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The Exchange Reaction between Bromine and Bromotrichloromethane

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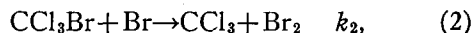
Thermal exchange of the bromine in CCl_3Br with Br_2 has been measured in the temperature range from 100° to 135°C in liquid CCl_3Br , in the range from 135° to 170°C in CCl_4 solution, and in the range from 150° to 220°C in the gas phase. The activation energy has been found to be approximately $29 \text{ kcal. mole}^{-1}$ in each phase. The rate of exchange has been found to be proportional to the first power of the CCl_3Br concentration and to the square root of the bromine concentration, indicating an atomic mechanism. The values of the rate constants obtained in the liquid and gas phases are approximately equal. From the results it may be deduced that the activation energy for the step which initiates the exchange, i.e., either $\text{CCl}_3\text{Br} + \text{Br} \rightarrow \text{CCl}_3 + \text{Br}_2$ or the reaction $\text{CCl}_3\text{Br} + \text{Br}^* \rightarrow \text{CCl}_3\text{Br}^* + \text{Br}$ is about $7 \text{ kcal. mole}^{-1}$. This value is in the range of values of $5\text{--}10 \text{ kcal. mole}^{-1}$ indicated by previous experiments on the analogous photochemical reaction in carbon tetrachloride solution. The thermal reaction has been found to be much less sensitive to oxygen than various previously studied photo-chemical halogenation reactions. Analysis of the results suggests that the "cage" effect may appreciably lower the quantum yield of the photo-chemical reaction in the liquid phase.

INTRODUCTION

MANY reactions of halogens with halogenated hydrocarbons have been studied for the purpose of establishing the reaction mechanisms and determining the activation energies of the elementary steps involving atoms or radicals.¹ Probably the simplest reactions of this type are those which involve only the exchange of atoms between elementary halogen molecules and the same halogen in organic combination. In such reaction systems only two molecular species are present and there is no change in the chemical composition of the system. The number of possible elementary reaction steps involving atoms and free radicals is smaller than in systems containing more species and consequently the possibility of certainty in assigning activation energies to these steps is increased. Several investigations² of such reactions have been reported but only in a very few have activation energies or quantum yields been determined.

In studying a variety of reactions of halogens with halogenated hydrocarbons we have ob-

tained information on the thermal and photochemical exchange of bromine with bromotrichloromethane. This reaction may be represented by the over-all equation $\text{CCl}_3\text{Br} + \text{BrBr}^* \rightarrow \text{CCl}_3\text{Br}^* + \text{BrBr}$, where Br^* is used to denote radioactive bromine tracer, which is used as a means of observing the exchange. Evidence for the existence of a reaction of this type was first reported by Wilson and Dickinson.^{2b,3} As might be expected, the results for the thermal reaction are consistent with a mechanism involving the following steps:



where the steady state concentration of bromine atoms is controlled solely by the thermal dissociation equilibrium for which the equilibrium constant is $K_c = k_1/k_4$. The rate law for this mechanism is simply: $R = \text{rate of exchange of halogen} = k_2[\text{CCl}_3\text{Br}](k_1[\text{Br}_2]/k_4)^{1/2} = k[\text{CCl}_3\text{Br}][\text{Br}_2]^{1/2}$. The same rate law will hold if the exchange occurs by the step $\text{CCl}_3\text{Br} + \text{Br}^* \rightarrow \text{CCl}_3\text{Br}^* + \text{Br}$ (having a rate constant

¹ See for example, E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946). Chapters IX, X, and XI.

² See, for example; a. G. K. Rollefson and W. F. Libby, *J. Chem. Phys.* **5**, 569 (1937); b. J. N. Wilson and R. G. Dickinson, *J. Am. Chem. Soc.* **61**, 3519 (1939); c. L. C. Liberatore and E. O. Wiig, *J. Chem. Phys.* **8**, 349 (1940); d. J. H. Hodges and A. S. Miceli, *J. Chem. Phys.* **9**, 725 (1941); e. L. B. Seely, Jr. and J. E. Willard, *J. Am. Chem. Soc.* **69**, 2061 (1947).

³ A study of the kinetics of the gas phase reaction has recently been made by N. Davidson and J. H. Sullivan of the California Institute of Technology (see article in this issue). We learned of this just as our work was being completed.

again designated as k_2) rather than by reactions 2 and 3 above. The over-all activation energy, which may be determined with the aid of the Arrhenius equation from the dependence of k on the temperature, is related to the activation energies of the elementary steps by the equation: $E_{\text{over-all}} = E_2 + \frac{1}{2}(E_1 - E_4)$ since $k = k_2(k_1/k_4)^{1/2}$. Since E_4 may be assumed to be zero and E_1 equal to the heat of dissociation of bromine the value of the activation energy for the elementary reaction $\text{Br} + \text{CCl}_3\text{Br} \rightarrow \text{CCl}_3 + \text{Br}_2$ may be calculated from the experimental data.

