stripped borazole ring. There are 6 B–N bonds in this ring, hence the average B–N bond strength in B-trichloroborazole is 82.5 kcal./mole bond at 25°.[10]

Gaydon[11] recommends 4.0 ± 0.5 e.v. (92 ± 11.5 kcal.) for the dissociation energy of gaseous diatomic boron nitride (BN) and states that this rather imprecise value has been obtained by a graphical Birge–Sponer extrapolation of spectral data. Certainly it is not surprising to find that the dissociation energy of gaseous BN exceeds the average B–N bond strength of the borazole ring.

It is instructive to compare the strength of the B–N bond in the B-trichloroborazole ring with values which have been estimated for donor–acceptor bonds involving boron and nitrogen. These latter bonds are in general weak and the compounds, while stable in the solid state, frequently undergo extensive dissociation in the vapor phase. Thus Burg and Green[12] have found evidence for boron–nitrogen bond strengths in the series $(CH_3)_3NBF_2CH_3$ to $(CH_3)_3NB(CH_3)_3$ varying from about 23 to 14 kcal./mole, respectively. Likewise Brown, Bartholomay and Taylor[13] have found B–N bond strengths in the range of 14 to 19 kcal./mole in a series of compounds of general formula $R_3NB(CH_3)_3$. Physical evidence is in accord with the much higher dissociation energy for the ring B–N bond in borazole and B-trichloroborazole. Thus it is found that the B–N internuclear distance is in the range of 1.6 Å. for the donor–acceptor compounds[14a] while in borazole[14b] it is 1.44 Å. and in B-trichloroborazole 1.41 Å.[5,6]

We believe that at least as a first estimate the average B–N bond strength in borazole itself can be considered to be of the order of 80 kcal./mole bond since the B–N internuclear distances closely approximate each other in borazole and B-trichloroborazole.

Acknowledgment.—We wish to thank Professor A. W. Laubengayer and Dr. Charles Brown for our supply of B-trichloroborazole. One of us (E.R.V.) wishes to express his sincere appreciation to the Faculty Research Grants Committee and the Office of the Vice President for Research of Cornell University for a grant in purchase of a calibrated, precision, platinum resistance thermometer used in this work.

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[10] One can arrive at the values of 100.6 and 78.6 kcal./mole bond, respectively, for the B–Cl and N–H bond strengths by using Bureau of Standards[8] data for heats of formation of the gaseous monatomic molecules BCl and NH which are known spectroscopically. When these bond strengths are used, one estimates the average B–N bond strength in B-trichloroborazole to be 81.5 kcal./mole bond. We, however, favor the value obtained in the text, 82.5 kcal./mole bond.

[11] A. G. Gaydon, "Dissociation Energies," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 205.

[12] A. B. Burg and A. A. Green, THIS JOURNAL, **65**, 1838 (1943).

[13] H. C. Brown, H. Bartholomay and M. D. Taylor, *ibid.*, **66**, 435 (1944).

[14] (a) S. H. Bauer, *ibid.*, **59**, 1804 (1937); (b) **60**, 524 (1938).

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Iodide-ion Catalysis of the Elimination of Iodine from *trans*-Diiodoethylene and of the Addition of Iodine to Acetylene[1,2]

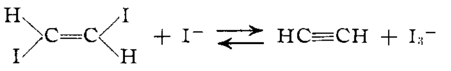
BY SIDNEY I. MILLER AND RICHARD M. NOYES

RECEIVED FEBRUARY 8, 1952

trans-Diiodoethylene in methanol reacts with iodide ion at temperatures below 110° with the formation of triiodide ion and acetylene. From studies of the final equilibrium and of the kinetics of this elimination reaction, we have obtained kinetic information concerning the rate of the reverse (addition) reaction. The rate of elimination of the *cis* isomer under the same conditions is immeasurably slow even at temperatures as high as 140°. Two reaction mechanisms appear plausible. In one mechanism the two carbon–iodine bonds break almost simultaneously in a concerted process. The other mechanism involves a neutral intermediate complex of acetylene and molecular iodine.

Introduction

Although it is well known that iodide ion can cause the elimination of halogen from 1,2-dihaloalkanes, there do not appear to be any reports of similar elimination reactions of 1,2-dihaloalkenes. We have found an example of such an elimination in the equilibrium reaction



(1)

This elimination reaction is first order in iodide ion and first order in *trans*-diiodoethylene. Apparently the *cis* isomer does not undergo elimination at a significant rate under the conditions of our experiments.

