

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Mechanism of Halogen-atom Catalyzed *cis-trans* Isomerization. Studies with Bromine and Dibromoethylene

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The bromine-catalyzed *cis-trans* isomerization of 1,2-dibromoethylene has been studied in degassed carbon tetrachloride, and the exchange reaction in the same system has been studied with the use of bromine-82. The reactions are autocatalytic in the presence of oxygen, and the kinetics are complicated by the concurrent addition of bromine to the double bond, but satisfactory rate constants have been obtained.

The data at 35° indicate that the rate constant for the reaction $\text{Br}^* + \text{Br}_2 \rightarrow \text{BrBr}^* + \text{Br}$ is about three times the rate constant for the reaction $\text{Br}^* + \text{C}_2\text{H}_2\text{Br}_2 \rightarrow \text{C}_2\text{H}_2\text{BrBr}^* + \text{Br}$. The rate constant for the latter reaction is about twice the rate constant for the reaction $\text{Br} + \text{cis-C}_2\text{H}_2\text{Br}_2 \rightarrow \text{Br} + \text{trans-C}_2\text{H}_2\text{Br}_2$. We have interpreted the results to indicate that isomerization takes place through the interconversion of two isomeric $\text{C}_2\text{H}_2\text{Br}_3$ radicals which differ by a rotation about the carbon-carbon bond. The energy barrier opposing this rotation appears to be almost identical in height with the barrier opposing dissociation of a bromine atom from the radical. We believe that the height of this barrier is greater than 3 kcal./mole, but even this limiting figure must be regarded as very tentative.

Introduction

Halogens act as catalysts for the *cis-trans* isomerization of compounds containing carbon-carbon double bonds, and kinetic studies by Dickinson and co-workers²⁻⁶ have demonstrated that the free halogen atoms are the active species in this type of reaction. It was also shown⁴ that the rate of the iodine-atom catalyzed isomerization of 1,2-diiodoethylene is much slower than the rate of exchange of either isomer with labeled iodine atoms. These observations were interpreted to indicate that exchange proceeds through a radical transition state having the empirical formula $\text{C}_2\text{H}_2\text{I}_3$ and that the transition states for exchange of the two isomeric diiodoethylenes are different and resist interconversion with an energy barrier of about 4 kcal./mole. We regard the process of interconversion to involve a relative rotation of about 180° around the carbon-carbon bond of a $\text{IHC}-\text{CHI}_2$ radical.

Although the experiments with iodine serve to clarify the mechanism of the catalyzed isomerization, they do not suggest whether the resistance to rotation arises because of steric forces between the bulky iodine atoms or because of interactions of the unshared electron which give some residual double-bond character to the carbon-carbon bond. In order to obtain information which might bear on this point, we have carried out similar studies with bromine and dibromoethylene. The isomerization and exchange reactions were both so rapid that thermal rates were easily measurable at room temperature and photochemical rates were much greater; therefore it was not feasible to make quantitative studies of the influence of light on the reaction.

Our results are all explicable in terms of the following individual steps for the isomerization and addition reactions.

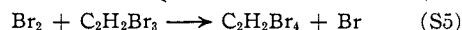
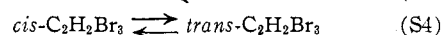
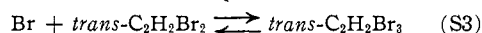
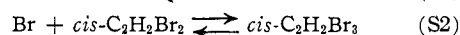
(1) Based on a Dissertation submitted by Hyman Steinmetz to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Persons wishing to see the original Dissertation or to obtain a microfilm thereof should address the Librarian, Columbia University, New York 27, New York.

(2) R. G. Dickinson and H. Lotzkar, *THIS JOURNAL*, **59**, 472 (1937).

(3) R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 3259 (1939).

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

(5) R. G. Dickinson, R. F. Wallis and R. E. Wood, *ibid.*, **71**, 1238 (1949).



Of these steps, all except the last are readily reversible. The rate of the addition reaction (S5) may depend upon the isomeric form of $\text{C}_2\text{H}_2\text{Br}_3$, but our data do not permit any differentiation in the rate constants.

Experimental

Materials—Dibromoethylene was prepared by the action of zinc on technical *sym*-tetrabromoethane, and the isomers were separated by fractionation of the azeotropes formed with absolute ethanol.⁶ Although it has been observed⁷ that pure *trans*-dibromoethylene isomerizes in the presence of air, carbon tetrachloride solutions of the freshly-separated isomer showed no isomerization even on standing for several weeks. Analyses by infrared absorption as described below indicated that the *cis* isomer contained not more than 0.2% of *trans* as impurity and that the *trans* isomer contained not more than 1.5% of *cis*.

The bromine was C.P. grade material which was distilled twice from anhydrous calcium bromide. Only the middle fraction of each distillation was retained.

Carbon tetrachloride was used as solvent in all experiments. A liter of C.P. grade material was refluxed with alkaline permanganate for 4 hours, washed, dried, and distilled. The middle fraction was retained and stored in the dark.

The bromine-82 used in the exchange experiments was obtained as pile-irradiated potassium bromide allocated by the Atomic Energy Commission. The salt was dissolved in water and shaken with a solution of bromine in carbon tetrachloride. This latter solution was washed with water and used directly.

