[Contribution from the Department of Chemistry of Columbia University]

Kinetics of Basic Elimination Reactions of the Dihaloethylenes and the Mechanism of *trans* Elimination

By Sidney I. Miller[1] and Richard M. Noyes

Kinetic studies are reported on the elimination reactions of methoxide ion with the *cis* and *trans* isomers of dichloro-, dibromo- and diiodoethylenes. The data indicate that *cis* and *trans* eliminations proceed by different mechanisms having identical kinetic orders. In all three pairs of isomers *trans* elimination is faster than *cis* elimination, but the difference is due to an entropy effect in the dichloroethylenes and to an energy effect in the diiodoethylenes. In the *trans* eliminations the entropies of activation are unusually large, and the energies of activation decrease during the sequence chloride–bromide–iodide. In the *cis* eliminations the energies of activation increase slightly during the same sequence, but the effect is more than counterbalanced by a large increase in the entropies of activation. These observations appear to be consistent with the theory that *trans* elimination takes place by a one-step concerted process, while the *cis* elimination process requires two or more steps such that the rate is determined either by removal of a proton or by inversion of the resulting carbanion.

In bimolecular elimination reactions, groups located in *trans* positions are removed more easily than those in *cis* positions. No certain exceptions have been found to this "*trans*-elimination" rule which was first formulated by Michael.[2] This difference in reactivity has sometimes been ascribed to electrostatic effects arising from differences in polarity of the isomers.[3] However, these forces are not large enough to account for observed differences in rate and sometimes (as in the example of bromofumarate and bromomaleate[4]) are even in the direction to favor *cis* elimination. After one-step substitution reactions at a secondary carbon were recognized to involve inversion, it was suggested that *trans* elimination might be a similar reaction in which an electron pair from one carbon atom acted as the displacing "group" in a substitution reaction at an adjacent carbon atom.[5] Recently Cristol, *et al.*,[6] have suggested that *trans* elimination proceeds by a one-step concerted mechanism, but that *cis* elimination proceeds through the formation of an intermediate carbanion which rearranges and completes the elimination in another step.

In the present paper we wish to report kinetic data on the reactions with methoxide ion of the various *cis*- and *trans*-dihaloethylenes. The reactions may be formulated by the equation

$$\mathrm{CHX{=}CHX + CH_3O^- \longrightarrow HC{\equiv}CX + CH_3OH + X^-} \quad (1)$$

where the two X's in the initial molecule are Cl, Br or I. Although all of these reactions are identical with regard to kinetic order, our data indicate that the *cis* and *trans* eliminations proceed by very different mechanisms. The Cristol mechanisms involving one-step and two-step processes appear to be entirely consistent with our results, but kinetic observations of elimination reactions alone can never demonstrate either mechanism unequivocally.

Experimental

Materials.—Anhydrous methanol was used as solvent throughout and was prepared from Mallinckrodt 99.5% "absolute methanol" by the method of Lund and Bjerrum.[7] Solutions of sodium methoxide were prepared by rinsing the surface of chemically pure sodium with methanol and dissolving the rinsed metal in the anhydrous solvent. The concentration was determined by titration of the solution with standard acid.

cis- and *trans*-dichloroethylenes were obtained from Columbia Organic Chemicals and were fractionally distilled under carbon dioxide as recommended by Wood and Dickinson.[8] At 765 mm. pressure the *cis* isomer boiled at 59.65–59.80°, and the *trans* boiled at 47.2°.

Dibromoethylene was prepared by the action of zinc on tetrabromoethane. The isomers were separated by fractionating the ethanol azeotropes as described by van de Walle.[9] The dibromoethylene was recovered from each azeotrope by washing repeatedly with water and drying with calcium chloride. The *cis* isomer could be kept indefinitely in a stoppered flask in a refrigerator. The pure *trans* isomer under the same conditions rapidly reverted to an equilibrium mixture; therefore, it was dissolved in solvent immediately after it was shaken with drying agent.

trans-Diiodoethylene was prepared from acetylene and iodine.[10] It was purified by successive recrystallizations from aqueous ethanol and melted sharply at 72.2°.

cis-Diiodoethylene was prepared by the isomerization of the *trans* isomer. A sample of dried impure *trans*-diiodoethylene contaminated with iodine was exposed for several days to two infrared lamps which emitted a significant amount of visible light. The flask was then cooled, and the liquid was poured off from the residue of *trans* isomer. The liquid consisted of a mixture of iodine with the two isomers. Irradiation of the residue was repeated until sufficient liquid was available for fractionation. The iodine was then removed by extraction with aqueous bisulfite, and the remaining brown oil was frozen. The resulting solid was placed on a sintered glass funnel and centrifuged while it was warming to room temperature. The melt from the centrifuging was refrozen, and the operation was repeated until a eutectic liquid freezing −13.5 to −13.6° was obtained. The crystals which separated on the filter plate always melted close to 72°. Evidence presented elsewhere[11] demonstrated that the liquid, the "*cis*-diiodoethylene" of the previous literature, is a eutectic containing about 20.5% of the *trans* isomer. The separated eutectic liquid was dried over calcium chloride or drierite and distilled in the dark at about 35° and 1 mm. Even though the material was a mixture, it distilled without observable change in melting point; this result is not surprising in view of the almost identical vapor pressures of the two isomers.[12] The water-white distillate was redried and used directly in the kinetic runs.

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[1] Based on a Dissertation submitted by Sidney I. Miller to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. Persons desiring to consult the more complete report or obtain a microfilm thereof may address the Library, Columbia University, New York 27, N. Y.

[2] A. Michael, *Ber.*, **34**, 4215 (1901); *J. prakt. Chem.*, **52**, 344 (1895).