By combining our kinetic observations with measurements on the equilibrium constant for reaction (1), we have also been able to calculate the rate of the reverse reaction involving the addition of iodine to acetylene. These results are of interest because of the paucity of kinetic data on the iodination of acetylenes.

Experimental

Materials.—The preparation of the anhydrous methanol solvent and of the eutectic and *trans*-diiodoethylene have been described elsewhere.[3] Since pure *cis*-diiodoethylene has not yet been obtained, we used the eutectic material which contained about 20% of the *trans* isomer.[4]

Dried reagent-grade sodium iodide was checked against standard silver nitrate 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.

[2] Persons desiring to consult the more complete report or to obtain a microfilm thereof may address the Library, Columbia University, New York 27, N. Y.

[3] S. I. Miller and R. M. Noyes, THIS JOURNAL, **74**, 629 (1952).

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

Procedure.—Methanolic solutions for the kinetic runs were made up in 250-ml. volumetric flasks from known amounts of diiodoethylene and sodium iodide. Ten-milliliter aliquots were pipetted into ampules which were then sealed and heated in oil thermostats.[3] In some attempts to study the *cis* elimination reaction, a xylene vapor thermostat was used at 140 ± 1°. At noted times, the ampules were removed, cooled, opened and analyzed.

The course of the elimination reaction was followed by titrating the produced iodine with a solution of sodium thiosulfate prepared and standardized by usual methods.[5] The organic compounds in our solutions appeared to interfere with the usual starch–iodine end-point; therefore we determined the end-point by the "dead-stop" procedure.[6]

Stoichiometry.—The acetylene produced in the elimination reaction was identified by qualitative tests. The kinetic behavior of the system demonstrated that the diiodoethylene consumed was equivalent to the iodine produced.

Methanolic solutions containing only sodium iodide or only *trans*-diiodoethylene produced no titratable iodine under the conditions of our experiments. Solutions of iodine in methanol showed small but measurable losses in titer. These losses were probably due at least in part to an impurity in the solvent, for the iodine was taken up more rapidly during the first hour. In order to make empirical corrections for this effect, observed concentrations of iodine in various runs were increased 10×10^{-5} mole/liter at 109°, 7×10^{-5} mole/liter at 94° and 3×10^{-5} mole/liter at 79°. These corrections did not affect the calculated values of k_1 by more than 1.5%; therefore no more refined treatment was deemed necessary.

We were unable to find more than traces of *cis*-diiodoethylene in any preparation of the *trans* isomer by the addition of iodine to acetylene. This observation is a necessary consequence of the failure of the *cis* isomer to undergo elimination at a significant rate.

Results

Methanolic solutions that were 0.05 *M* in eutectic diiodoethylene and 0.14 *M* in sodium iodide were heated for 12 hours at 109 and at 140°. These solutions showed no production of iodine in excess of that expected from the 20% of *trans* isomer present in the eutectic mixture. It was feared that on prolonged heating the product iodine would catalyze isomerization to the more reactive *trans* form[7] and cause spurious indications of *cis* elimination. Therefore, these experiments were not carried further.

In order to treat the kinetics of the reaction of *trans*-diiodoethylene with iodide ion, we have used the standard expression for a reversible second-order reaction

$$\mathrm{d}x/\mathrm{d}t = k_1(a - x)(b - x) - k_2x^2 \qquad (2)$$

where

a = initial concn. of $C_2H_2I_2$ in mole/liter
b = initial concn. of I^- in mole/liter
x = concn. of C_2H_2 or of titratable iodine at time t
k_1 = rate constant for forward (elimination) reaction
k_2 = rate constant for reverse (addition) reaction

Equation (2) can be integrated to give

$$k_1t = \frac{2.303}{m}\log\frac{\left[\frac{K(a+b+m)}{2(K-1)} - x\right](a+b-m)}{\left[\frac{K(a+b+m)}{2(K-1)} - x\right](a+b+m)} \qquad (3)$$

where

$$m = \sqrt{(a+b)^2 - 4ab(K-1)/K}$$
$$K = k_1/k_2 = \text{equilibrium constant for reaction (1)}$$

The use of this treatment involves some assumptions. In the first place, the treatment assumes that the rate of the addition reaction is first order in acetylene and first order in triiodide ion. If the kinetics of a reaction have been determined, the kinetics of the reverse reaction are not uniquely established but must be such that the forward and reverse rates are equal at all conditions of thermodynamic equilibrium. The kinetic form assumed for the addition reaction is the only acceptable expression, provided the equilibrium

$$I_2 + I^- \rightleftarrows I_3^- \qquad (4)$$

is rapid compared to the addition and elimination reactions. Studies in aqueous solution[8] have established that reaction (4) is very rapid. Additional confirmation for the assumption is provided by the satisfactory fit of the data to equation (3) and by the fact the assumed kinetics were actually observed by Moelwyn-Hughes and Legard[9] for the addition of iodine to phenyl propiolate ion.