Procedure for Kinetic Runs.—Preliminary studies of the isomerization reaction indicated that it was very sensitive to light and that different rates were obtained under atmospheres of air and of tank nitrogen. Therefore, the runs described here were prepared in a vacuum system. Carbon tetrachloride solutions of bromine and of dibromoethylene were degassed separately by repeatedly freezing with liquid nitrogen and evacuating with a mercury diffusion pump. Each solution was distilled separately through phosphorus pentoxide and trapped with liquid nitrogen. The combined solution was degassed again. Finally, the melted solution was distributed about equally in six ampules which were chilled simultaneously and sealed off. The ampules were warmed together to the reaction temperature, and one was opened and analyzed to establish zero time.

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

(7) R. M. Noyes and R. G. Dickinson, *THIS JOURNAL*, **65**, 1427 (1943).

Analysis for Extent of Isomerization.—In isomerization experiments, the solution from an ampule was thoroughly mixed with aqueous bisulfite until all of the free bromine had been reduced. The organic layer was then washed with several portions of water and dried with calcium chloride. The extent of isomerization was determined by infrared absorption with a Perkin-Elmer Model 12B spectrometer. *trans*-Dibromoethylene absorbs strongly at 900 cm^{-1} . Carbon tetrachloride and *sym*-tetrabromoethane (the product of bromine addition to dibromoethylene) are transparent in this region, but the purest samples of *cis*-dibromoethylene showed a slight absorption. This absorption was assumed to be due to about 0.2% of *trans* impurity.

Analysis for Free Bromine.—Since bromine also added slowly to the double bond, it was necessary to analyze some of the ampules for free bromine. In these determinations, a pipetted 2-ml. sample from an ampule was shaken with freshly-boiled water containing potassium iodide and dilute sulfuric acid. The resulting iodine was titrated with thio-sulfate.

Analysis for Isotopic Exchange.—In experiments containing bromine-82, the contents of an ampule were poured into a separatory funnel containing carbon tetrachloride and dilute aqueous bisulfite. The funnel was shaken immediately to reduce the bromine, the layers were separated, and the water layer was washed with two portions of carbon tetrachloride which were added to the other layer. Both layers were made up to volume and counted with a liquid counter described previously.⁸ The counts were corrected for background and for the fact that the counting rate for bromine-82 in carbon tetrachloride was observed to be $(2.4 \pm 0.6)\%$ higher than for the same amount of activity in water.

Results

Rates of Isomerization.—If the rate of isomerization is first-order in the isomerizing species and half-order in molecular bromine, then we may write

$$k_i = - \frac{2.303K_i}{(1 + K_i)[\text{Br}_2]^{1/2}} \frac{d \log (1 - [\text{Tr}]/[\text{Tr}]_{\text{eq}})}{dt} \quad (1)$$

where k_i is the rate constant for the isomerization of the *cis* isomer, K_i is the equilibrium constant for the reaction $\text{cis} \rightleftharpoons \text{trans}$, $[\text{Tr}]$ is the concentration of the *trans* isomer, and $[\text{Tr}]_{\text{eq}}$ is the concentration at equilibrium.

In Table I are presented the results of a series of runs carried to equilibrium in solutions containing 0.525 mole per liter (at 25°) of initially *cis*-dibromoethylene. The values for the fraction of *trans* at equilibrium are almost certainly good to 2% and probably to half that amount. In the following calculations we have assumed that the fraction of *trans* isomer at equilibrium is 0.441 at 59°, 0.438 at 49°, and 0.435 at 39°. These data indicate that for the equilibrium reaction $\text{cis-C}_2\text{H}_2\text{Br}_2 \rightleftharpoons \text{trans-C}_2\text{H}_2\text{Br}_2$ in carbon tetrachloride solution at 50°, $K_i = 0.78 \pm 0.02$, $\Delta F^\circ = 160 \pm 20$ cal./mole, $\Delta H^\circ = 260 \pm 200$ cal./mole, and $\Delta S^\circ = 0.3 \pm 0.5$

TABLE I

ISOMERIC EQUILIBRIUM OF DIBROMOETHYLENE IN CARBON TETRACHLORIDE

Temperature, °C.	Time of reaction, hours	Fraction of <i>trans</i> isomer
58.9	60	0.440
	90	.446
	100	.440
	100	.441
	150	.440
49.0	120	0.435
	120	.440

(8) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

cal./mole deg. Olson and Maroney⁹ report that an equilibrium mixture of pure dibromoethylenes at room temperature has 0.37 ± 0.02 mole fraction *trans*. An extrapolation to 50° of the vapor-phase equilibrium studies of Noyes and Dickinson⁷ indicates 0.49 ± 0.02 mole fraction *trans*. The differences between the various results are in the direction to be expected if the more polar isomer is more strongly solvated and if the effect is increased by increasing polarity of the solvent.

The results of the rate measurements are summarized in Table II. The fraction of *trans* isomer in each run was measured as a function of time, and $-\log (1 - [\text{Tr}]/[\text{Tr}]_{\text{eq}})$ was plotted against t . Plots for two representative runs are illustrated in Fig. 1. The slope of the straight line from each run was used in equation (1) to calculate the rate constant, k_i , for isomerization of *cis*-dibromoethylene. In making the calculations, it was also necessary to correct for the fact that an average of about 4% of the bromine was consumed in side reactions during the course of a run. Therefore, the concentration of bromine used in the calculation of k_i was the average concentration present during the run rather than the initial concentration reported in Table II. The data do not justify any more refined treatment for this effect.