[3] W. Huckel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[4] S. J. Cristol, private communication, November, 1950.

[5] S. Winstein, D. Pressman and W. G. Young, This Journal, **61**, 1645 (1939).

[6] (a) S. J. Cristol, *ibid.*, **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951).

[7] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[8] R. E. Wood and R. G. Dickinson, This Journal, **61**, 3259 (1939).

[9] H. van de Walle, *Bull. soc. chim. Belg.*, **27**, 209 (1913).

[10] R. M. Noyes, R. G. Dickinson and V. Schomaker, This Journal, **67**, 1319 (1945).

[11] S. I. Miller and R. M. Noyes, *ibid.*, **73**, 2376 (1951).

[12] R. M. Noyes, Win. A. Noyes and H. Steinmetz, *ibid.*, **72**, 33 (1950).

Aqueous solutions of hydrochloric and nitric acids were standardized against anhydrous sodium carbonate by standard procedures.[13] Solutions of sodium hydroxide and sodium methoxide were standardized against the hydrochloric acid.

Standard solutions of chemically pure silver nitrate were prepared by direct weighing. Potentiometric titrations[14] against pure sodium chloride checked their calculated concentrations to one part in a thousand.

Procedure at Low Temperatures.—The "low temperature" runs include those at temperatures below 45°. At 0° the thermostat consisted of a large dewar flask containing an ice-water slush. The other constant temperatures in this range were obtained in conventional water thermostats. Temperature control was good to at least ±0.03°. All the thermometers were calibrated against a National Bureau of Standards thermometer.

Most of the runs at temperatures below 45° were carried out in a stoppered erlenmeyer reaction flask containing a central compartment of about 50-ml. capacity. A stock solution of sodium methoxide was pipetted into the outer compartment, and a stock solution of dihaloethylene was pipetted into the inner; more solvent methanol was pipetted into the flask if desired. The total volume was taken as the sum of all pipetted volumes. The flask was allowed at least 45 minutes to reach thermostat temperature, and the reaction was started by tipping and shaking the flask. At known time intervals 10-ml. samples were withdrawn, emptied into water containing an excess of dilute acetic acid, and analyzed for halide potentiometrically. The total uncertainty in the time interval is no more than thirty seconds; this uncertainty may be important in the initial points for the rapidly-reacting *cis*-diiodoethylene and dibromoethylene.

Procedure at High Temperatures.—The "high temperature" runs include those at temperatures above 58°. These were carried out in oil thermostats controlled by conventional regulators to within 0.1 to 0.2°.

The dihaloethylenes in these experiments were so unreactive that it was possible to prepare stock solutions which also contained methoxide ion. Small glass ampules were filled with 10-ml. portions of these stock solutions, capped, cooled with Dry Ice, uncapped, and sealed. The sealed ampules were stored in a refrigerator until they had reacted. Identical stock solutions which had been allowed to stand in the laboratory for three to five days did not contain any significant amounts of halide ion; therefore, solutions in the ampules did not undergo appreciable reaction before they were placed in the thermostats. A blank correction of 0.1% was made for runs with *trans*-dibromoethylene because of the presence of a reactive impurity which was probably the *cis* isomer.

To carry out kinetic runs, the ampules were first brought to room temperature and were then placed in the thermostats. Ampules to be left in for periods of less than 500 minutes were shaken vigorously in the bath, and zero time was taken about two minutes after they were added. At the conclusion of a run the ampule was chilled rapidly with cold water and stored in a refrigerator until it was analyzed. The uncertainty in the time of heating is no more than 3 minutes.

In order to analyze the results of a run, the contents of the ampule were rinsed into a slight excess of dilute acetic acid. The amount of free halide ion was then estimated potentiometrically as described above. Blank titrations for halide were made on all reagents. Ampules containing dihaloethylene but no methoxide did not form any free halide ion under identical conditions.

Stoichiometry.—We have assumed that the elimination described by equation (1) was the initial net reaction in all of these systems. Pure $HC\equiv CCl$ and $HC\equiv CBr$ have been isolated from the action of strong bases on equilibrium mixtures of dichloro- and dibromoethylene[15]; the preparation of $HC\equiv CI$ by this method has not been reported.

The subsequent behavior of the products in equation (1) was not studied in detail. Runs which were allowed sufficient time contained more than the theoretical amount of halide regardless of which reactant was initially in excess. The chloro- and bromoacetylenes are known to inflame spontaneously in air above a partial pressure of several millimeters,[15] and they may not be stable in these solutions. It is known also that, in the presence of alcoholic alkoxide, haloacetylenes may undergo several reactions, including the formation of the acetylene, an olefinic ether or a carboxylic acid.[16] All of these reactions consume base and produce halide ion.

The *cis* isomers (*trans* eliminations) showed "clean" kinetics with rate constants which did not vary during a run until the reaction was at least 50% and sometimes as much as 80% complete. These observations indicate that one molecule of dihaloethylene neutralized on methoxide ion with the formation of one halide ion. This stoichiometry was more fully confirmed in the reaction of *cis*-diiodoethylene by titrating both the residual base and the iodide produced.

The *trans* isomers (*cis* eliminations) were not as well behaved. In any given run the calculated second-order rate constant increased steadily after the initial stages of the reaction were over. However, initial rates measured with widely varied concentrations demonstrated that the halide was first produced by a reaction which was first order in dihaloethylene and first order in methoxide ion. It would appear that the autocatalytic nature of these reactions may be attributed to side reactions of the haloacetylenes which were favored by the higher temperatures, the longer reaction times, and the frequently greater methoxide concentrations compared to those in the corresponding *trans* eliminations.

