10^{2}$
$HCBr{=}CHN(CH_3)_3{}^+Br^-$–$(C_2H_5)_3N$	DMF	39.51	0.61×10^{-4} [c]	$\sim 2.5 \times 10^{3}$
		50.10	2.3×10^{-4} [d]	
cis-$C_2H_2Cl_2$–$(C_2H_5)_3N$	DMF	101.0	1.3×10^{-8} [d]	$\sim 6.4 \times 10^{-3}$
		123.3	6.0×10^{-8} [d]	
trans-$C_2H_2Br_2$–$(C_2H_5)_3N$	DMF	101.76	6.7×10^{-9} [d]	$\sim 3 \times 10^{-3}$
		121.21	3.5×10^{-8}	
cis-$C_2H_2Br_2$–$CH_3O^-Na^+$	CH_3OH	60	1.8×10^{-2} [e]	1.5×10^{5}

[a] The comparison in the last column is with the standard system, *cis*-dibromoethylene–triethylamine at the indicated temperature. All rate constants have been corrected for solvent expansion. [b] Based on one direct determination and three computed in Table III. [c] Ten runs. [d] One run. [e] References 2 and 12.

Results and Discussion

Although we have referred to the first step of the reaction between *cis*-dibromoethylene and triethylamine as an elimination, *e.g.*, eq 4, this really has to be established. The absence of an isotope rate effect, $k_H/k_D = 1.00$, did at first seem more consistent with the SN rather than the EN process. There is some precedent for small secondary isotope effects, *e.g.*, 0.9–1.1, in substitution reactions, and the observed value is certainly within this range. If this were the sole piece of evidence, we believe that a choice between the SN and EN paths in (4) could not be made.

Consider the observations as they bear on the alternatives. In determining the stoichiometry of this process, we have found 2 mol of bromide ion for every mol of starting *cis*-dibromoethylene. The salts, triethylammonium bromide and tetraethylammonium bromide, could be isolated from the product mixture. Indirect evidence for diethylethynylamine (or the corresponding ethynyltriethylammonium salt) as a product was obtained by the isolation of its hydration product, N,N-diethylacetamide. There is, in fact, ample precedent for the postulated conversions, which involve replacement of the weak base, ethynylamine, by triethylamine in the quaternary salt, followed by facile hydration even on exposure to the atmosphere.[24]

$$(HC{\equiv}CN(C_2H_5)_3{}^+) \xrightarrow[\text{fast}]{(C_2H_5)_3N} (HC{\equiv}CN(C_2H_5)_2) + (C_2H_5)_4N^+$$
$$(HC{\equiv}CN(C_2H_5)_2) \xrightarrow[\text{very fast}]{H_2O} CH_3CON(C_2H_5)_2 \qquad (9)$$

From the rate law, 5, that fits the data for bromide ion production, it was clear that two bromide ions were released either simultaneously or in quick succession from the *cis*-dibromoethylene by the triethylamine. Indeed, the treatment of reaction 4 as a single pseudo-first-order process succeeded because of the relatively large rate ratio, $k_{12}/k_{11} \simeq 100$. This was demonstrated when we analyzed reaction 4 as two successive pseudo-first-order steps. A computer analysis of several runs turned out precise rate constants for k_{11} but gave values of k_{12} which showed considerable scatter (Table III). Nevertheless, these values of k_{12} were sufficiently close to the rate constant found independently for the reaction of bromoacetylene with triethylamine, so that this reaction is very probably the one in which the second bromide ion is produced from *cis*-dibromoethylene.