TABLE II

RATE OF BROMINE-CATALYZED ISOMERIZATION OF DIBROMOETHYLENE

Temperature, °C.	$[\text{C}_2\text{H}_2\text{Br}_2]_0$, mole/liter	Initial $[\text{Br}_2]$, mole/liter	$10^4 k_i$ (mole/ml.) ^{-1/2} sec. ⁻¹
38.94	0.510	0.01343	3.32
	.510	.01343	3.30
	.510	.01343	3.28
	.510	.00672	3.32
	.510	.00672	3.42
	.510	.00672	3.57
		Av.	3.37 ± 0.12
49.03	0.500	0.01316	9.70
	.500	.01316	10.31
	.500	.01316	10.08
	.500	.00658	9.49
	.500	.00658	10.02
	.500	.00658	9.86
		Av.	9.91 ± 0.33
58.82	0.489	0.01288	27.8
	.489	.01288	27.3
	.489	.01288	28.6
	.489	.00643	26.8
	.489	.00643	25.8
	.489	.001288	28.4
	.245	.01288	26.5
		Av.	27.3 ± 1.1

^a The reported concentrations have been corrected for thermal expansion of the carbon tetrachloride.

The variation of the rate constant with temperature is such that it can be fitted by the equation

$$k_i = 10^{11.71 \pm 0.37} e^{-(21,700 \pm 600)/RT} (\text{mole/ml.})^{-1/2} \text{ sec.}^{-1}$$

Two other experiments were made to test the effects of air and water on the reaction. In one run about 10 mm. of air was introduced into the system;

(9) A. R. Olson and W. Maroney, *This Journal*, **56**, (32) (1934).

and in the other, enough water was added to form a second phase. In both experiments, the rate of isomerization increased autocatalytically.

Rates of Addition of Bromine.—Several tests indicated that negligible amounts of inorganic bromide were formed even when considerable amounts of bromine were consumed. It was therefore assumed that the bromine disappeared through addition to dibromoethylene. Since this addition had a measurable effect on the apparent rate of exchange and an almost significant effect on the rate of isomerization, a few semi-quantitative rate experiments were carried out with the *cis* isomer. These experiments, which are summarized in Table III, represent three separate runs, in two of which some of the ampoules were placed in thermostats at different temperatures. The data are neither extensive nor accurate enough to establish the kinetics of the addition reaction, but they are consistent with the rate expression

$$-d[\text{Br}_2]/dt = k_a[\text{Br}_2]^{1/2}[\text{C}_2\text{H}_2\text{Br}_2] \quad (2)$$

where k_a is the rate constant for the addition reaction. Values of k_a are included in Table III. In spite of the crudeness of these measurements, they are sufficiently precise to establish the corrections to apply to the other rate expressions.

TABLE III

RATE OF ADDITION OF BROMINE TO DIBROMOETHYLENE

Temp., °C.	$[\text{C}_2\text{H}_2\text{Br}_2]$, mole/liter	Initial $[\text{Br}_2]$, mole/liter	Br consumed per hour, %	k_a , (mole/ml.) ^{-1/2} sec. ⁻¹
45.05	0.504	0.0132	0.24 ± 0.02	0.36 ± 0.03
45.05	.101	.0663	.124 ± .012	.42 ± .04
29.93	.104	.0684	.037 ± .007	.120 ± .023
45.05	.152	.0198	.088 ± .009	.36 ± .04
29.93	.156	.0204	.014 ± .002	.055 ± .008

* The reported concentrations have been corrected for thermal expansion of the carbon tetrachloride.

Rates of Exchange of Bromine.—The reaction with radioactive bromine was not a simple exchange reaction because of two complicating effects. The first complication arose because considerable but not complete isomerization of dibromoethylene occurred during a run. However, runs in which the *trans* isomer was used as starting material gave exchange rates that agreed within experimental error with those obtained when the *cis* isomer was used. Also, if the two isomers exchanged by rates that differed by 50%, significant deviations from linearity would have been observed in the logarithmic plots used to determine the rate of exchange. Therefore, changes in isomeric composition of dibromoethylene will be neglected in further considerations of the exchange reaction.

The second complication arose because up to 5% of the bromine added to the double bond during the course of a run. Since our experimental procedure distinguished only between free and organically-bound bromine, we measured radioactivity present in $\text{C}_2\text{H}_2\text{Br}_2$ because of exchange and in $\text{C}_2\text{H}_2\text{Br}_4$ because of addition. Fortunately, the amount of addition was small enough to permit the use of some approximations in correcting for the effect on the

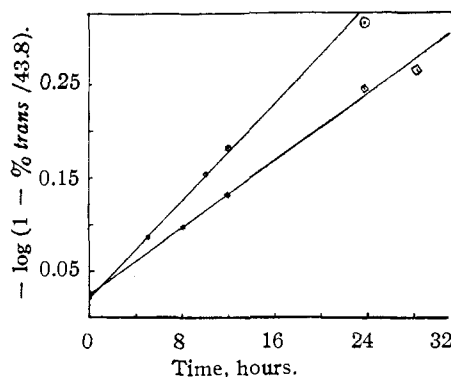
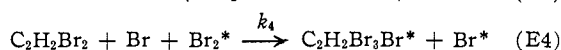
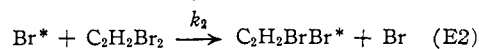


Fig. 1.—Two isomerization runs at 49.03°: ○ $[\text{C}_2\text{H}_2\text{Br}_2] = 0.500 M$, $[\text{Br}_2] = 0.01316 M$; □ $[\text{C}_2\text{H}_2\text{Br}_2] = 0.500 M$, $[\text{Br}_2] = 0.00691 M$.

apparent rate of exchange. We have postulated that the following processes are involved



In these equations, the asterisks are used merely to indicate the way in which bromine atoms present in the reactants are distributed in the products, and they do not necessarily indicate radioactive species. Presumably processes E2 and E4 take place through the formation of a $\text{C}_2\text{H}_2\text{Br}_3$ radical intermediate which subsequently either dissociates or reacts with a Br_2 molecule; however, it is permissible to treat them mathematically as simple processes obeying second- and third-order kinetics, respectively.