The over-all stoichiometry of the reaction of *cis*-diiodoethylene was shown to be

$$2C_2H_2I_2 + 2CH_3O^- \longrightarrow 2CH_3OH + 2I^- + IC\equiv CI + HC\equiv CH \quad (2)$$

As was mentioned earlier, the rate of disappearance of base was shown to be equal to the rate of formation of iodide. The acetylene was analyzed as $C_2Ag_2 \cdot AgNO_3$.[17] Only about 90% of the theoretical amount was obtained, but the discrepancy may be attributed to the difficulty of collecting all of the gas. The presence of C_2I_2 was established by comparing the properties of the purified product with a sample prepared and purified by the method of Dehn.[18] Melting point, infrared spectrum and other properties served to demonstrate the identity of the two materials. The same products were identified in the reaction of *trans*-diiodoethylene with methoxide, but the quantitative stoichiometry was not worked out. Equation (2) is in agreement with the observations of Emschwiller[19] for the reaction of the *trans* isomer with sodium ethoxide. The data do not provide any information on the mechanism of the fast disproportionation of monoiodoacetylene, but the following sequence of reactions is plausible

$$HC\equiv CI + CH_3O^- \rightleftharpoons CH_3OH + IC\equiv C^- \quad (3)$$

$$IC\equiv C^- + IC\equiv CH \longrightarrow IC\equiv CI + HC\equiv C^- \quad (4)$$

$$HC\equiv C^- + CH_3OH \longrightarrow HC\equiv CH + CH_3O^- \quad (5)$$

Experiments with synthetic C_2I_2 showed that it did not decompose at a significant rate under the conditions of these eliminations; although it is known that both of the iodines in either isomeric diiodoethylene can be removed quantitatively by refluxing with concentrated alcoholic potassium hydroxide.[10] It appears therefore that in the runs at 58° and above with *trans*-diiodoethylene the acceleration observed after the initial stages was caused by some reaction of $HC\equiv CI$ which produced excess iodide. However, we can say that in general any reaction subsequent to equation (1) which produced halide and consumed base did not have an important effect on the rate in the early stages of our runs.

Results

The rate constants for these reactions are defined by the standard expression

$$k = \frac{2.303}{t(b - a)} \log \frac{a(b - x)}{b(a - x)} \quad (6)$$

where

a = initial concentration of $C_2H_2X_2$
b = initial concentration of CH_3O^-
x = concentration of X^- at time t

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[13] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 130.

[14] E. Zintl and K. Betz, *Z. anal. Chem.*, **74**, 330 (1928).

[15] L. A. Bashford, H. J. Emeleus and H. V. A. Briscoe, *J. Chem. Soc.*, 1358 (1938).

[16] R. Truchet, *Ann. chim.*, [10] **16**, 309 (1931).

[17] J. A. Shaw and E. Fisher, *Anal. Chem.*, **20**, 533 (1948).

[18] W. M. Dehn, THIS JOURNAL, **33**, 1598 (1911).

[19] G. Emschwiller, *Bull. soc. chim.*, [5] **2**, 1625 (1935).

TABLE I

RATES OF ELIMINATION REACTIONS OF DIHALOETHYLENES WITH METHOXIDE ION

Compound	Temp., °C.	a, $C_2H_2X_2$ mole/liter	b, $NaOCH_3$ mole/liter	k, liter/mole sec.
cis-$C_2H_2Cl_2$	58.25 ± 0.10	0.1645	0.06291	
		.00638	.1258	
		.02909	.03679	$(9.13 \pm 0.08) \times 10^{-6}$
		.08592	.1258	
	72.46 ± 0.17	0.02909	0.03679	
		.05818	.03679	
		.1645	.06291	$(8.22 \pm 0.07) \times 10^{-5}$
		.08592	.1258	
		.00638	.1258	
	85.36 ± 0.15	0.02909	0.03679	
		.08592	.1258	
		.1645	.06291	$(5.13 \pm 0.05) \times 10^{-4}$
		.00638	.1258	
trans-$C_2H_2Cl_2$	95.8 ± 0.1	0.5212	0.2748	
		.7151	.1310	
		1.5674	.4128	
		0.2620	.8717	$(3.48 \pm 0.08) \times 10^{-7}$
		.4469	.2547	
		.1975	.5094	
	108.9 ± 0.1	0.5212	0.2748	
		.7151	.1310	
		1.5674	.4128	
		0.2620	.8717	
		.4469	.2547	$(1.44 \pm 0.03) \times 10^{-6}$
		.1975	.5094	
		.3024	1.5938	
		.3893	1.2750	
	121.7 ± 0.4	0.5212	0.2748	
		.7151	.1310	
		.2620	.8717	
		.4469	.2547	$(6.02 \times 0.95) \times 10^{-6}$
		.1975	.5094	
		.3024	1.5938	
		.3893	1.2750	
	133.4 ± 0.3	1.5674	0.4128	
		0.4469	.2547	
		.1975	.5094	$(1.64 \pm 0.18) \times 10^{-5}$
		.3893	1.2750	
		.3024	1.5938	
cis-$C_2H_2Br_2$	23.90 ± 0.03	0.03362	0.3820	$(1.18 \pm 0.05) \times 10^{-4}$
		.1303	.2865	
	24.90 ± 0.03	0.00981	0.2520	$(1.22 \pm 0.01) \times 10^{-4}$
		.01192	.1224	
	25.00 ± 0.03	0.00831	0.1271	
		.01603	.09807	$(1.24 \pm 0.02) \times 10^{-4}$
		.01320	.2019	
	35.20 ± 0.02	0.01121	0.1635	
		.02967	.1348	$(6.03 \pm 0.05) \times 10^{-4}$
		.06514	.2865	
	40.00 ± 0.03	0.00981	0.02526	
		.01192	.01227	$(1.23 \pm 0.05) \times 10^{-3}$
		.01756	.02526	
	44.95 ± 0.05	0.01121	0.1635	$(2.55 \pm 0.02) \times 10^{-3}$
		.01868	.08490	
trans-$C_2H_2Br_2$	78.92 ± 0.05	0.1420	0.3371	
		.04827	.5886	
		.1207	.2943	$(5.92 \pm 0.22) \times 10^{-7}$
		.2413	.1471	
		.02057	.4585	