In an exchange reaction of this type the measured rate of change of the radiobromine from one chemical form to the other becomes progressively slower, as the equilibrium distribution of radioactivity is approached, although the true exchange reaction continues at a constant rate. Regardless of the mechanism of the exchange reaction the observed rate of equilibration of the radiobromine will follow a first order rate law⁴ for which the observed rate constant is $k' = (2.3/t) \log(1/1 - F)$ where F equals the concentration of radioactivity in the CCl_3Br relative to that at equilibrium and t equals the time of reaction. Equilibrium will be attained when the activity per gram atom of bromine in the CCl_3Br and Br_2 fractions is equal. It can be shown that if the true rate of the exchange reaction is given by: $R = k[\text{Br}_2]^m \times [\text{CCl}_3\text{Br}]^n$ where k is the true velocity constant that

$$k' = R \frac{(2[\text{Br}_2] + [\text{CCl}_3\text{Br}])}{2[\text{Br}_2][\text{CCl}_3\text{Br}]}$$

If, as in the case of the present work, the bromotrichloromethane concentration is much greater than the bromine concentration,

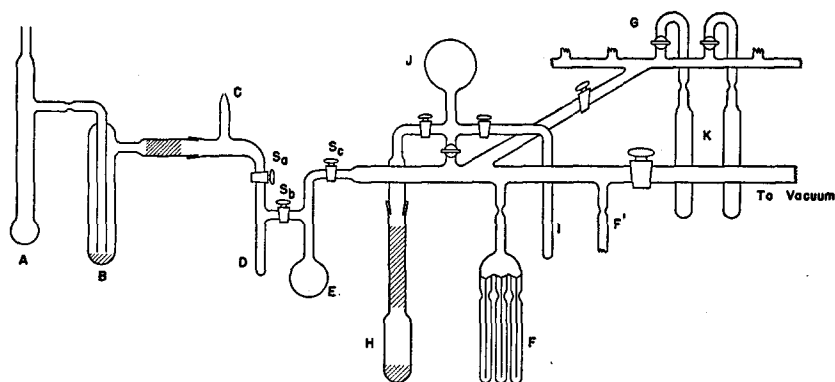
$$k = 2k'([\text{Br}_2]^{1-m}/[\text{CCl}_3\text{Br}]^n).$$

The over-all activation energy can be determined from the temperature coefficient of k or, if the concentration of each reactant is constant in a series of experiments at different temperatures, can be obtained directly from the temperature coefficient of the experimental velocity constant, k' .

EXPERIMENTAL

In order to minimize the possibility that the results of these experiments would be affected by air, water, or other impurities the reactants were degassed, dried and distilled into the reaction tubes on the vacuum system illustrated in Fig. 1. Radiobromine, Br^{82} (34 hr.), was prepared from active KBr^5 by reaction with the stoichiometric equivalent of KBrO_3 and an excess of 85 percent H_3PO_4 in tube *A* of Fig. 1. With the aid of heat the Br_2 was driven into trap *B*; tube *A* was removed from the system and outlet *C* was closed with a flame. The system was then evacuated while the bromine was frozen in *B*, following which the bromine was distilled from the P_2O_5 in *B* through a train of P_2O_5 on glass wool and condensed in the tube *D* where it was further degassed by several cycles of alternate freezing and evacuation. From a knowledge of the vapor pressure-temperature curve of bromine it was then possible to obtain a desired pressure of bromine gas in the bulb *E*

FIG. 1. Apparatus for filling reaction tubes in study of $\text{CCl}_3\text{Br}-\text{Br}_2$ reaction.



⁴ a. H. A. C. McKay, *Nature* **142**, 997 (1938); b. S. Z. Roginsky, *Acta Physicochemica URSS* **14**, 1 (1941); c. R. B. Duffield and M. Calvin, *J. Am. Chem. Soc.* **68**, 557 (1946).

⁵ U. S. Atomic Energy Commission, Item No. 11, *Radioisotopes Catalogue*, No. 2, September 1947.

TABLE I. $\text{CCl}_3\text{Br}-\text{Br}_2$ exchange in liquid CCl_3Br .