Let us define the quantity Γ as the fraction of free bromine atoms which came from Br_2 molecules in the step which produced them, and $1 - \Gamma$ as the fraction of free bromine atoms which came from $\text{C}_2\text{H}_2\text{Br}_2$ molecules.

$$\Gamma = \frac{k_3[\text{Br}_2] + k_4[\text{C}_2\text{H}_2\text{Br}_2][\text{Br}_2]}{k_2[\text{C}_2\text{H}_2\text{Br}_2] + k_3[\text{Br}_2] + k_4[\text{C}_2\text{H}_2\text{Br}_2][\text{Br}_2]} \quad (3)$$

This treatment assumes that at least some of the processes E2, E3 and E4 occur at a much greater rate than E1 so that there is a negligible probability that a specific free bromine atom was formed by the dissociation of a bromine molecule. It also assumes that the concentrations of Br atoms and $\text{C}_2\text{H}_2\text{Br}_3$ radicals are negligible compared to the concentrations of non-radical species containing bromine. We have previously used a similar treatment of a somewhat simpler exchange reaction.¹⁰

Let R be the rate at which atoms from Br_2 become incorporated in $\text{C}_2\text{H}_2\text{Br}_2$. In terms of the mechanism we have proposed

$$R = k_2[\text{C}_2\text{H}_2\text{Br}_2][\text{Br}]\Gamma \quad (4)$$

where the factor Γ is introduced because the isotopic composition of the free Br atoms is not the same as that of the Br_2 molecules.

If all of the organically-bound bromine were

(10) R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950).

produced by the exchange process E2, we could evaluate R from our data by means of the standard exchange expression

$$R = -\frac{2ab}{a+b} \frac{d}{dt} \ln \left[\frac{(a+b)x - a}{b} \right] \quad (5)$$

where a is the concentration of molecular bromine, b is the concentration of dibromoethylene, and x is the fraction of radioactivity (initially all present in the bromine) extractable with aqueous bisulfite at time t . Figure 2 illustrates a plot used to obtain such a preliminary value of R from the individual observations taken in one of our runs. Values of R obtained in this way were corrected for that portion of the activity which became organically-bound because of addition rather than exchange. The method of correction involved a complicated algebraic treatment described in the original Dissertation¹ and in a manuscript available from the American Documentation Institute.¹¹ The corrected values of R were less by 3 to 12% than those calculated on the assumption that only the exchange reaction was important. Our use of the corrected values of R is justified by the fact that they gave better straight-line relationships in the plots which were used to determine the rate constants for the individual exchange steps. The values obtained in our individual runs are available elsewhere.^{1,11}

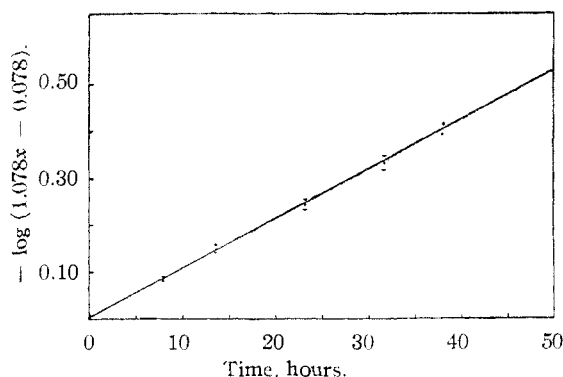


Fig. 2.—Exchange run at 45.05°: $[C_2H_2Br_2] = 0.1680 M$, $[Br_2] = 0.01327 M$. The estimates of error for individual points are calculated from the statistical fluctuations anticipated in counting the radioactive events.

In order to use values of R at different concentrations to evaluate individual rate constants, we have found it convenient to define the quantity Δ .

$$\Delta = \left[1 + \frac{k_2[C_2H_2Br_2]}{k_3[Br_2]} \right] \Gamma \quad (6)$$

In this equation, the term in brackets is the reciprocal of the value of Γ if there is no addition of bromine. Therefore, Δ would be unity if there were no addition. In our experiments, Δ varied between 1.01 and 1.04.

By combining Equations (4) and (6), we obtain

$$\frac{[C_2H_2Br_2][Br]\Delta}{R} = \frac{1}{k_2} \left[1 + \frac{k_2[C_2H_2Br_2]}{k_3[Br_2]} \right] \quad (7)$$

The evaluation of absolute rate constants requires

(11) Order Document 3605 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 × 8 inches) readable without optical aid.

knowledge of the concentration of free bromine atoms. We can obtain relative rate constants by using the relation

$$[Br] = K_1^{1/2}[Br_2]^{1/2} \quad (8)$$

where K_1 is the equilibrium constant for step E1. For convenience in discussion, we shall use the relation

$$k_e = k_2K_1^{1/2} \quad (9)$$

where k_e is the rate constant for the exchange reaction calculated in terms of the concentration of molecular bromine. This k_e can be compared to the k_i obtained for the isomerization reaction, which proceeds by identical kinetics.