TABLE I (*Continued*)

Compound	Temp., °C.	*a*, $C_2H_2X_2$ mole/liter	*b*, $NaOCH_3$ mole/liter	*k*, liter/mole sec.
trans-$C_2H_2Br_2$ (continued)	94.46 ± 0.12	0.04827	0.5886	(4.22 ± 0.40) × 10^{-6}
		.1207	.2943	
		.2413	.1471	
		.02057	.4585	
	109.15 ± 0.05	0.05193	0.1042	(2.55 ± 0.08) × 10^{-5}
		.04827	.5886	
		.1207	.2943	
		.2413	.1471	
		.02057	.4585	
cis-$C_2H_2I_2$[a]	0.00 ± 0.03	0.02333	0.01235	(3.90 ± 0.02) × 10^{-4}
		.01921	.02543	
	25.02 ± 0.05	0.01414	0.02151	(1.78 ± 0.02) × 10^{-2}
		.03532	.02151	
		.02001	.03047	
		.01091	.03324	
		.01921	.02519	
trans-$C_2H_2I_2$	58.25 ± 0.15	0.01684	0.01470	(8.1 ± 1.5) × 10^{-6}
		.02046	.00589	
		.02672	.00830	
		.01193	.01660	
	69.0 ± 0.1	0.03481	0.02147	(5.1 ± 0.7) × 10^{-5}
		.01547	.02147	
	72.5 ± 0.1	0.01684	0.01470	(6.6 ± 0.7) × 10^{-5}
		.02046	.00589	
		.02672	.00830	
		.01193	.01660	
		.08045	.00415	
	83.2 ± 0.1	0.00857	0.01828	(3.95 ± 0.17) × 10^{-4}
		.01791	.01828	
		.01684	.01470	

[a] These solutions were prepared from "eutectic" diiodoethylene.[11] The concentrations are calculated on the assumption that the material used contained 79.5% *cis* isomer and 20.5% *trans*. The *trans* isomer is unreactive at these temperatures.

In the data presented below, the values of *a* and *b* are expressed in moles/liter at 25°. At other temperatures the calculated values of *k* were corrected with the use of data[20] for the density of methanol as a function of temperature. The largest correction was 17% at 133°. The solutions probably did not have the same coefficients of expansion as pure methanol, but the temperature range in any one series was small enough that the calculated energy of activation cannot have been seriously affected by this assumption.

In Table I are presented the concentrations used in the various runs and the best value of the rate constant for each compound at each temperature. This value was calculated from the initial slope of the plot of *kt* against *t* for all of the runs in the series, extrapolated to zero ionic strength if necessary. Detailed results for each run are reported in the original dissertation.[1] Some runs for *cis*-dibromoethylene and diiodoethylene with methanolic solutions of sodium hydroxide gave rate constants identical with those obtained when the solution of base was prepared by dissolving metallic sodium.

Figures 1 to 6 illustrate the nature of the data (uncorrected for solvent expansion) for each compound at one of the temperatures studied. The data for the *cis* isomers (*trans* eliminations) give plots having identical slopes for all concentrations and showing no deviations from linearity until the reaction is much more than half-way to completion. The subsequent increases, which are probably due to reaction of the product haloacetylenes, do not affect the accuracy of the initial rate constants. The rate constant at each temperature was determined from the slope of the best straight line through the data for all runs. The activation energy, E_{exp}, was calculated from the least squares fit of a plot of log *k* against $1/T$ as illustrated in Fig. 7. The entropy of activation, $\Delta S^{\ddagger}$, was calculated from the standard expression[21]

$$k = \frac{\mathbf{k}Te}{h}\, e^{\Delta S^{\ddagger}/R}\, e^{-E_{\mathrm{exp}}/RT} \qquad (7)$$

where **k** is the Boltzmann constant and *k* is the rate constant corrected for thermal expansion and expressed in liters/mole sec.

The data for the *trans* compounds (*cis* eliminations) are not nearly as satisfactory. The plots of *kt* against *t* are concave upward, being especially bad for the iodide. Moreover, even the initial rates of the chloride and bromide reactions show a dependence on the concentration of base. In order to obtain the best values for the energies of activation, we have treated these data by two completely independent procedures.

One procedure is illustrated by the plots in Figs. 2 and 4. The best value for the rate constant was estimated for each run from the initial slope of the curve as shown. These initial rate constants were then plotted against ionic strength, *b*, as shown in the insets, and the straight line obtained by least squares was used to extrapolate the rate constants to zero ionic strength.[22] The logarithms of these extrapolated rate constants were plotted against $1/T$, the points were

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(20) Landolt–Börnstein, "Tabellen," Vol. I, Verlag von Julius Springer, Berlin, 1923, p. 278.

(21) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Company, Inc., New York, N. Y., 1941, p. 199.