In order to examine the SN route of reaction scheme 4 directly, we required compound **5E**. Though we encountered difficulties in preparing this triethyl salt, we could obtain the trimethyl analog **5M**. Therefore, we used this as a model for **5E**, assuming that the substitution of methyl for ethyl would not alter the reactivity significantly. Since substitution of haloalkenes goes with retention,[5,6] the *cis* configuration of **5M** was correct. Among all compounds in this study, compound **5M** had the highest reactivity toward the triethylamine in DMF (Table IV). In fact, the rate constant of **5M** at 40–50° is about the same as that for monobromoacetylene at 101°, perhaps *ca.* 25 times that of monobromoacetylene at the same temperature. This means that whatever the fate of **5E**, it does not lie on the same reaction path as monobromoacetylene. Hence we exclude a connection between the two in reaction scheme 4. All of this implies, of course, that the rate constant, k_{22}, of **5E** is too large to qualify as k_{12} in reaction 4; **5E** cannot be the first stable intermediate, and the SN path is precluded.

Structure–reactivity comparisons provide additional evidence for the elimination EN path in (4). It is well known that dehydrohalogenation is much faster when the departing groups are *trans* than when they are *cis*.[12,25,26] This factor in the second-order rate constants is 10^5 for the 1,2-dibromoethylenes in methoxide–methanol at 60°. Moreover, dehydrochlorination is slower than dehydrobromination in corresponding haloalkenes.[12,26] In Table IV, the factor of *ca.* 300 at 121 and 101° in the rate constants of *cis*-dibromoethylene over those for *trans*-dibromoethylene and *cis*-dichloroethylene is wholly consistent with EN processes.

With respect to substitution at an unsaturated center, this appears to involve prior addition of the nucleophile to the π system in a slow step followed by rapid loss of halide.[5–7] Normally, the mechanism of direct substitution is not very sensitive to the configuration of the reagents or to the nature of the leaving group. Accordingly, the rate constants of the reactions of phenylthiolate ion with *cis*- and *trans*-bromo- and chlorostyrenes are all included within a factor of 10.[6] Not infrequently in the SN process, in haloalkenes,[5,6] haloalkynes,[27] or halobenzenes,[28] the chloro compound

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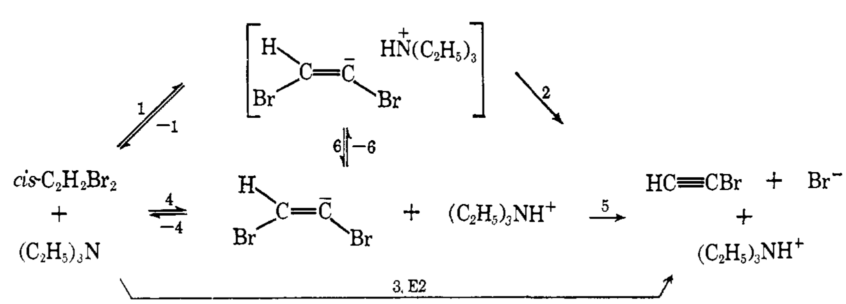

(10)

may even react somewhat faster than the bromo compound. Again, the rate comparisons in Table IV of *cis*-dibromoethylene with *trans*-dibromoethylene or *cis*-dichloroethylene would seem to exclude the SN process in reaction scheme 4.

An Ion-Pair Elimination Mechanism, $(ElcB)_{ip}$. We have established that the *second* step in (4) is relatively fast and probably involves monobromoacetylene. This was formulated as an SN process.[24,27] As the first step in the reaction of *cis*-dibromoethylene with triethylamine, the SN process seems ruled out. We consider, therefore, the detailed description of the first step as a rate-determining elimination.

Three possible first steps in elimination are given in reaction scheme 10. The concerted E2 process is step 3. Above it in steps 4 and 5 is an ElcB mechanism *via* separated ions.[8,9] Across the top in steps 1 and 2 is an $(ElcB)_{ip}$ mechanism *via* an intimate ion pair (ip). The difference in the two ElcB mechanisms is in the nature of the first products: as opposed to the separated ions, the intimate ion pair either returns (collapses) to reactants or falls apart to give products, without exchanging triethylammonium ions with those in the solvent pool.