According to Equation (7), a plot of $[C_2H_2Br_2] \cdot [Br_2]^{1/2} \Delta / R$ against $[C_2H_2Br_2] / [Br_2]$ should give a straight line with intercept $1/k_2K_1^{1/2}$ ($= 1/k_e$) and with slope $1/k_3K_1^{1/2}$. Figure 3 illustrates such a plot for the data at 35.56°; Table IV contains values for the rate constants at each temperature obtained from the equations of lines fitted by a method of weighted least squares. The values of R

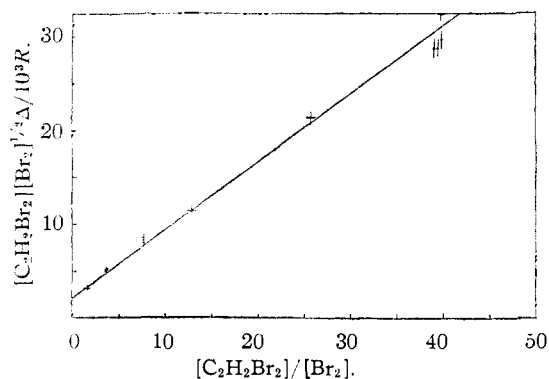


Fig. 3.—Plot for evaluating rate constants for exchange reactions at 35.56°. In addition to the data shown, there is one point at $[C_2H_2Br_2]/[Br_2] = 116.6$ and $[C_2H_2Br_2] \cdot [Br_2]^{1/2} \Delta / 10^3 R = 87.0$. (The line as drawn passes through the value of 87.1).

obtained in the 29 individual runs agree with those calculated from these rate constants with an average deviation of 4.1% and a maximum deviation of 10.1%. Such agreement is very satisfactory for rate data on radical chain reactions of this type.

TABLE IV
RATE CONSTANTS FOR EXCHANGE OF BROMINE ATOMS WITH Br_2 AND $C_2H_2Br_2$

Temp., °C.	Rate constant for $C_2H_2Br_2$, $10^4 k_e =$ $10^4 k_2 K_1^{1/2}$, (mole/ml.) ^{-1/2} sec. ⁻¹	Rate constant for Br_2 , $10^4 k_3 K_1^{1/2}$, (mole/ml.) ^{-1/2} sec. ⁻¹	k_2/k_3
29.92	2.36 ± 0.16	6.79 ± 0.17	0.348 ± 0.025
35.56	$4.82 \pm .14$	$13.72 \pm .19$	$.351 \pm .011$
45.05	$13.8 \pm .8$	$45.5 \pm .9$	$.303 \pm .019$

The variation of these rate constants with temperature is such that they can be fitted by the equations

$$k_2 K_1^{1/2} = 1(1)^{12.50 \pm 0.75} e^{-(22,300 \pm 1100)/RT} \text{ (mole/ml.)}^{-1/2} \text{ sec.}^{-1} = k_e$$

$$k_3 K_1^{1/2} = 1(1)^{14.21 \pm 0.27} e^{-(24,190 \pm 400)/RT} \text{ (mole/ml.)}^{-1/2} \text{ sec.}^{-1}$$

A few experiments were carried out to test the effect of air on the rate of the exchange reaction. Runs containing even a few mm. of air in the system went much faster than the vacuum runs and frequently showed autocatalytic features.¹

Discussion

The rates of exchange and isomerization can be compared most satisfactorily at 35.56°, the temperature at which the exchange was studied most fully. At this temperature, the rate constant for exchange of either isomer is $k_e = (4.82 \pm 0.14) \times 10^{-4}$ (mole/ml.)^{-1/2} sec.⁻¹. At the same temperature, the rate constant for the isomerization of the *cis* isomer is $k_i = (2.28 \pm 0.09) \times 10^{-4}$ (mole/ml.)^{-1/2} sec.⁻¹, and the rate constant for the isomerization of the *trans* isomer is $k_i/K_i = (2.98 \pm 0.15) \times 10^{-4}$ (mole/ml.)^{-1/2} sec.⁻¹. These results seem to demonstrate conclusively that the C₂H₂Br₃ radical is capable of existing in two isomeric forms and that the free energy barrier opposing their interconversion is of a height comparable to the height of the barrier opposing dissociation of either radical into a bromine atom and the corresponding isomer of dibromoethylene.

Our interpretation of the system can be illustrated by the free energy diagram in Fig. 4. In this diagram, levels A and B refer to the isomeric radicals and levels X, Y and Z to the transition states for the processes we are studying. Let P_{AC} be the probability that a system in state A will pass over X to C before it has passed over Y to B. Similarly, let P_{BT} be the probability that a system in state B will pass over Z to T before it has passed over Y to A. If the system is in state A, it will eventually pass either to state C or to state T. The probability that it will get to C before it gets to T is given by

$$P_{AC} + (1 - P_{AC})(1 - P_{BT})P_{AC} + [(1 - P_{AC})(1 - P_{BT})]^2P_{AC} + \dots = \frac{P_{AC}}{1 - (1 - P_{AC})(1 - P_{BT})} = \frac{P_{AC}}{P_{AC} + P_{BT} - P_{AC}P_{BT}} \quad (10)$$

Moreover, the probability that a system in state A will pass to T before it gets to C is given by

$$(1 - P_{AC})P_{BT} + (1 - P_{AC})^2(1 - P_{BT})P_{BT} + (1 - P_{AC})^3(1 - P_{BT})^2P_{BT} + \dots = \frac{(1 - P_{AC})P_{BT}}{1 - (1 - P_{AC})(1 - P_{BT})} = \frac{P_{BT} - P_{AC}P_{BT}}{P_{AC} + P_{BT} - P_{AC}P_{BT}} \quad (11)$$