(22) S. Glasstone, K. J. Laidler and H. Eyring (*ibid.*, p. 441) claim that in the reaction of a negative ion and a neutral molecule the rate constant will increase linearly with the ionic strength. E. S. Amis ("Kinetics of Chemical Change in Solution," The Macmillan Company, New York, N. Y., 1949, p. 174), however, maintains that the rate constant should decrease with increasing ionic strength. It is not clear whether this extrapolation corrects for a positive salt effect or for some reactions involving methoxide ion to a higher order, or both.

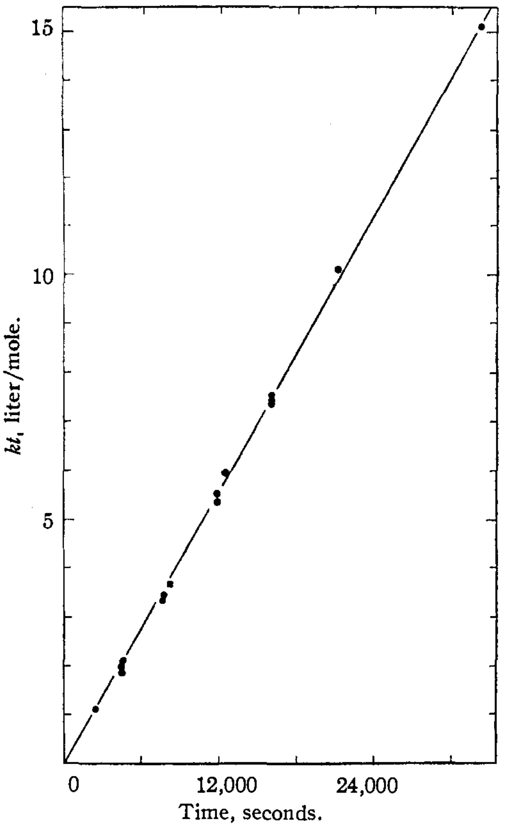

Fig. 1.—*cis*-$C_2H_2Cl_2$-$NaOCH_3$ reaction at 85°; figure includes four runs.

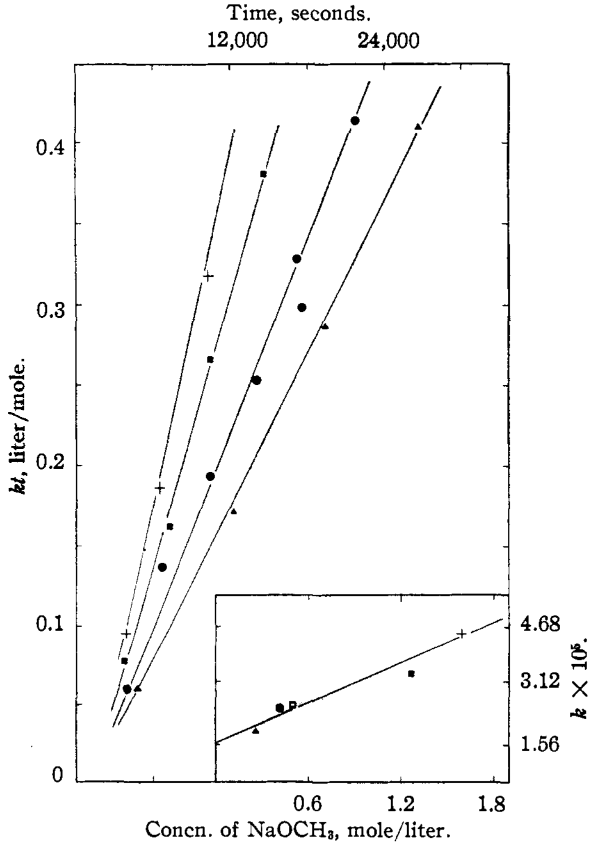

Fig. 2.—*trans*-$C_2H_2Cl_2$-$NaOCH_3$ reaction at 133°; inset includes five runs.

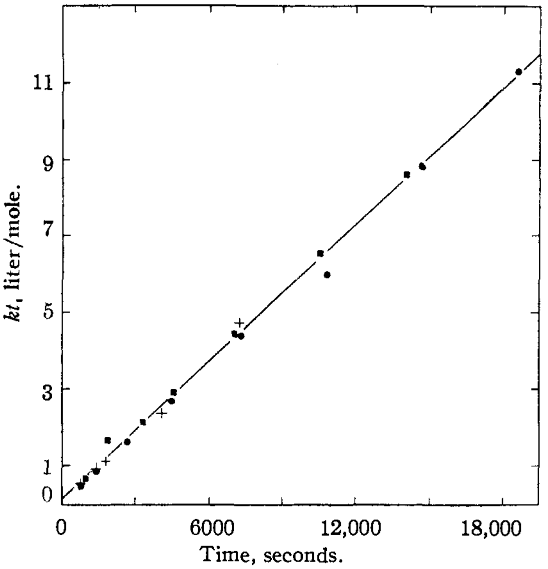

Fig. 3.—*cis*-$C_2H_2Br_2$-$NaOCH_3$ reaction at 35.2°; figure includes three runs.