For simplicity, we shall consider the two ElcB paths as independent alternatives, although one might as plausibly proceed from reactants to products *via* step 1, step 6, and step 5 in scheme 10. The rate law for the $(ElcB)_{ip}$ mechanism has the form

$$k_{\text{obsd}} = k_1k_2/(k_{-1} + k_2) \qquad (11)$$

while that for the usual ElcB process has the form[9]

$$k_{\text{obsd}} = k_4k_5/(k_{-4}[\text{BH}^+] + k_5) \qquad (12)$$

in which B is triethylamine. If $k_5 \gg k_{-4}[\text{BH}^+]$ or $k_2 \gg k_{-1}$, then k_{obsd} for the three mechanisms cannot be distinguished among k_1 or k_3 or k_4. All three would be subject to general base catalysis. One would have to use extra-kinetic arguments to choose among the three mechanisms.

If $k_5 \ll k_{-4}$, specific base catalysis (implicit in eq 12) and hydrogen exchange between substrate and a protonic solvent should be observable. In the $(ElcB)_{ip}$ mechanism, with $k_2 \ll k_{-1}$, general base catalysis and no hydrogen exchange with a protonic solvent should be observable. Now, $k_{\text{obsd}} = K_1k_2$. Here, one would need extra-kinetic arguments to distinguish k_3 of the E2 process from K_1k_2 of the $(ElcB)_{ip}$ process.

Structural effects on the elimination indicate, but do not prove, that carbon–halogen bond breaking is involved in the rate-determining step. On this basis we would have to include both preequilibrium ElcB processes as well as the concerted elimination of step 3 as mechanistic possibilities. At the same time, limiting cases of $k_{\text{obsd}} = k_1$ or k_4 may be discarded.

Now, the next pertinent observations on mechanism are these. The rate data in Table II and Figure 3 indicate that the deuterium isotope effect on the dehydrobromination of *cis*-dibromoethylene is $k_H/k_D = 1.00$. Salts such as triethylamine hydrochloride or hydrobromide do not appear to affect the dehydrobromination rate (Table I). In the reaction of triethylamine with *cis*-dibromoethylene in the presence of triethylammonium deuteriobromide, the unreacted dibromoethylene does not become deuterated. Finally, there are the observations of the related dehydrobromination and hydrogen exchange in methanol, which are contained in (1).[2]

At the outset, the absence of a retarding salt effect and of deuterium uptake from deuterated salt suggests that, if separated ions are formed at all, $k_{-4} \simeq 0$ in eq 10. This effectively excludes the preequilibration ElcB mechanism.

The observed isotope effect can now be considered for one of the limiting single-step processes, *i.e.*, k_1 or or k_3 or k_4, *vs.* K_1k_2 of the $(ElcB)_{ip}$ mechanism. Observed values of the isotope rate effects in eliminations involving carbon–hydrogen bond breaking normally fall in the range $k_H/k_D \simeq 2$–7.[29] On the other hand, the isotope rate effect for the $(ElcB)_{ip}$ mechanism should be close to unity, for the effect on k_{obsd} of eq 11 is made up of equilibrium (K_1)[30] and secondary (k_2) isotope effects, which are close to unity.[31] This oversimplified argument suggests that the E2 mechanism, and those mechanisms which are kinetically equivalent to it, are improbable. On the basis of *all* of the evidence to this point, the choice is between the $(ElcB)_{ip}$ and E2 mechanisms, with the $(ElcB)_{ip}$ mechanism strongly favored.

We would like to believe that our mechanistic conclusions are free both from unwarranted extrapolations from other systems and unproved assumptions about what k_H/k_D is expected to be for a given mechanism. More O'Ferrall and Kouba have made extensive calculations bearing on hydrogen transfer in four- and five-center transition states; they find that transfer of a proton from carbon to trimethyamine leads to k_H/k_D = 1.0, 6.3, and 0.9 for reactant-like, symmetric, and product-like transition states, respectively.[32] (It is unlikely that these ratios would change appreciably, if the proton abstraction were accompanied by departure of β-bromide in the rate-determining step.) It should be noted that the calculated value of $k_H/k_D = 1.00$ would presumably hold for the El process, which hardly ap-

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(32) R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc.*, *B*, 985 (1967).