Tube	Temp., °C	Time, hours	$[\text{CCl}_3\text{Br}]$, mole/l	$[\text{Br}_2]$, mole/l	$F \times 100$	k' , hr. ⁻¹	k_{AV} , (mole/l) ⁻¹ hr. ⁻¹
A1	100	2.0	9.3	0.0293	15.8	0.087	0.0034
A2	100	4.0	9.3	0.0293	30.8	0.092	
A3	100	8.0	9.3	0.0293	78.5	0.090	
A4	125	0.5	8.95	0.0282	49.0	1.35	0.050
A5	125	0.75	8.95	0.0282	60.5	1.24	
A6	125	1.0	8.95	0.0282	78.5	1.53	
A7	R.T.	70	10	0.030	0.7	—	—
C1	100	2	9.3	0.0785	12.4	0.066	0.0038
C2	100	4	9.3	0.0785	22.0	0.062	
C3	100	8	9.3	0.0785	39.8	0.063	
C4	100	12	9.3	0.0785	52.5	0.062	
B1	115	1	9.1	0.0735	26.9	0.315	0.0184
B2	115	2	9.1	0.0735	45.0	0.300	
B3	125	0.5	8.95	0.0720	32.1	0.770	0.048
B4	125	1.0	8.95	0.0720	56.6	0.830	
B5	125	1.5	8.95	0.0720	70.8	0.820	
B6	125	2.0	8.95	0.0720	80.2	0.810	
C5	135	0.33	8.8	0.0745	46.5	1.89	0.118
C6	135	0.66	8.8	0.0745	72.2	1.94	

by regulating the temperature of *D* and allowing the vapor to fill the system between stopcocks *S_A* and *S_C*. The volume of the bulb *E* together with its connecting tubes was known. By introducing bromine at a known pressure from *D*, then closing *S_B* and opening *S_C* it was therefore possible to introduce variable known amounts of bromine into the liquid phase reaction tubes *F* and *F'* or into the gas phase tubes attached to the manifold *G*.

Bromotrichloromethane, prepared by the photo-bromination of boiling chloroform in a nitrogen atmosphere,⁶ and subsequent fractional distillation, was degassed by alternate freezings and evacuations in the bulb *H*, and distilled from P_2O_5 through a train of P_2O_5 on glass wool into the metering tube *I* of which the volume per unit length was known.

To fill the liquid phase reaction tubes a known amount of bromotrichloromethane was distilled from *I* into the six tubes in the cluster at *F*

TABLE II. Effect of bromine concentration on the $\text{CCl}_3\text{Br}-\text{Br}_2$ exchange in liquid CCl_3Br .

Temp. °C	$[\text{Br}_2]$, mole/l	k' , hr. ⁻¹	$k'[\text{Br}_2]$	$k'[\text{Br}_2]^{\dagger}$	$k'[\text{Br}_2]^{-1}$
100.	0.0293	0.090	0.0026	0.015	3.07
	0.0785	0.063	0.0049	0.018	0.80
125	0.0282	1.37	0.40	0.23	48.5
	0.0720	0.81	0.58	0.22	11.2

⁶ E. G. Bohlmann and J. E. Willard, J. Am. Chem. Soc. **64**, 1342 (1942).

cooled with liquid air. (Each of these tubes was made of 2.5 mm I.D., 9 mm O.D. Pyrex capillary tubing and contained 0.3 ml of solution when half-filled.) The stopcock *S_C* was then opened and the known amount of bromine from bulb *E* was condensed with the bromotrichloromethane in *F*. Following further degassing cycles, continued until no Tesla coil discharge was obtained while the liquid was frozen, the cluster of six tubes was sealed off from the system, the liquid was thawed, mixed and refrozen, and the individual tubes were sealed off from the manifold. From the total amounts of Br_2 and CCl_3Br the concentration, which was the same in each tube, could be calculated. Since no data were found on the coefficient of thermal expansion of liquid CCl_3Br , this information, which was needed for use in calculating the concentrations in the reaction tubes at different temperatures, was estimated from data for carbon tetrachloride. Final calculations of the amount of bromine were based on the total radioactive counting rate obtained when the tubes were opened and the contents analyzed. The counting rate per unit weight of bromine was determined for each shipment by counting an aliquot of the stock KBr solution and weighing the solid KBr from a second aliquot.