Similarly, the probability that a system in state B will get to T is given by $P_{BT}/(P_{AC} + P_{BT} - P_{AC}P_{BT})$, and the probability that it will get to C is given by $(P_{AC} - P_{AC}P_{BT})/(P_{AC} + P_{BT} - P_{AC}P_{BT})$. We have previously used a very similar mathematical device¹² to calculate the ultimate fate of a system which can oscillate between two metastable configurations. The treatment assumes that the energies of molecules in the various states become canonically distributed rapidly enough that there are no momentum effects and that therefore the value of P_{AC} is independent of whether the system entered A from C or from B. This assumption is fundamental to any treatment involving absolute

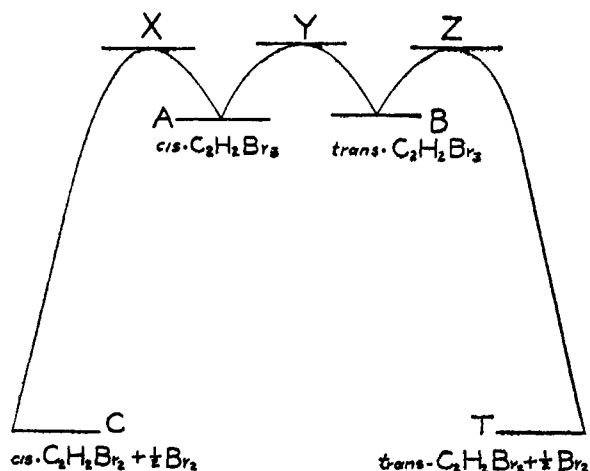


Fig. 4.—Free energy diagram for isomerization and exchange reactions of bromine and dibromoethylene.

reaction rate theory and is probably justifiable for these complicated molecules in liquid phase.

If k_{CA} is the rate constant for the system to react from C to A through transition state X, then k_i , the rate constant for isomerization of the *cis* isomer, will be equal to k_{CA} multiplied by the probability expression (11).

$$k_i = \frac{k_{CA}(P_{BT} - P_{AC}P_{BT})}{P_{AC} + P_{BT} - P_{AC}P_{BT}} \quad (12)$$

By applying absolute reaction rate theory to Fig. 4, we obtain

$$P_{AC} = \frac{e^{-(F_X - F_A)/RT}}{e^{-(F_X - F_A)/RT} + e^{-(F_Y - F_A)/RT}} = \frac{1}{1 + e^{-(F_Y - F_X)/RT}} \quad (13)$$

where the F 's are the molar free energies of the various states. By similar reasoning, we obtain

$$P_{BT} = \frac{1}{1 + e^{-(F_Y - F_Z)/RT}} \quad (14)$$

Equations (12), (13) and (14) can be combined to obtain

$$\frac{k_i}{k_{CA}} = \frac{1}{1 + e^{-(F_X - F_Y)/RT} + e^{-(F_X - F_Z)/RT}} \quad (15)$$

Equation (15) permits us to evaluate the difference in the free energies of the transition states X and Y provided we can evaluate the quantities k_i , k_{CA} and $F_X - F_Z$. Of these quantities, k_i is obtained by experimental measurement. Since bond-energy values indicate that C₂H₂Br₃ should be stabilized with respect to C₂H₂Br₂ + Br, it is hard to see how exchange of the *cis* isomer can occur unless the system passes through transition state X. Therefore, k_{CA} should be directly proportional to the experimentally measured k_e . The value of the constant of proportionality will depend on whether the entering atom becomes equilibrated with one or both of the original bromine atoms in the dibromoethylene molecule. If the entering atom becomes equilibrated with only one bromine, then $k_{CA} = 2k_e$. However, if the process BrHC-CHBr₂ → Br₂HC-CHBr can take place with retention of *cis-trans* isomeric configuration and is faster than the dissociation to C₂H₂Br₂ + Br, then the entering atom be-

(12) R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950).

comes equilibrated with both the atoms of the original molecule and $k_{CA} = 1.5k_e$. At the present time we are unable to distinguish between these two possibilities.

Finally, since the rate of exchange appears to be independent of isomeric composition of the dibromoethylene, $F_X - F_Z = F_C - F_T$. The data on the isomerization equilibrium reported above indicate that at 35° $F_C - F_T = -165$ cal./mole. Then, if $k_{CA} = 2k_e$, we find that $F_X - F_Y = -396$ cal./mole. If $k_{CA} = 1.5k_e$, $F_X - F_Y = +92$ cal./mole. Therefore, the data permit us to say that the free energies of transition states X and Y are nearly equal and differ by no more than a few hundred cal./mole.

The activation energy calculated for the thermal exchange reaction is 22.3 kcal./mole. This activation energy is greater than the activation energy for the process $\text{Br} + \text{C}_2\text{H}_2\text{Br}_2 \rightarrow \text{C}_2\text{H}_2\text{Br}_3$, and the difference should be equal to half the energy of dissociation of bromine in carbon tetrachloride solution. In the gas phase, half the energy of dissociation of bromine is 22.7 kcal./mole. Presumably the energy of dissociation in carbon tetrachloride solution is less than in the gas phase because the free atoms of bromine are solvated more strongly than the molecules, but probably the difference is not large. Therefore, the reaction of a free bromine atom with a dibromoethylene molecule takes place with a very low activation energy which is probably little, if any, more than the energy required for the diffusion process which brings the reactants together. This conclusion is consistent with the observations of Müller and Schumacher that in the gas phase bromine atoms add to acetylene¹³ and to dichloroethylene¹⁴ without activation energy.