In the second place, this treatment assumes that all of the liberated iodine is present as triiodide ion. Dillon[10] concluded that the equilibrium for reaction (4) in methanol at 75° is shifted almost completely to the right if iodide ion is present in an excess concentration of 0.1 *M* or more. Our experiments were at only slightly higher temperatures and contained sufficient excess iodide that the concentration of I_3^- throughout a run was certainly proportional to the concentration of titratable iodine even if it was not almost equal to it.

Similarly, the treatment assumes that all of the acetylene remains dissolved in the solution. The free air space in the ampules varied from 3 to 20 ml., while the volume of solution was always 10 ml. The solubility of acetylene in methanol has not been reported, but data for other solvents[11] suggest that the concentration of acetylene in the methanol was at least 2 or 3 times the concentration in the vapor phase. Moreover, Henry's law requires that throughout any particular run the amount of dissolved acetylene was proportional to the amount of acetylene produced. Therefore, we feel sufficiently justified in setting x equal to the concentrations of acetylene and of triiodide ion. Any systematic failure of this assumption might change the reported value of the equilibrium constant, K, by perhaps as much as 30% but would have a much smaller effect on the value of the rate constant, k_1.

In Table I we present the results of our kinetic measurements. The concentrations of the reactants are given for 25° and the rate constants have been corrected for thermal expansion of methanol.[12] In Fig. 1 we illustrate the individual data for all

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(5) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1938, pp. 590, 593.

(6) C. W. Foulk and A. T. Bawden, THIS JOURNAL, **48**, 2045 (1926).

(7) R. M. Noyes, R. G. Dickinson and V. Schomaker, *ibid.*, **67**, 1319 (1945).

(8) R. W. Dodson and R. D. Fowler, *ibid.*, **61**, 1215 (1939).

(9) E. A. Moelwyn-Hughes and A. R. Legard, *J. Chem. Soc.*, 424 (1933).

(10) R. T. Dillon, THIS JOURNAL, **54**, 952 (1932).

(11) A. Seidell, "Solubilities of Organic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 1941, p. 75.

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

TABLE I

RATE OF ELIMINATION OF IODINE FROM *trans*-DIIODOETHYLENE

a, *trans*-$C_2H_2I_2$, mole/liter	*b*, NaI, mole/liter	$k_1 \times 10^6$, liter/mole sec. 78.92 ± 0.05°	94.46 ± 0.17°	109.15 ± 0.05°
0.01779	0.1044	1.79	11.3	49.1
.06430	.1089	1.83	11.4	48.5
.04944	.2129	1.77	10.8	44.8
.02306	.3521	1.72	10.1	43.5

measurements at the intermediate temperature. The values of the equilibrium constant, K, were needed for the calculations and were obtained from ampules left in the thermostats for several weeks. The precision of the small number of equilibrium measurements is not as good as that obtained from the larger number of kinetic measurements. This lack of precision may be due in part to the fact that variations in free air space exert more effect on calculated values of K than of k_1.

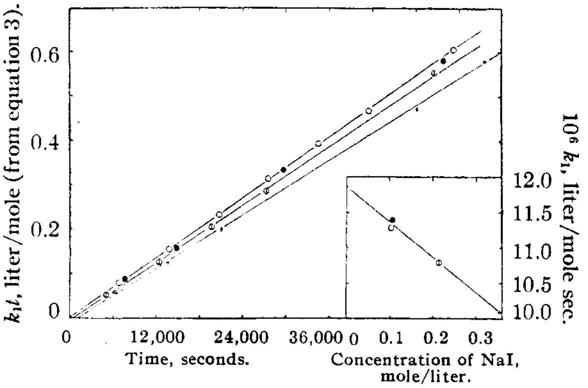


Fig. 1.—*trans*-$C_2H_2I_2$–NaI reaction at 94.46°. The inset figure shows how the rate constant changes with the ionic strength.

The rate constants are independent of diiodoethylene concentration but decrease slightly with increasing concentration of sodium iodide. This small apparent negative salt effect is in the same direction as that observed by Dillon[10] for the elimination reaction of $C_2H_4Br_2$ with iodide ion. Values of the rate constants at zero ionic strength were obtained by extrapolation of least-squares plots similar to the inset in Fig. 1. Table II contains these extrapolated rate constants and the best values of constants for the equilibrium and reverse reactions.