The reaction tubes in which carbon tetrachloride was used as a solvent were filled in the same manner using a second calibrated tube similar to *I* (Fig. 1) to introduce the desired amount of CCl_4 into the system. The carbon tetrachloride was purified by the method described by Dickinson and Leermakers.⁷

In the preparation of the gas phase reaction tubes a known amount of bromine vapor from the bulb *E* was allowed to expand into the system including the twelve reaction tubes *K* on the manifold *G*, after which the stopcocks were closed. These tubes had a uniform volume of 20 ml; it was thus possible to obtain approximately equal amounts of bromine in each. Equal amounts of bromotrichloromethane were then metered into each of the tubes by maintaining the liquid in *I* at 20°C, allowing the vapor to expand into the known volume of bulb *J* and then condensing it from this volume into one of

⁷ R. G. Dickinson and J. A. Leermakers, J. Am. Chem. Soc. **54**, 3853 (1932).

the tubes by cooling the tube in liquid air and opening the corresponding stopcock. After degassing, the tube was sealed off at the constriction below the stopcock. The exact amount of bromine in each vapor phase tube was determined from the measured counting rate following reaction. The exact amount of bromotrichloromethane was determined from the weight of the tube following reaction before it was opened (a buoyancy correction was applied) and the weight of the clean dry pieces after it was emptied. About 0.06 to 0.08 gram of bromotrichloromethane was normally used in each tube.

In all cases the reaction tubes were kept at 0° in the dark until they were reacted, and were wrapped in aluminum foil to exclude light during heating and subsequent handling. The reactions were carried out in an oil bath with temperature controlled to within $\pm 0.5^\circ$. After removal from the bath each tube was rapidly cooled in an air blast and frozen in dry ice until it was analyzed.

All stopcocks on the system shown in Fig. 1 were lubricated with silicone high vacuum stopcock grease, tests with radiobromine having demonstrated that this grease is much less reactive toward bromine than other common types. All reaction tubes were prepared by boiling in fuming nitric acid and rinsing with triply distilled water. The reaction tubes and all other parts of the apparatus for which it was feasible were degassed prior to use by flaming while evacuated.

In order to determine the extent of reaction in a tube, the contents were frozen in the bottom with dry ice. The top was broken off, carbon tetrachloride was added, and the contents were transferred together with the carbon tetrachloride rinses to a separatory funnel containing 20 percent aqueous sodium iodide. The aqueous and carbon tetrachloride layers were separated, made up to 10 ml each and counted in a Technical Associates solution-type Geiger-Mueller tube. Preliminary experiments showed that under our conditions of measurement the counting rate of radiobromine in carbon tetrachloride was 90 percent of that of the same amount of bromine in 20 percent aqueous sodium iodide solution. This correction and corrections for background and decay were applied where necessary. The fraction of the radiobromine

TABLE III. $\text{CCl}_3\text{Br}-\text{Br}_2$ exchange in CCl_4 solution.

Tube	Temp., $^\circ\text{C}$	Time, hours	$[\text{CCl}_3\text{Br}]$, mole/l	$[\text{Br}_2]$, mole/l $\times 10^4$	$F \times 100$	k' , hr.^{-1}	k , $(\text{mole/l})^{-1}\text{hr.}^{-1}$
A1	135	1.0	0.207	2.84	18.5	0.21	0.110
A2	135	2.0	0.207	2.84	28.9	0.17	0.090
A3	150	1.0	0.201	2.93	42.7	0.56	0.30
A4	150	2.0	0.201	2.93	73.6	0.66	0.34
A5	170	0.25	0.194	2.74	57.0	3.36	1.82
A6	170	0.50	0.194	2.74	86.2	3.96	2.12
B1	135	1.0	0.942	7.90	43.5	0.59	0.112
B2	135	2.0	0.942	7.90	66.6	0.51	0.096
B3	150	0.5	0.916	7.68	44.8	1.14	0.22
B4	150	1.0	0.916	7.68	64.5	1.10	0.20

which had exchanged was then given by the ratio of the count in the carbon tetrachloride to the total count. A total count of 5000 was usually measured giving a probable statistical counting error of about 1 percent.

RESULTS

The conditions and results of exchange experiments carried out with liquid phase mixtures of bromine and bromotrichloromethane are given in Table I, where F is the fraction of radiobromine equilibrium attained and k' is the observed first order velocity constant for the transfer of radiobromine from Br_2 to CCl_3Br . The letters A , B , and C each indicate a separate series of reaction tubes prepared as a unit. Series B and C were prepared from a single bromine shipment under conditions as nearly identical as possible while A was prepared from a different bromine shipment and with a much lower bromine concentration.

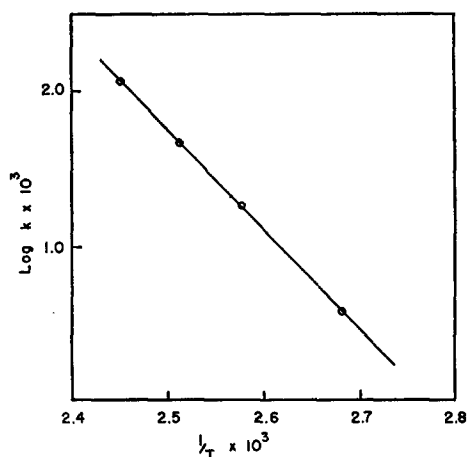
FIG. 2. Temperature dependence of rate of $\text{CCl}_3\text{Br}-\text{Br}_2$ exchange in liquid CCl_4 .