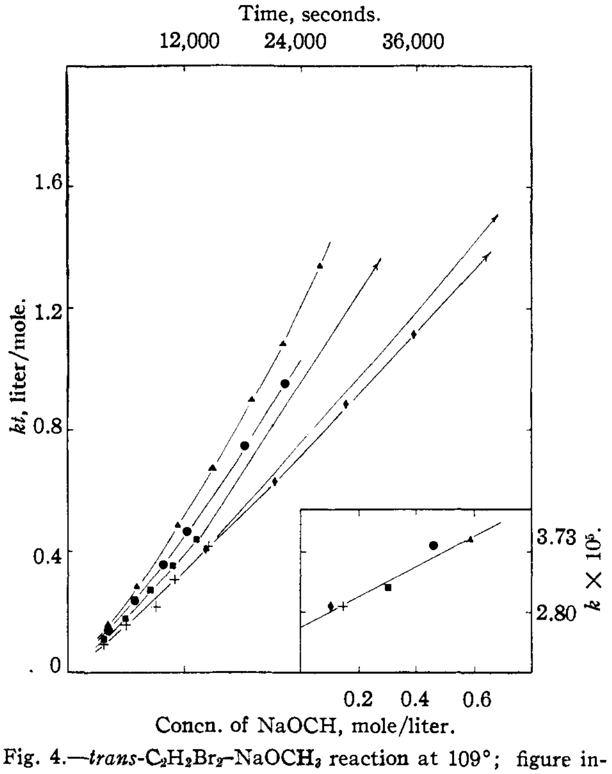

Fig. 4.—*trans*-$C_2H_2Br_2$-$NaOCH_3$ reaction at 109°; figure includes five runs.

fitted with a straight line by the method of least squares, and the activation energies were calculated. These plots are illustrated in Fig. 7.

The other procedure was suggested by the method of Crowell and Hammett.[23] At each temperature values of log k (defined by equation (6)) were plotted against kt on transparent paper. Then each pair of plots was superimposed, while the left margins were kept identical, and the difference in log k was determined for the best fit of data at all times and all concentrations. The energy of activation was calculated from the relation

$$E_{\text{exp}} = \frac{2.303RT_1T_2\Delta(\log k)}{(T_2 - T_1)} \quad (8)$$

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[23] T. I. Crowell and L. P. Hammett, This Journal, **70**, 3444 (1948).

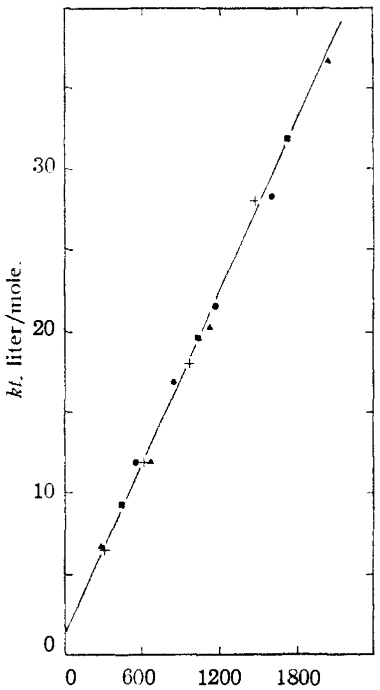


Fig. 5.—*cis*-$C_2H_2I_2$-$NaOCH_3$ reaction at 25°; figure includes four runs.

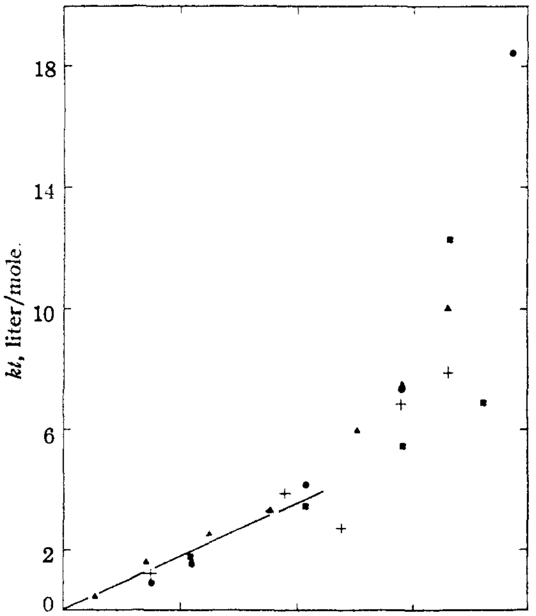


Fig. 6.—*trans*-$C_2H_2I_2$-$NaOCH_3$ reaction at 58°; figure includes four runs.

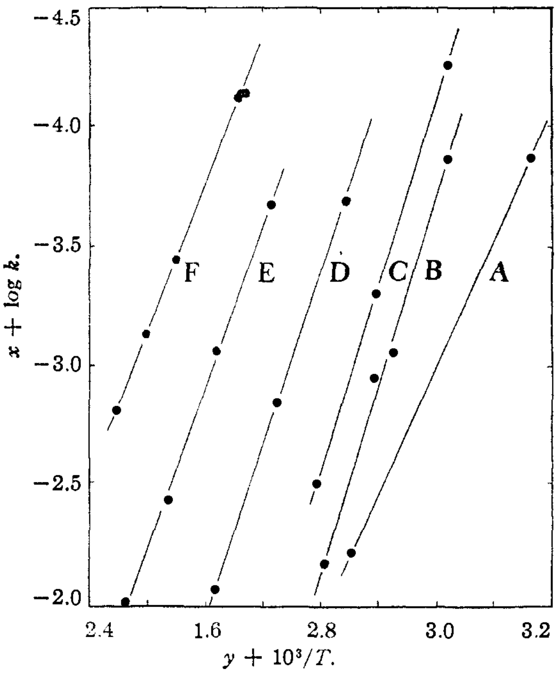


Fig. 7.—Dependence of rate contents on temperature: A, *cis*-$C_2H_2I_2$, $x = -0.47$, $y = -0.5$; B, *trans*-$C_2H_2I_2$, $x = +1.23$, $y = 0$; C, *cis*-$C_2H_2Cl_2$, $x = +0.78$, $y = 0$; D, *trans*-$C_2H_2Br_2$, $x = +2.53$, $y = 0$; E, *trans*-$C_2H_2Cl_2$, $x = +2.78$, $y = 0$; F, *cis*-$C_2H_2Br_2$, $x = -0.22$, $y = -0.7$.

and the best value was obtained by averaging the values calculated for all possible pairs of temperatures but weighting in favor of large temperature differences. This method has the advantage of avoiding an extrapolation which puts undue emphasis on the points measured after the shortest time intervals. It essentially compares each solution at different temperatures at the same fraction reaction and is justified in this case by the fact that for a specific solution the plots of log k against kt are superimposable at all temperatures.