During a study of the bromine-catalyzed isomer-

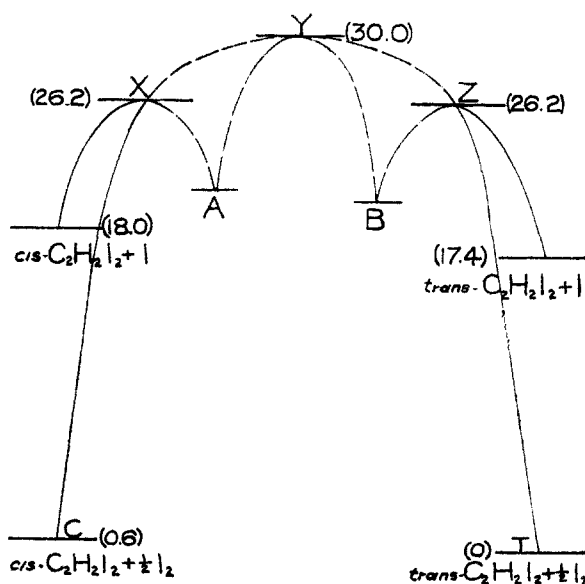
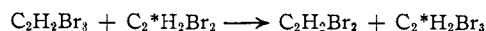


Fig. 5.—Energy diagram for isomerization and exchange reactions of iodine and diiodoethylene. Numbers in parentheses are energies in kcal./mole.

(13) K. L. Müller and H.-J. Schumacher, *Z. physik. Chem.*, **B39**, 352 (1938).

(14) K. L. Müller and H.-J. Schumacher, *ibid.*, **B42**, 327 (1939).

ization of the dichloroethylenes, Ketelaar, Van Velden, Broers and Gersmann¹⁵ proposed a slightly different mechanism of chain propagation. In our system, their mechanism could be formulated as

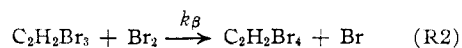
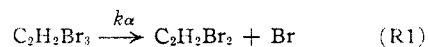


where the asterisks are used merely to clarify the equation. The last experiment presented in Table II indicates that the rate constant for isomerization is independent of dibromoethylene concentration in this range. Therefore, in our experiments the $\text{C}_2\text{H}_2\text{Br}_3$ radicals dissociated much more frequently than they transferred bromine atoms with dibromoethylene molecules. Ketelaar, *et al.*, were working in pure dichloroethylene without added solvent, and the mechanism which they propose may well have been important in their system even though it was not applicable in ours.

It is interesting to compare the results of this study with the previous experiments with diiodoethylene and iodine.⁴ In those studies the rate constant for thermal exchange of the *cis* isomer in non-polar solvents could be described by the expression $4.1 \times 10^{12}e^{-25,600/RT}$. The corresponding rate expression for *cis*-dibromoethylene and bromine is $3 \times 10^{12}e^{-22,300/RT}$. The reactions presumably proceed by identical mechanisms, and the remarkable agreement of the temperature-independent factors helps to vindicate the rather complicated treatment of the data which had to be used in the present investigation.

The energy relations for the iodine system are presented in Fig. 5. The dotted lines indicate the uncertainty as to whether there is any stabilization of $\text{C}_2\text{H}_2\text{I}_3$ relative to $\text{C}_2\text{H}_2\text{I}_2 + \text{I}$. However, since a bromine atom adds to dibromoethylene with little or no activation energy, we might expect that the 8 kcal./mole activation energy for exchange in diiodoethylene indicates that $\text{C}_2\text{H}_2\text{I}_3$ is little if any stabilized against dissociation.

We would like especially to know the difference in the energies of a $\text{C}_2\text{H}_2\text{X}_3$ radical in its stablest configuration and in the transition state for isomerization to the other form of the radical. Although we cannot obtain this information from our data, we can set minimum values. Thus, for the iodine case we can be confident that the energy of Y in Fig. 5 is at least 3.8 kcal./mole greater than that of A or B, and we do not believe the difference is much more than this. For the bromine case, we are able to make an even cruder estimate of the energy difference. The ultimate fate of a $\text{C}_2\text{H}_2\text{Br}_3$ radical is determined by a competition between two processes



We can say that $k_\alpha/k_\beta[\text{Br}_2] = k_{CA}/k_a[\text{Br}_2] = 2$ (or 1.5) $k_e/k_a[\text{Br}_2]$. At 45° , $k_e = 1.38 \times 10^{-3}$ (mole/ml.)^{-1/2} sec.⁻¹ and $k_a = 0.38$ (mole/ml.)^{-1/2} sec.⁻¹. Then $k_\alpha/k_\beta = 0.0073$ (or 0.0054) mole/ml. Even if step R2 takes place at every encounter in solution, k_β can hardly be greater than 1.1×10^{13} (mole/ml.)⁻¹ sec.⁻¹, the rate constant for the

(15) J. A. A. Ketelaar, P. F. Van Velden, G. H. J. Broers and H. R. Gersmann, *J. Phys. Colloid Chem.*, **55**, 987 (1951).

recombination of iodine atoms in hexane.⁸ Then the maximum possible value of k_a would appear to be 8×10^{10} sec.⁻¹. If the temperature-independent term for k_a has the "normal" value of 10^{13} sec.⁻¹, the minimum energy of activation for step R1 is 3.0 kcal./mole. This value is undoubtedly minimal, for k_β is almost certainly distinctly less than 10^{13} (mole/ml.)⁻¹ sec.⁻¹.