plies here to a bromoalkene, for elimination is almost invariably promoted by base,[12,26] and solvolysis is almost unknown. In any case, this calculated value rises quickly from the reactant-like limit so that it is already *ca.* 2.6 at a transition state 90% reactant-like and 10% product-like.[32]

At the product-like limit, we arrive at the E1cB process. Subject to the reasonable assumption that the isotope effect is largely given by the zero point energy (ZPE) contribution to the partition functions,[30,31] we can make estimates of the isotope rate effect. For the preequilibrium we sum vibration frequencies as follows.

$$(\mathrm{ZPE})_1 = \frac{1}{2}\left(\sum_{1}^{12}(\nu_{\mathrm{H}} - \nu_{\mathrm{D}})_{\mathrm{C_2H_2Br_2}} - \sum_{1}^{9}(\nu_{\mathrm{H}} - \nu_{\mathrm{D}})_{\mathrm{C_2HBr_2^-}} - \sum_{1}^{36}(\nu_{\mathrm{H}} - \nu_{\mathrm{D}})_{\mathrm{(CH_3)_3NH^+}}\right) \quad (13)$$

$$= \frac{1}{2}(2634 - 1442 - (1350 \pm 50)) = -79 \pm 50\ \mathrm{cm^{-1}}$$

Vibration frequencies of *cis*-dibromoethylene[3] and trimethylammonium ion and their deuterated analogs are available.[33] Although some of the assignments for the trimethylammonium ion are somewhat uncertain,[33] we believe that the frequency difference we require is *ca.* 1350 ± 50 cm.$^{-1}$ Moreover, we do not believe that this quantity will be altered greatly in the triethylammonium ion, which is really directly involved in our measurement of $k_{\mathrm{H}}/k_{\mathrm{D}}$. Since we have no way to evaluate ZPE of the carbanion, we approximate by setting it equal to the ZPE term of the *cis*-dibromoethylene *less* contributions from three asymmetric hydrogenic modes (ν_8, ν_9, ν_{12}).[3] The $(\mathrm{ZPE})_1 = -79 \pm 50\ \mathrm{cm^{-1}}$ translates into $K_{1\mathrm{H}}/K_{1\mathrm{D}} = 0.90 \pm 0.06$ at 100°, which agrees with the product-like value computed from fewer frequencies by More O'Ferrall and Kouba.[32] We believe the close

$$(\mathrm{ZPE})_2 = \frac{1}{2}\left(\sum_{1}^{9}(\nu_{\mathrm{H}} - \nu_{\mathrm{D}})_{\mathrm{C_2HBr_2^-}} - \sum_{1}^{7}(\nu_{\mathrm{H}} - \nu_{\mathrm{D}})_{\mathrm{C_2HBr}}\right) \quad (14)$$

$$= \frac{1}{2}(1442 - 1172) = 135\ \mathrm{cm^{-1}}$$

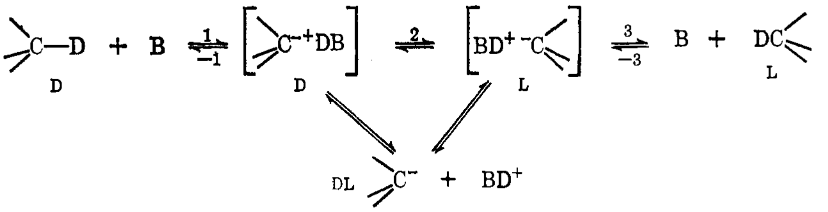
agreement is partly fortuitous, because our calculation involves more vibrational modes, alkene rather than alkane frequencies, and both primary and secondary isotope effects.

In the step from vinyl carbanion to product, we estimate the *total* change (eq 14). The vibrational frequencies of the monobromoacetylenes were taken from the literature.[34] Note that the *maximum* for this secondary isotope rate effect on the rate would be $k_{2\mathrm{H}}/k_{2\mathrm{D}} = 1.20$ at 100°. Such a value is not unreasonable, for it falls in the range of secondary isotope rate effects of 1.10–1.20 per deuterium on the same carbon (α) as the leaving group.[31]

The over-all isotope effect on k_{obsd} of eq 10 is therefore calculated to be 0.90 × 1.20 = 1.08, where this is an upper limit. We believe this estimate is sufficiently close to our observed value of unity, so that one may be confident that the $(\mathrm{E1cB})_{\mathrm{ip}}$ model is reasonable. We shall come back to the problem of "low" deuterium isotope rate effects in elimination presently.