The energies of activation obtained by the two procedures were in fortuitously good agreement for the *trans*-dibromo- and diiodoethylenes. The activation energy from the extrapolated rate constants of *trans*-dichloroethylene was 1.6 kcal./mole higher than the value reported below. This reported value was based on two different matching procedures carried out by three independent workers and all agreeing to 0.2 kcal./mole.

In Table II we have summarized the best values of the energies and entropies of activation for these reactions and have also presented extrapolated values for the rate constants at 60°.

Discussion

The results presented in Table II clearly illustrate the futility of attempting to discuss mechanisms on the basis of relative rates measured at a single temperature. For each pair of isomers *trans* elimination is faster than *cis*. For each series involving the same type of elimination the iodide reacts fastest and the chloride slowest. However, the reasons for these relative rates are very different in different instances. In the diiodoethylenes *trans* elimination is favored for energetic reasons, and in the dichloroethylenes the difference is due to entropy considerations which overcome an unfavorable difference in energy of activation. In the dibromoethylenes *trans* elimination is favored by both energy and entropy considerations. In the examples of *trans* elimination the rate increases on going from the chloride to the iodide because of a decrease in energy of activation, while in the examples of *cis* elimination the rate increases because of a large increase in entropy of activation which much more than counteracts a small increase in energy of activation.

The free energies of activation invariably favor *trans* elimination by at least 5 kcal./mole. The isomers in each pair of dihaloethylenes have free en-

TABLE II

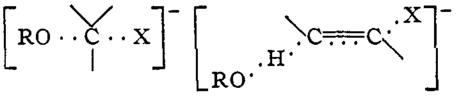
SUMMARIZED ENERGIES AND ENTROPIES OF ACTIVATION FOR ELIMINATION REACTIONS

	cis isomers (*trans* eliminations)			*trans* isomers (*cis* eliminations)		
Compound	E_{exp}, kcal./mole	$\Delta S^{\ddagger}$, cal./mole deg.	k_{60}, liter/mole sec.	E_{exp}, kcal./mole	$\Delta S^{\ddagger}$, cal./mole deg.	k_{60}, liter/mole sec.
$C_2H_2Cl_2$	35.1 ± 0.3	22 ± 1	1.4×10^{-5}	29.0 ± 1.0	−12 ± 3	4.2×10^{-9}
$C_2H_2Br_2$	28.1 ± 0.3	16 ± 1	1.8×10^{-2}	33.4 ± 0.5	5 ± 2	3.3×10^{-8}
$C_2H_2I_2$	24.7 ± 0.3	14 ± 1	1.6	35.8 ± 1.5	24 ± 5	1.2×10^{-6}

ergies which differ by no more than a few hundred calories per mole in vapor phase or non-polar solvent.[8,24,25,10] Solution in methanol would not shift the isomerization equilibria greatly, and it therefore appears certain that not only is *trans* elimination faster than *cis* in each pair of isomers, but the transition state for *trans* elimination has a lower free energy than the isomeric transition state for *cis* elimination. The data also require that any process leading to isomerization in these systems must have a free energy of activation which is greater than that required for *trans* elimination from the more reactive isomer.

The data cannot provide an unambiguous description of the difference between the mechanisms of *cis* and *trans* elimination, but they can suggest requirements to be satisfied by any explanation. Electrostatic and dipolar forces are completely inadequate to account for the observed differences in reactivity,[6b] and steric forces provide an even less plausible interpretation. We must conclude that the relative rates are influenced much more by the relative positions of the groups which are eliminated than by any of the properties of the groups themselves.

Cristol[6] has suggested that *trans* elimination takes place in a one-step concerted process which is not available to the elimination of groups which are located *cis* to each other. We do not know of any quantum-mechanical justification for this proposal, but it appears to be a good working hypothesis. We have also found an interesting analogy between bimolecular substitutions and the *trans* eliminations of this study. Comparable transition states may be represented as



In both structures the breaking of old bonds and the formation of new ones can proceed simultaneously. In the substitution the reacting centers are collinear, while models indicate that they are almost collinear in the elimination. In both reactions a carbon atom is sterically inverted and a new bond is formed on a side remote from the old bond. Since these conditions cannot all be easily fulfilled in *cis* eliminations, it may be that these considerations will be useful in an exact explanation of the favoring of *trans* elimination over *cis*.

One of the most striking features of the data for *trans* eliminations in Table II is the abnormally large entropy of activation associated with each reaction. These entropy effects seem much too large to be explained in terms of loosening of bonds in the dihaloethylene alone, and we propose tentatively that they are associated with the ordering of the surrounding solvent molecules. The electrostatic field around an isolated methoxide ion will cause an orienting of the dipolar solvent molecules which may extend for a distance of several molecular diameters. If *trans* elimination takes place as a one-step process, the charge in the transition state is distributed throughout the length of the grouping —O · · H · · C═C · · X. This "smeared out" charge would have much less orienting effect on the surrounding solvent molecules, resulting in a large positive entropy of activation. Moreover, if *trans* elimination takes place in a one-step process, the energy of activation would be expected to increase with increasing strength of the C–X bond; the results in the left side of Table II are in agreement with this hypothesis.