TABLE II

SUMMARY OF KINETIC AND EQUILIBRIUM MEASUREMENTS

Temperature, °C.	78.92	94.46	109.15
k_1, liter/mole sec.	$(1.83 \pm 0.02) \times 10^{-6}$	$(11.8 \pm 0.1) \times 10^{-6}$	$(50.7 \pm 0.5) \times 10^{-6}$
K	$(1.45 \pm 0.12) \times 10^{-2}$	$(3.0 \pm 0.4) \times 10^{-2}$	$(4.4 \pm 0.3) \times 10^{-2}$
k_2, liter/mole sec.	$(1.27 \pm 0.12) \times 10^{-4}$	$(4.0 \pm 0.7) \times 10^{-4}$	$(11.5 \pm 0.8) \times 10^{-4}$

In Fig. 2 we present conventional plots of ln k_1 and ln k_2 against $1/T$. From these plots, we calculate that for the elimination reaction in this temperature range the energy of activation is 29.4 ± 0.4 kcal./mole, and the entropy of activation is −3.7 ± 1.2 cal./mole deg. For the addition reaction, the energy of activation is 19.5 ± 1.2 kcal./mole, and the entropy of activation is −23 ± 4 cal./mole deg. For the equilibrium indicated in reaction (1), $\Delta H = 9.9 \pm 1.2$ kcal./mole, and $\Delta S = 19 \pm 4$ cal./mole deg.

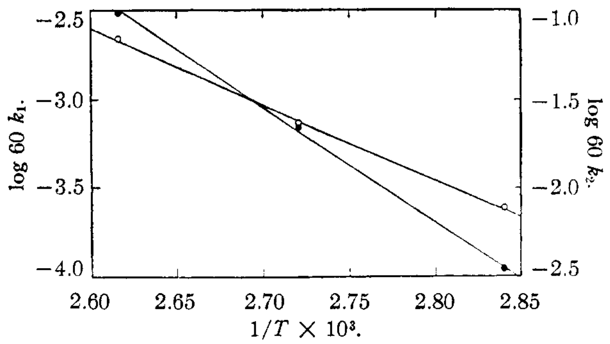
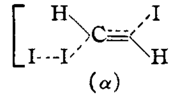


Fig. 2.—Activation energy plots: ●, k_1 for the elimination reaction of *trans*-$C_2H_2I_2$ + NaI; ○, k_2 for the addition reaction of $C_2H_2 + I_3^-$.

Discussion

The principle of microscopic reversibility requires that the mechanism of the addition reaction must be the exact reverse of that for the elimination reaction. This requirement serves to rule out several mechanisms which have been considered plausible when applied to the reaction in one direction only. Thus, our opinions as to the possible mechanisms of the elimination reaction make us doubt that the addition involves a rate-determining attack by triiodide ion as proposed by Moelwyn-Hughes and Legard.[9]

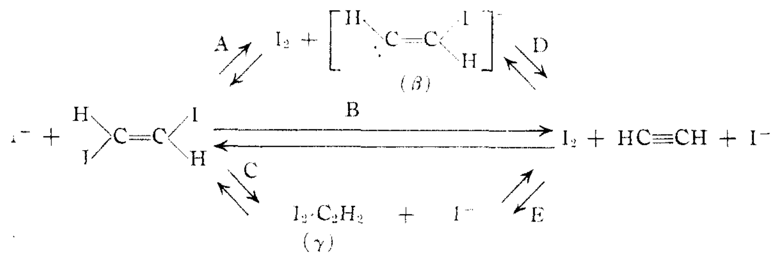
We believe that the only plausible mechanisms for the elimination reaction involve an initial attack by an iodide ion on one of the iodines in a molecule of *trans*-diiodoethylene. We consider that



(α)

is the best representation of the transition state. In making the representation, we have used dashed lines to indicate the three single bonds which must be broken or formed by heterolytic processes during the completion of the over-all reaction. The electrons of the I–I and C–I bonds are provided by the iodide ions involved; the electrons of the C–I_2 bond are provided by the organic molecule. The complete reaction could proceed in three distinct sequences depending upon whether the C–I and C–I_2 bonds break simultaneously or in either order. These sequences are indicated in the formulation. In this formulation, we do not attempt to describe the structure of the neutral intermediate γ, but it is probably a complex of the type Mulliken[13] has postulated for the interaction between molecular iodine and Lewis bases.

[13] R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950).