In view of the preceding analysis of the isotope effect on the possible mechanisms of dehydrobromination, we believe that the evidence for the tight ion pair $(\mathrm{E1cB})_{\mathrm{ip}}$ process is compelling. But is it plausible? How reasonable is the existence of an undissociated ion pair at 90–130°? It turns out that this $(\mathrm{E1cB})_{\mathrm{ip}}$ process fits in nicely with reaction schemes in apparently unrelated systems. Our discussion begins with the behavior of the tight ion pair of (10).

In the area of electrophilic substitution, Cram, *et al.*, has provided numerous examples of contact ion pairs, *e.g.*, $[\mathrm{R_1R_2R_3C^-\ {}^+DNR_3}]$, in which the rates of hydrogen exchange (k_{ex}) and carbon racemization (k_α) were studied.[35–37] When $k_{\mathrm{ex}}/k_\alpha < 0.5$, isoracemization or racemization without exchange predominates. In the reaction of tri-*n*-propylamine with a substituted 9-methylfluorene at 75° in tetrahydrofuran–*t*-butyl alcohol, $k_{\mathrm{ex}}/k_\alpha < 0.1$.[36] Examples in which the tri-*n*-propylamine conducts one proton on a tour of several sites on the carbanion without losing it to the solvent pool are also known.[36] Even in a solvent as dissociating as methanol, contact ion pairs may racemize at rates comparable to hydrogen exchange.[36] Since identity collapse along steps −1 or −3 in eq 15 would not be detected in this work, the first ion pair is probably formed many times faster than revealed by k_α. Such data provide precedents and analogies for the tight ion pair of reaction 10, in which recombination (step −1) or decomposition (step 2) appears to predominate over dissociation (step 6).



(15)

The matter of the lifetime of the carbanion, HCBr=CBr⁻, is something of a problem. This, however, can be estimated for the present system from the previous work with dibromoethylene in methanol.[2] The steady-state treatment applied to process 1 yields

$$k_{\mathrm{elim}} = k_1k_2/k_{-1}(\mathrm{CH_3OH}) \quad (16)$$

Since $K = k_1/k_{-1} \simeq 3.3 \times 10^{-14}$ and $k_{\mathrm{elim}} \simeq 2\ M^{-1}\ \mathrm{sec^{-1}}$ at 100°,[2] $k_2 \simeq 10^{15}\ \mathrm{sec^{-1}}$ at 100°. If the first-order rate of decomposition of the carbanion is assumed to be independent of solvent, the same values of $k \simeq 10^{15}\ \mathrm{sec^{-1}}$ would hold for DMF at 100°. Even if

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(37) D. J. Cram, W. T. Ford, and L. Gosser, *ibid.*, **90**, 2598 (1968).

errors were involved in both the estimates and extrapolations, the half-life of the carbanion should still be exceedingly small. (If the carbanion were a blind alley intermediate,[4] our estimate of the half-life would be a lower limit, of course, and of little use in this context.)

To compare k_2 with k_{-6} in eq 10, we require data on the hypothetical equilibrium of the tight ion pair with separated ions. It has been reported that tetrabutylammonium chloride has an almost temperature-independent dissociation constant, K_D, of $(4.1 \text{ to } 2.3) \times 10^{-2} M$ in DMF at 30–120°.[38] If we assume $k_{-6} \simeq 10^{10}\ M^{-1}\ \text{sec}^{-1}$, or the diffusion-controlled limit,[39] $k_6 \leq 10^{12}\ \text{sec}^{-1}$. On this basis, we find $k_2/k_6 \simeq 10^3$, or the tight ion falls apart before it dissociates. None of these figures, of course, are precise, but they do provide a satisfying rationale for the $(\mathrm{E1cB})_{\mathrm{ip}}$ mechanism.