TABLE IV. $\text{CCl}_3\text{Br}-\text{Br}_2$ exchange in the gas phase.

Tube	Temp., °C	Time, hours	$[\text{CCl}_3\text{Br}]$, mole/l $\times 10^3$	$[\text{Br}_2]$, mole/l $\times 10^3$	$F' \times 100$	$F_\infty \times 100$	$F \times 100$	k_1 , (mole/l) ⁻¹ hr. ⁻¹	k_{app} , (mole/l) ⁻¹ hr. ⁻¹
1	150	0.5	5.5	0.33	2.0	89.3	2.2	0.26	0.26
2	170	0.5	7.2	0.34	9.6	91.3	10.5	1.16	
3	170	2.0	4.2	0.37	17.4	84.5	20.6	1.06	1.11
4	170	4.75	20.3	0.41	86.6	96.0	90.4	1.12	
5	200	0.5	3.9	0.36	34.8	84.4	41.2	10.30	
6	200	1.0	6.9	0.36	76.4	90.5	84.5	10.26	10.28
7	220	0.25	3.9	0.47	43.2	80.5	53.6	34.2	34.2
8	220	0.50	10.6	0.37	92.8	93.5	99.4		

Experiment A7, in which a reaction mixture was allowed to stand for 70 hours at room temperature and then analyzed, shows that reaction is negligible at this temperature.

In Table II data from Table I for experiments made at two different bromine concentrations at each of two temperatures are tabulated, together with the values of k' multiplied by different powers of the bromine concentration. From the equations stated in the Introduction, $R = k[\text{Br}_2]^m \times [\text{CCl}_3\text{Br}]^n$ and $k = 2k'[\text{Br}_2]^{1-m}/[\text{CCl}_3\text{Br}]^n$ it is evident that if the CCl_3Br concentration is held constant and k' is determined at different concentrations of bromine then the value of m which gives a constant value of the product $k'[\text{Br}_2]^{1-m}$ will be equal to the order of the bromine dependency of the exchange reaction. The results of Table II indicate that the rate of exchange of bromine with liquid bromotrichloro-

methane is proportional to the square root of the bromine concentration.

The first power dependency of the rate on the concentration of CCl_3Br is indicated by the results listed in Table III for experiments in CCl_4 as a solvent⁸ and by the results of the gas phase experiments listed in Table IV. Except for the discrepancy of unknown origin shown by the results at 150°C in Table III, the values of k calculated using the formula for first order dependency on CCl_3Br concentration, $k = (2k' \times [\text{Br}_2]^1)/[\text{CCl}_3\text{Br}]$, are essentially constant over three and fourfold variations in CCl_3Br concentration.

A calculation of the activation energy of the reaction on the basis of the two temperatures of Table I, series A gives a value of 32 kcal. mole⁻¹. The data of Table I, series B and C, for four temperatures, plotted in Fig. 2, give 29.8 kcal. mole⁻¹. The latter is probably a more accurate value since the experiments of series A were exploratory in nature and run under less carefully controlled conditions. The data of Table III for CCl_4 solutions give a value of about 29 kcal. mole⁻¹.

In the gas phase experiments (Table IV) the $\text{CCl}_3\text{Br}-\text{Br}_2$ ratio was usually less than 100, so that, in contrast to the liquid phase runs, where the excess of bromotrichloromethane was greater, a measurable fraction of the activity would have remained in the form of elemental bromine at equilibrium. In Table IV the observed fraction of the activity in the organic layer is denoted by F' , the calculated equilibrium fraction by F_∞ , and the fraction of equilibrium achieved

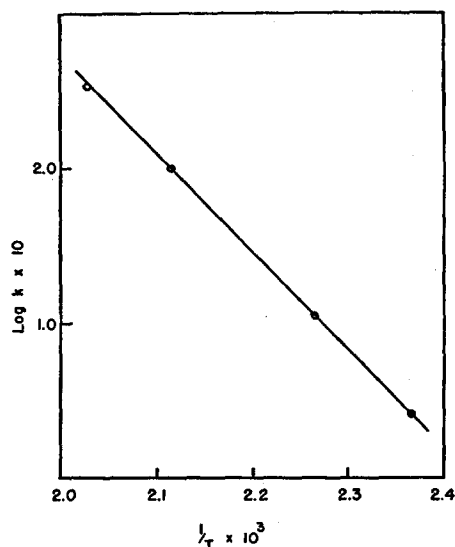


FIG. 3. Temperature dependence of rate of $\text{CCl}_3\text{Br}-\text{Br}_2$ exchange in the gas phase.