There are a few other quantitative studies of elimination reactions of isomeric haloölefins in anhydrous alcoholic solvents.[26,27] In these reactions the entropy of activation for *trans* elimination is invariably at least 14 cal./mole deg. However, the presumably *trans* elimination reactions of various saturated halides show more "normal" entropy effects,[6b,28] and the factors suggested in the preceding paragraph are obviously inadequate for a complete description of the observations.

In order to describe *cis* elimination, Cristol[6] suggests that a proton is first removed and that the subsequent loss of halide ion either accompanies or follows the inversion of the carbanion formed in the first step. This two- (or three-) step process is assumed to be necessary because the electrons from the C–H bond are not available to act in the concerted elimination of a *cis* halide ion. For such a step-wise process the rate-determining step may be the removal of the proton, the inversion of the carbanion, or the loss of the halide. There is no *a priori* reason to predict which step will be rate-determining, but we can distinguish certain consequences of each possibility.

If the rate-determining step in *cis* elimination is the removal of the proton, the step-wise mechanism will be kinetically indistinguishable from the one-step mechanism postulated for *trans* elimination, but the pattern of energies and entropies of activation for various reactions might be different.

If the rate-determining step in *cis* elimination is the inversion of the carbanion, then removal of the

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[24] R. E. Wood and D. P. Stevenson, THIS JOURNAL, 63, 1650 (1941).

[25] R. M. Noyes and R. G. Dickinson, *ibid.*, 65, 1427 (1943).

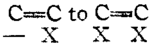
[26] S. J. Cristol, A. Begoon, N. L. Hause and J. S. Meek, 116th Meeting of American Chemical Society, Atlantic City, N. J., September 20, 1949.

[27] H. A. Smith and W. H. King, THIS JOURNAL, 72, 95 (1950). The authors were studying substitution reactions of dichloropropenes, but they suggest that elimination may have been the chief reaction in certain cases.

[28] K. A. Cooper, E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. MacNulty, *J. Chem. Soc.*, 2049 (1948).

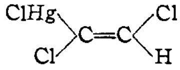
proton would be reversible, and the compound should exchange with deuterated solvents. Leitch and Bernstein[29] have shown that trichloroethylene is deuterated when it is refluxed with $Ca(OD)_2$. Under more strenuous conditions, hydrogen chloride is eliminated with the formation of $ClC{\equiv}CCl$.[30] These results indicate that reversible carbanion formation may occur without elimination if the molecule contains groups which are sufficiently electron-attracting; the evidence is not sufficient to determine whether carbanion formation is reversible during elimination reactions in general.

Loss of halide ion from a carbanion cannot be the rate-determining step in *cis* elimination, for in that case proton removal and inversion of the carbanion would both be reversible. Then, if the free energy of the transition state for inversion of the carbanion were lower than that for either type of elimination, each isomer would revert to a mixture of the two, and both would undergo elimination at very nearly the same rate. If the free energy of the transition state for inversion of the carbanion were more than that for concerted *trans* elimination but less than that for loss of halide from a carbanion, the mechanism of *cis* elimination would involve isomerization followed by *trans* elimination. Such a mechanism would be experimentally indistinguishable from the Cristol step-wise mechanism with inversion the rate-determining step; therefore, it is meaningless to differentiate between the two alternatives.

Our data for *cis* eliminations are not inconsistent with a step-wise mechanism. The trend in activation energies on going from chloride to iodide is in the opposite direction from that observed in the *trans* eliminations, and the magnitude of the change is less. This result suggests (but does not in any way prove) that breaking of the C–X bond is not involved in the rate-determining step. If the rate-determining step is removal of a proton, then (since chlorine is most electronegative) we might expect the proton to be removed most easily in dichloroethylene, all other factors being equal. If the rate-determining step is inversion of the carbanion, the steric repulsions of the halogen atoms might affect the energy barrier for the conversion of  $\overset{X\ \ H}{\underset{-\ \ X}{C{=}C}}$ to $\overset{-\ \ H}{\underset{X\ \ X}{C{=}C}}$. Such an effect would be least for the chloride and greatest for the iodide.

We are somewhat at a loss to account for the large change in entropy of activation on going from chloride to iodide. If the rate-determining step is removal of a proton, it may be that the bulky iodine atoms prevent solvent molecules from getting as close to the localized negative charge; and therefore the solvent is not as ordered as in the case of dichloroethylene. If the rate-determining step is inversion of the carbanion, it may be that the charge on the $C_2HCl_2^-$ ion is fairly localized, but that it is spread out more in the more polarizable iodine carbanion. Such spreading of charge will, of course, increase randomness in the surrounding solvent molecules. Finally, it may be that the relative importance of the steps changes and that the rate-determining step is proton removal at the chloride end of the series and carbanion inversion at the iodide end.

In the course of a literature survey we have found in a different system strong supporting evidence for a dual interpretation of elimination reactions. Fitzgibbon[31] found that in alkaline mercuric cyanide at room temperature *cis*-dichloroethylene gave the acetylide $Hg(C{\equiv}CCl)_2$. However, the *trans* isomer slowly gave the ethylenide.



from which it could be recovered on acidification. It is difficult to suggest a mechanism for this reaction which does not involve the formation of a carbanion intermediate from the *trans*-dichloroethylene. At reflux temperatures both isomers react quantitatively to form the same acetylide.[32] To our knowledge these observations constitute the most direct evidence that in certain systems *trans* elimination takes place in a single step while *cis* elimination involves the intermediate formation of a comparatively stable carbanion.

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