A General $(\mathrm{E1cB})_{\mathrm{ip}}$ Mechanism. Ingold has pointed out that there is a spectrum of transition states for elimination. From one extreme, E1 (or SN1), in which a carbonium ion has formed, one passes through E2 transition states to the E1cB (or SE2) extreme, in which a carbanion has formed.[40] Just as it has been necessary to include a variety of ion pairs in carbonium mechanisms, it has been recognized that an analogous series of ion pairs may participate in carbanion (SE) processes.[35–37] With respect to elimination mechanisms of the E1cB type, ion pairs have occasionally been mentioned in discussions of certain *syn* eliminations.[41] What we have proposed is an elaboration of Ingold's mechanistic spectrum to include $(\mathrm{E1cB})_{\mathrm{ip}}$.

$$\mathrm{E1} \text{———} (\mathrm{E1})_{\mathrm{ip}} \text{———} \mathrm{E2} \text{———} (\mathrm{E1cB})_{\mathrm{ip}} \text{———} \mathrm{E1cB}$$

The proposal is novel in the sense that a new rate law with specific consequences can be tested, and a probable example has been found.

Recent interest in E1cB type mechanisms has centered on finding unambiguous examples and/or establishing criteria for their identification.[9] The preequilibrium E1cB process, which is subject to specific base catalysis, can be separated out, as in the last section. For the rest, it has become popular to characterize certain apparently E2 reactions as "carbanion-like" (E1cB-like), and conversely. To cope with the total problem, one can draw on several types of measurement, *e.g.*, acidity dependence (H_-), *syn vs. anti* stereoselectivity and reactivity, isotope effects, leaving group effects, structure and reactivity (Hammett ρ or Brønsted α), medium effects, etc. The problem is to sort out mechanisms in eq 10, which lead to k_1, k_3, k_4, K_1k_2, and $k_1k_2/(k_{-1} + k_2)$ for k_{obsd}. Although distinctions may be difficult to find (or measure), the difference between the simple and composite constants, *e.g.*, k_3 and K_1k_2, is clear-cut. On the other hand, we see no way to make the choice between the two E1cB mechanisms, in which k_{obsd} is either k_1 or k_4. As between k_1 (or k_4) *vs.* k_3, it may be necessary to define more precisely what is meant, say by E1cB-like, in terms of extra-kinetic properties or assumptions.

Of necessity, our discussion must be limited to the example of this paper. We believe it will be valuable to emphasize that deuterium isotope effects make a choice between K_1k_2 and k_1 or k_3 or k_4 possible, and to give a recipe for the interpretation of "low" hydrogen isotope effects. (There may of course be E1 or E1-like mechanisms, which may lead to an isotope effect in the range of the E1cB limit. We assume these can be recognized.)

Our recommendation is simple: if an observed primary isotope effect is in the range estimated for K_1k_2, the preequilibrium E1cB mechanisms are indicated. In the title system, the observed $k_H/k_D = 1.00$ appears to result from cancellation in K_{1H}/K_{1D} and k_{2H}/k_{2D}. The model calculations of More O'Ferrall and Kouba indicate the values with different bases (K_{1H}/K_{1D}) are CH_3O^- (1.1), CH_3S^- (2.7), CN^- (1.6), $(CH_3)_3N$ (0.9), F^- (1.2), Cl^- (2.6), Br^- (3.2), and I^- (4.0).[32] Secondary deuterium isotope effects, either on K_1 or k_2, may change these figures a little.[31] Since complete assignments of vibrational frequencies are not normally available, it would be desirable to have experimental values to check or calibrate the calculated values. These K_{1H}/K_{1D}'s could be obtained by analysis of solutions obtained by dissolving suitable pairs of compounds in an aprotic solvent, and adding catalytic quantities of potassium methoxide, *e.g.*

$$R_3CH + CH_3OD \underset{\text{glyme}}{\overset{CH_3O^-K^+}{\rightleftharpoons}} R_3CD + CH_3OH \qquad (17)$$

Although some old data of this general type are available, they are of uncertain quality.[30] The point is that the equilibrium deuterium isotope effect of interest here is accessible, either by calculation or by experiment. In principle, one has a rigorous method for inclusion or exclusion of the preequilibrium E1cB mechanisms.