The above argument is very qualitative but suggests how some additional information could be obtained. At concentrations of a few moles per liter of bromine, the rates of processes R1 and R2 should be comparable. Under these conditions, kinetic studies of the addition reaction could evaluate k_{CA} and k_a/k_β at various temperatures.¹⁶ Such results could es-

(16) Data of this sort were obtained by Müller and Schumacher for the vapor-phase bromination of dichloroethylene. Unfortunately, they made a mistake in algebra on p. 368 of Reference 13 and thought they could calculate absolute energies of activation for reactions corresponding to our processes R1 and R2.

tablish the constant of proportionality between k_{CA} and k_e and determine whether one or both of the bromines in the dibromoethylene become equilibrated with the entering bromine atom. The results could also provide a better minimum value for the energy difference between Y and A or B. However, all of our studies serve only to provide us fleeting glimpses of the peaks represented by transition states X, Y and Z, and to measure their heights relative to the surrounding plains (C and T). Kinetic measurements alone can never explore the mountain valleys to locate levels A and B. We have a slight hope that the concentration of $C_2H_2Br_3$ radicals might be measurable in an equilibrium or photostationary state, and that the quantitative picture in Fig. 4 could thereby be completed, but we do not see how to make the measurements by any techniques available to us at present.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

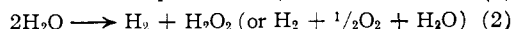
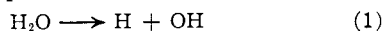
The Molecular Yield in the Decomposition of Water by Hard X-Rays¹

BY EVERETT R. JOHNSON AND AUGUSTINE O. ALLEN

RECEIVED FEBRUARY 16, 1952

Dilute aqueous solutions of a number of oxidizing and reducing agents at various concentrations give on irradiation with hard X-rays identical initial yields of hydrogen gas. This yield of molecular hydrogen is therefore characteristic of the action of X-rays on water, and occurs simultaneously with the formation of free radicals which react with solutes. The molecular yield is decreased about 18% by addition of 4% of sulfuric acid to the water.

A number of observations on the radiation chemistry of water and aqueous solutions have been correlated by the idea that the systems behave as though the water were reacting simultaneously in two ways²⁻⁵—a decomposition into free radicals and also a decomposition into molecules



The radicals formed in (1) are assumed to be responsible for most of the reactions undergone by solutes in irradiated solutions. Consequently in the presence of solutes which are sufficiently reactive toward the radicals produced in (1) a constant initial yield of hydrogen gas should appear from reaction (2).

Hydrogen yields from a variety of oxidizing and reducing solutions have been determined with the object of testing this prediction.

Experimental

Reagents and Materials.—The water used in all these experiments was obtained by redistilling ordinary distilled water, first from alkaline permanganate, then acid dichromate, then dilute sodium hydroxide into a Pyrex vessel from which the final distillation was made. The distillate from this last flask was condensed in a silica system and col-

lected in a silica vessel. All reagents were C.P. and were used without further purification, with the exception of ferrous ammonium sulfate which was recrystallized several times.

The sample bulbs (approximately 10-cc. volume) were blown from 2-mm. Pyrex capillary tubing. All sample bulbs were soaked in purified water prior to use.

X-Rays were obtained by bombarding a gold target with 2-Mev. electrons from an electrostatic generator made by High Voltage Engineering Corp. of Cambridge, Mass.

Preparation of Samples and Methods of Analyses.—The procedure for filling the bulbs is as follows: The solution to be irradiated is placed in bulb A (Fig. 1), outgassed at room temperature, and frozen with liquid nitrogen while the entire system is being pumped down. When the pressure is less than 1×10^{-6} mm. (as measured by an ion gage), the liquid nitrogen trap is removed from the solution bulb and solution boiled (about 40–50°) and refrozen. When the pressure is again less than 1×10^{-6} mm., that part of the line containing the solution and reaction bulbs is sealed off from the remaining portion by means of the heavy-walled

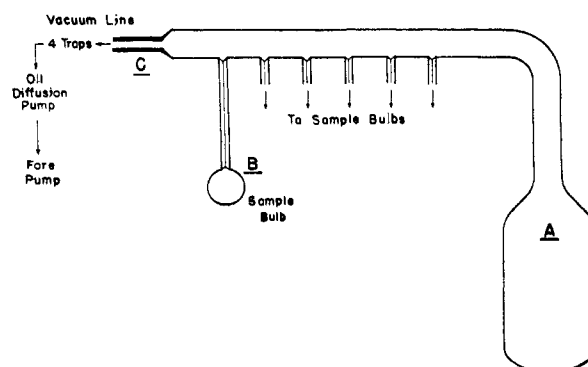


Fig. 1.—Arrangement for filling sample bulb.

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

(2) (a) A. O. Allen, *J. Phys. Colloid Chem.*, **52**, 479 (1948); (b) A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, Report AECU-1413; *J. Phys. Chem.*, **56**, 601 (1952).

(3) C. J. Hochanadel, *ibid.*, **56**, 587 (1952).

(4) E. J. Hart, *This Journal*, **73**, 1891 (1951).

(5) E. J. Hart, Reports AECU-1250 and ANL-4636; *J. Phys. Chem.*, **56**, 594 (1952).