⁸ We have found that the rate of the reaction of Br_2 with the solvent is negligible even at the highest temperature used in this work. The reaction between CCl_4 and Br_2 does take place with an easily measurable rate above 200°C, the activation energy being about 40 kcal./mole.

by F

$$F = F'/F_\infty; \quad F_\infty = 1/1+r; \quad r = 2[\text{Br}_2]/[\text{CCl}_3\text{Br}].$$

Fig. 3 shows the plot of $\log k$ vs. $1/T$ for the gas phase experiments. The slope of this line yields a value of 28.7 kcal. mole⁻¹ for the activation energy.

In order to prove the identity of the organic radiobromine compound resulting from these experiments the organic fractions from one series of tubes were combined and fractionally distilled with carriers covering a wide boiling point range and including CCl_3Br . The separate fractions were counted with a Geiger-Mueller counter. Essentially all of the activity was found in the CCl_3Br fraction.

A series of experiments was made to determine whether or not added constituents affect the rate of the $\text{CCl}_3\text{Br}-\text{Br}_2$ exchange reaction in the gas phase at 170° and at concentrations similar to those used in the experiments of Table IV. The results indicate that a pressure of O_2 15 percent as great as that of the Br_2 , of H_2O 12 percent as great as that of the Br_2 , or of Cl_2 40 percent as great as that of the Br_2 causes a decrease in the rate constant of approximately 50 percent. A test in which a quartz tube was used in place of the usual Pyrex tube showed no change in the rate constant. These results are of qualitative rather than quantitative significance but are adequate to indicate that the reaction is not extremely sensitive to any of the variables tested.

Day⁹ has shown that a bromine-sensitized photo-chemical formation of C_2Cl_6 from CCl_3Br ($2\text{CCl}_3\text{Br} \xrightarrow{\text{Br}_2, h\nu} \text{C}_2\text{Cl}_6 + \text{Br}_2$) occurs at very low bromine concentrations. We have determined qualitatively that this reaction also occurs as a thermal reaction but is not observable at bromine concentrations as high as those used in the work of this paper.

DISCUSSION

The results presented above establish the fact that the rate of equilibration of the radiobromine between the inorganic and organic phases in a mixture of Br_2 and CCl_3Br follows a first order law, in agreement with the belief that it is a

⁹ W. U. Day, Ph.D. thesis, University of Wisconsin (1942).

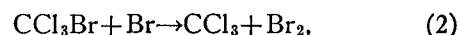
TABLE V. Comparison of rate constants of $\text{CCl}_3\text{Br}-\text{Br}_2$ exchange in liquid and gas phase.

Table	Series	Temp., °C	Conditions	k , (mole/l) ⁻¹ hr. ⁻¹
I	C	135	Liquid Phase	0.118
III	A	135	CCl_4 Solution	0.100
	B	135	CCl_4 Solution	0.104
III	A	150	CCl_4 Solution	0.32
	B	150	CCl_4 Solution	0.22
IV		150	Gas Phase	0.26
III	A	170	CCl_4 Solution	1.96
I	B, C	170	Liquid Phase	1.92*
IV		170	Gas Phase	1.11

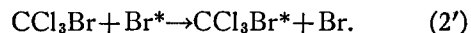
* Obtained by extrapolation on Fig. 2.

simple exchange reaction. This belief is further established by the distillation experiment showing the organically bound activity to be in the form of bromotrichloromethane.

The fact that the rate of the over-all exchange reaction is proportional to the square root of the bromine concentration is strong evidence that the exchange occurs through the medium of bromine atoms whose concentration is controlled by the thermal equilibrium $\text{Br}_2 \rightleftharpoons 2\text{Br}$. This suggests that the mechanism of the exchange is either



or



It is impossible to distinguish between these two mechanisms on the basis of the results reported in this paper.

Selected rate constants which afford the best comparison of the exchange reaction in liquid CCl_3Br , in CCl_4 solution, and in the gas phase have been taken from Tables I, III, and IV and listed in Table V.

The near equivalence of the activation energy (Figs. 1 and 2) and of the rate constants (Table V) in the gas and liquid phases suggests that the elementary steps are the same in the two phases and that at the same temperature the steady state concentration of the bromine atom intermediate is the same in the two cases.