Having established the E1cB limit of K_{1H}/K_{1D} under specified conditions of base, solvent, temperature, etc., one can decide that a higher observed isotope effect pertains to k_{1H}/k_{1D} or k_{3H}/k_{3D} or k_{4H}/k_{4D}. According to the model calculations of More O'Ferrall and Kouba, the isotope effect should rise fairly steeply from the limiting values, and the region of uncertainty of what is "high" and what is "low" is small.[32] Other model calculations either show a gentler rise or do not relate the change in k_H/k_D to the transition asymmetry;[42] in either case, the region of uncertainty is larger. In large measure, the basic problems or reaction rate theory is involved. Further mechanistic differentiation will therefore have to depend on other data, *e.g.*, leaving-group effects, etc.

It has become necessary to reexamine so-called "low" isotope effects. We consider that either of the preequilibrium E1cB mechanisms applies to the following eliminations on the basis of the observed isotope effects: (1) $k_H/k_D = 1.26$ for methoxide–1,1,1-trifluoro-2,2-dichloroethane;[43] (2) $k_H/k_D = 1.41$ for methoxide–1,1,1-trifluoro-2-bromo-2-chloroethane;[43] (3) $k_H/k_D = 1.2$ for *t*-butoxide–1,1,1-trifluoro-2-methyl-3-phenylpropane;[44] (4) $k_H/k_D = 0.9$–1.1 for *t*-butoxide–*ethythro*-2,-3-dimethyl-3-(trimethylammonium)nonane;[45] (5) $k_H/k_D = 1.6$ for *cis*-β-chloro-*p*-nitrostyrene with methoxide in methanol.[26] In the first two cases base-promoted

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[45] M. Panková, J. Sicher, and J. Závada, *Chem. Commun.*, 394 (1967).

hydrogen exchange of reactant and solvent was observed, while none was detected in the others. In the third system, racemization of the optically active starting material could not be found under conditions of the elimination. Rather than term these reactions "carbanion-like," the primary isotope effect k_H/k_D "low," and the transition state "asymmetric E2," we believe that the magnitude of the isotope effect is strong evidence for the preequilibrium E1cB or $(\mathrm{E1cB})_{\mathrm{ip}}$ processes. We cite only two of many other reactions which have received much attention and which we consider as possible candidates for the $(\mathrm{E1cB})_{\mathrm{ip}}$ mechanism: $k_H/k_D \simeq 1.9$ for *syn* eliminations of various cyclic trimethylammonium hydroxides;[46] the "carbanion-like elimina-tions in the 2-arylsulfonylcyclohexyl tosylates.[47]

Although the $(\mathrm{E1cB})_{\mathrm{ip}}$ mechanism may be difficult to prove, we can perhaps discern some of the factors associated with it. In the series of *cis*- or *trans*-dihaloethylenes, dehydrohalogenation in methanolic methoxide follows the order $k_{\mathrm{elim}}(\mathrm{C_2H_2I_2}) > k_{\mathrm{elim}}(\mathrm{C_2H_2Br_2}) > k_{\mathrm{elim}}(\mathrm{C_2H_2Cl_2})$,[12] while hydrogen exchange with alkaline deuterium oxide is in the reverse order $k_{\mathrm{ex}}(\mathrm{C_2H_2Cl_2}) > k_{\mathrm{ex}}(\mathrm{C_2H_2Br_2}) > k_{\mathrm{ex}}(\mathrm{C_2H_2I_2})$.[2] *cis*-Diiodoethylene, however, seems to be exceptional and significant in that no exchange was observed, possibly because $k_{\mathrm{elim}} > k_{\mathrm{ex}}$.[2] A change from preequilibrium E1cB to a non-preequilibrium E1cB or an E2 mechanism seems to be indicated. The title system is inserted in the elimination spectrum at $(\mathrm{E1cB})_{\mathrm{ip}}$, presumably because of the less dissociating solvent DMF. Again, there is the parallel with $\mathrm{S_E}$ reactions in which the degree of racemization increases roughly with the polarity of the medium.[35]