The kinetics require that the transition state for these reactions lies along path A, B or C, whichever is appropriate, and does not lie along path D or E. James and Sudborough[14] observed that ortho- and para-nitrophenyl propiolate ions add iodine under these conditions more slowly than phenyl propiolate ion does. This observation indicates that the free energy of activation is increased by groups which withdraw electrons from the reacting carbon atoms; therefore, we consider that the electron density at these carbon atoms is less in the transition state than it is in the original acetylene.[15] This condition is presumably fulfilled for a transition state lying along path C; it is fulfilled for a transition state lying along path A or B only if either the C–I or I–I bond is more nearly broken than the C–I_2 bond.

Two arguments serve to render the sequence A–D implausible. In the first place, it is doubtful that an ionic intermediate like species β would be formed at significant rate by the direct attack of iodide ion on an acetylenic carbon.[16] In the second place, we observe that the rate of *cis* elimination is very much smaller than the rate of *trans* elimination. We find it hard to believe that an intermediate like species β could retain a stereospecific configuration at these temperatures, and the free energy of formation would be nearly the same from either isomer of diiodoethylene. These conditions require that *trans* elimination proceeds through a transition state which is unattainable for the *cis* isomer and which has a lower free energy than the transition state for the formation of species β.

We know of no compelling arguments to favor path B or sequence C–E. Acetylene and iodine probably tend to form a complex like species γ, whether or not it is an intermediate in these reactions. Either of the two mechanisms could be formulated to account plausibly for the stereospecificity of the reactions if we accept theories that the electronic configuration is most favorable when bond making or breaking occurs on opposite sides of adjacent carbon atoms.[3,17] The only restriction which we can apply is that the concerted mechanism (path B) is permissible only if the C–I or I–I bond in the transition state is more nearly broken than the C–I_2 bond.

[14] T. C. James and J. J. Sudborough, *J. Chem. Soc.*, **91**, 1037 (1907).

[15] This argument is suggested by the recent treatment of substituent effects by C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951).

[16] M. J. Murray, *ibid.*, **60**, 2662 (1938).

[17] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2117 (1948).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Heats of Combustion of Thorium and Uranium[1,2,3]

BY ELMER J. HUBER, JR., CHARLES E. HOLLEY, JR., AND E. H. MEIERKORD

RECEIVED FEBRUARY 8, 1952

Precise measurements of the heats of combustion of thorium, uranium and uranium dioxide have been made and from the results the heats of formation of ThO_2, UO_2 and U_3O_8 have been calculated. The final values for the various materials are listed as follows: Thorium: heat of combustion in 25 atm. oxygen = 5274 ± 7 joules/g.; heat of formation of ThO_2, $\Delta H_{25}° = -1{,}226.9 \pm 1.5$ kjoules./mole. Uranium dioxide: heat of combustion in 25 atm. oxygen = 389.23 ± 0.46 joules/g.; heat of the reaction $3UO_2 + O_2 = U_3O_8$, $\Delta H_{25}° = -318.01 \pm 0.37$ kjoules. Uranium: heat of combustion to U_3O_8 in 25 atm. oxygen = 4984.7 ± 9.7 joules/g.; heat of formation of U_3O_8, $\Delta H_{25}° = -3570.9 \pm 6.9$ kjoules./mole. It was necessary to cut the uranium into small pieces and mix it with UO_2 in order for it to oxidize completely to U_3O_8. The heat of formation of UO_2 calculated from the above results is $\Delta H_{25}° = -1{,}084.3 \pm 2.5$ kjoules./mole.

Introduction

The heats of formation of the oxides of thorium and uranium are of interest for thermodynamic calculations. Since it is only recently that these metals have become available in high purity, an experimental redetermination of their heats of combustion was thought desirable. The heat of combustion of uranium dioxide was also redetermined.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the material in question with oxygen at a known pressure in a bomb calorimeter. The energy equivalent of the calorimeter was determined from the heat of combustion of standard benzoic acid, and the heat of combustion was evaluated from this value and the measured temperature rise per unit mass of metal. The details of the method and apparatus have been described.[4]

Units and Precision.—The results of this work are expressed in absolute joules. For purposes of comparison with the older literature the results are also expressed as calories using the definition 1 calorie = 4.1840 absolute joules.

The unit of mass is the gram mass *in vacuo*. The materials to be burned were weighed to the nearest 0.0001 g. The water for the calorimeter was weighed to the nearest 0.01 g.

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[1] This work was done under the auspices of the A.E.C.

[2] Presented before the Section on Physical and Inorganic Chemistry, XIIth International Congress of Pure and Applied Chemistry, at New York, N. Y., September 13, 1951.

[3] For detailed table order Document 3576 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 x 8 inches) readable without optical aid.

[4] Charles E. Holley, Jr., and Elmer J. Huber, Jr., THIS JOURNAL, **73**, 5577 (1951).