The over-all activation energy for the thermal $\text{CCl}_3\text{Br}-\text{Br}_2$ exchange may be expected to be derived from the activation energies of the primary steps by the relation $E_{\text{over-all}} = E_2 + \frac{1}{2}(E_1 - E_4)$. Substituting the average experi-

TABLE VI. Photo-chemical exchange of Br₂ with CCl₃Br in CCl₄ solution.⁹ [CCl₃Br]=0.47 m/l.

	[Br ₂], mole/l ×10 ³	T, °C	% of Equilib. exchange	Quanta abs sec. ⁻¹ cc. ⁻¹ ×10 ⁻¹⁴	Quantum yield	Activation energy, kcal. mole ⁻¹
1a	0.335	28	25	4.37	0.63	5.1
1b	0.335	50	42	3.74	1.27	
2a	0.370	28	8.6	3.90	0.26	9.7
2b	0.370	50	20.5	3.71	0.68	

mental value of 29.2 kcal. mole⁻¹ for $E_{\text{over-all}}$; 45.2 kcal. for E_1 , the heat of dissociation of Br₂; and 0 for E_4 , the activation energy of combination of bromine atoms, gives a value of 7 kcal. mole⁻¹ for E_2 . This appears to be the activation energy for either the reaction $\text{CCl}_3\text{Br} + \text{Br} \rightarrow \text{CCl}_3 + \text{Br}_2$ or $\text{CCl}_3\text{Br} + \text{Br}^* \rightarrow \text{CCl}_3\text{Br}^* + \text{Br}$, whichever accounts for the observed bromine exchange. This result is in agreement with results of Day which gave a value of 5–10 kcal. mole⁻¹ for the activation energy of the photo-chemical exchange based on the data reproduced in Table VI and also with the deductions of Franke and Schumacher¹⁰ from a study of the bromine-sensitized photo-oxidation of CCl₃Br. Determinations 1a and 1b of Table VI were made on two cells filled from the same reaction mixture, and 2a and 2b on two filled from another reaction mixture. In both cases considerable care was taken to have the system free from oxygen, moisture and other impurities.

The difference in the quantum yields of the two sets of experiments and the variation in the temperature coefficient may mean that this reaction, like the photo-chemical exchange of Br₂ with CBr₄^{2e}, is very sensitive to impurities. If so, the mechanisms of the photo-chemical and thermal exchange reaction are different, or possibly oxygen-bromine complexes which use up bromine atoms at the temperature of the photo-chemical studies are unstable at the temperatures of the thermal studies. Further experiments should be made to clarify this question.

If the activation energy of 7 kcal. mole⁻¹ is correctly ascribed to the elementary reaction $\text{CCl}_3\text{Br} + \text{Br} \rightarrow \text{CCl}_3 + \text{Br}_2$ it may be concluded that the heat of dissociation of the carbon-

bromine bond in bromotrichloromethane is equal to or less than 52 kcal. mole⁻¹, i.e., the heat of formation of the bromine molecule formed plus this energy of activation.

A calculation of the rate of collisions between Br atoms and CCl₃Br molecules leads to the result that the rate of collisions involving an energy of at least 7 kcal. mole⁻¹ is about 20 times the observed rate of exchange. In this calculation the collision diameter of Br is assumed to be 2.2Å¹¹ and that of CCl₃Br is assumed to be equal to 6.4Å, the diameter of a CCl₄ molecule in the liquid phase,¹² and the bromine atom concentration is determined from K_p ¹³ for the $\text{Br}_2 \rightleftharpoons 2\text{Br}$ equilibrium.

In the work reported in this paper the maximum activity of the radiobromine used in any experiment was about 4×10^{10} disintegrations liter⁻¹ hour⁻¹. If it is assumed as a limiting case that all of the energy of the β -radiations from these disintegrations was absorbed in the reaction mixture and resulted in the cleavage of C—Br bonds in CCl₃Br, it may be estimated that the rate of breaking of C—Br bonds by this means is only 10^{-6} of the observed rate of exchange of Br₂ with CCl₃Br. This indicates that the effect of the beta- (and also the gamma-) radiations on the rate of the exchange can be neglected. This conclusion is in accord with the experimental observation that the rate of the CCl₃Br-Br₂ exchange is independent of the specific activity of the bromine in the 10-fold range (4×10^{10} dis/1 hr.⁻¹ down to 4×10^9 dis/1 hr.⁻¹) covered in these experiments.

SOLVENT EFFECTS

By comparing the data for the thermal and photo-chemical CCl₃Br-Br₂ exchange in the liquid phase it is possible to deduce that only one out of every 400 bromine molecules which absorb a photon in solution produces atoms which escape primary recombination. The steps of reasoning involved are in part similar to those used by Bodenstein and Lütke Meyer¹⁴ in calculating the

¹¹ E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. 32, 907 (1936).