Methoxide *vs.* Triethylamine in Dehydrobromination. The rate of elimination from *cis*-dibromoethylene at 60° is *ca.* 10^5 larger with sodium methoxide in methanol than with triethylamine in DMF (Table IV). What is remarkable about the two systems, however, is the strong reversal in the effect of the activation parameters (E_a, kcal/mol; $\Delta S^{\ddagger}$, eu): $\mathrm{NaOCH_3{-}CH_3OH}$, 28.1, 16; $\mathrm{(C_2H_5)_3N{-}DMF}$, 18.7, −32. We are inclined to believe that these figures, which span opposing factors in the rates of *ca.* 10^6 in energy and *ca.* 10^{11} in entropy, reflect gross changes in the role of the solvent, as suggested by Parker.[48] In methanol, the reactants and, in DMF, the ion-pair product are highly solvated; specifically, hydrogen bonding of methanol to methoxide and of DMF–triethylamine to triethylammonium ion is proposed. In this simple picture, it is reasonable that solvation energy and entropy effects should be opposed.

The present results do suggest an interesting application. In order to increase the rate of elimination, *e.g.*, dehydrohalogenation, one can do several things, *i.e.*, increase the base strength and decrease ground-state solvation. Both of these seem to be accomplished, when one uses potassium *t*-butoxide in dimethyl sulfoxide.[48] If, too, a strong donor, *e.g.*, triethylamine, is added, one could conceivably enhance the solvation of the transition state and/or ion pair and thus align the factors that enhance the rate.

The preceding comments are not intended to encompass, in any broad sense, the activation parameters for elimination from all haloalkenes. Indeed, these quantities can show large and often unexplained variations.[25] Certain rationalizations designed to fit limited sets of data can be misleading. It should be noted, therefore, that many, but not all, *anti* dehydrohalogenations have positive entropies of activation,[12,25] and some, but not all, *anti* eliminations have lower energies of activation than those of corresponding *syn* eliminations.[49]

Nucleophilic Reactivity at an Acetylenic Carbon. Although our data were not intended for this purpose, it is possible to make a comparison of the relative reactivity of nucleophiles with several carbon centers. The reaction type is the displacement

$$\mathrm{RBr} + \mathrm{(C_2H_5)_3N} \longrightarrow \mathrm{RN(C_2H_5)_3{}^+Br^-} \qquad (18)$$

The reactivity scale for DMF is summarized by the order $\mathrm{C_2H_5Br(sp^3)} \sim \mathrm{HC{\equiv}CBr(sp)} > \mathrm{H_2C{=}CHBr(sp^2)} > \mathrm{C_6H_5Br(sp^{2.5})}$. A similar order was noted when iodide was the nucleophile.[50]

Of necessity, we put this sequence together by extrapolating from structurally related compounds or from rate data in other solvents. Fortunately, solvent effects on molecule–molecule reactions are less pronounced than those involving ions;[48] the range of reactivity of saturated chlorides or bromides with several amines in solvents such as nitrobenzene, pentanone, amyl acetate, or xylene is usually less than a factor of 10 and almost invariably less than 10^2.[51] To estimate the rate constant of ethyl bromide in DMF, we took the data for triethylamine and propyl bromide in benzene and came up with $10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$.[52] Vinylic bromides do not react with amines at 100° in 1000 hr,[51] and bromobenzene does not react with piperidine at 130° in 200 hr.[53] By considering the literature on activated bromides, *e.g.*, with arylsulfonyl substituents, we judge substitution at ethylenic carbon[7] to be faster than substitution at aryl carbon.[53] It should not be surprising to find changes in this particular order, *e.g.*, with changes in solvent or nucleophile.[24b,27]

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