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¹³ A. R. Gordon and Colin Barnes, J. Chem. Phys. 1, 693 (1933).

¹⁴ M. Bodenstein and H. Lütke Meyer, Zeits. f. Physik. Chemie 114, 208 (1924).

¹⁰ W. Franke and H. J. Schumacher, Zeits. f. physik. Chemie B42, 297 (1939).

rate constants for the dissociation of Br_2 molecules and recombination of Br atoms in the gas phase and in part related to problems of determining the primary photo-chemical yield in solution which have been discussed by Dickinson¹⁵ and others.

The conclusion is in agreement with the "cage" hypothesis originally proposed by Franck and Rabinowitch.¹⁶ Attempts to verify the existence of the process of primary recombination and determine its quantitative significance have in general supported the hypothesis but have not been conclusive.¹⁵ Perhaps the most conclusive evidence of the effect of solvent in favoring the combination of atoms and radicals which are formed in the same solvent envelope is furnished by a study of reactions activated by nuclear processes.⁶

The method and assumptions involved in the present discussion are outlined below.

(1) The equilibrium constant for the reaction $\text{Br}_2 \rightleftharpoons 2\text{Br}$ is assumed to be the same in solution as in the gas phase. This assumption is a plausible one, since it is probable that k_2 is the same in the liquid phase as in the gas phase and since it has been observed that the rate constants in gas, solution, and liquid CCl_3Br are approximately the same, implying equal Br atom concentrations at equal Br_2 concentrations.

(2) The collision frequency between Br atoms in solution is assumed to be given by the expression for the rate of collisions in the gas phase: $Z_{\text{Br-Br}} = 2n^2\sigma^2 \cdot (\pi RT/M)^{1/2}$, and this is assumed to be equal to the maximum possible rate of combination of Br atoms.

(3) The thermal equilibrium concentration of Br atoms (at a specified temperature and Br_2 concentration) calculated by $[\text{Br}] = (K_c[\text{Br}_2])^{1/2}$ is employed in (2) to calculate the maximum rate of recombination of Br atoms which must equal the rate of dissociation of Br_2 molecules, that is to say, $k_4[\text{Br}]^2 = k_1[\text{Br}_2]$ where $k_1/k_4 = K_c$.

(4) Assuming that the elementary reaction steps and the corresponding velocity constants, except for the initial step which produces Br atoms, are the same in the photo-chemical and

thermal reactions, we have

$$\frac{R'}{R} = \left(\frac{2\beta Q}{k_1[\text{Br}_2]} \right)^{1/2},$$

where R' and R represent the rates of the photo-chemical and thermal reactions, respectively, at the same temperature and concentrations, Q is the rate of light absorption in the photo-chemical reaction, and β is the fraction of the absorbed quanta which produce dissociation of the bromine molecules without primary recombination within the solvent cage.

The numerical data used in determining the value of β by the method outlined above are as follows. From Table VI, Experiment 1b, $[\text{CCl}_3\text{Br}] = 0.47$ mole/l; $[\text{Br}_2] = 0.00335$ mole/l; $t = 50^\circ\text{C}$; $Q = 0.225$ Einsteins/l hr.⁻¹; $R' = 0.352$ mole/l hr.⁻¹. For the thermal reaction, $k = 7.6 \times 10^{-6}$ (mole/l)⁻¹ hr.⁻¹ at 50°C by extrapolation on Fig. 2, giving $R = 2.1 \times 10^{-7}$ mole/l hr.⁻¹ for the concentrations listed above. At 50°C , $K_c = 9.4 \times 10^{-28}$ mole/l, this value being derived from K_p for the gaseous equilibrium.¹³

The value of β obtained is 0.0025. Subject to the validity of the assumptions and to an uncertainty of a factor of at least 2 in the experimental value of the rate of the photo-chemical reaction, this means that only one bromine molecule in 400 which absorbs photons in CCl_4 solution escapes primary recombination and yields free bromine atoms to the solution. If the number of encounters between bromine atoms in solution is less than in the gas phase the value calculated for β , i.e., the quantum yield for dissociation of Br_2 , would be even lower than 0.0025. Since the observed quantum yield for the exchange of bromine with CCl_3Br is about unity the chain length of the observed photo-chemical reaction must be at least 400 and the quantum yield of the exchange in the gas phase, where negligible primary recombination may be assumed, should be about $(400)^{1/2}$ at 50°C and a light absorption rate of 4×10^{16} quanta sec.⁻¹ cc⁻¹, if the calculated value for β is correct.

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¹⁶ J. Franck and E. Rabinowitch, Trans. Faraday Soc. **30**, 120 (1934).