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The Kinetics of the Forward and Reverse Reactions for the Vapor Phase Thermal Bromination of Chloroform*

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The rates of the forward and reverse reactions for the homogeneous vapor phase thermal bromination of chloroform, $CHCl_3+Br_2=CBrCl_2+HBr(A)$, have been measured in the range 420-455°K and are given by $-d(Br_2)/dt = k_f(CHCl_3)(Br_2)^{\frac{1}{2}} [1 + k_2(HBr)/k_3(Br_2)]^{-1} - k_r(CBrCl_3)(Br_2)^{\frac{1}{2}} [1 + k_3(Br_2)/k_2(HBr)]^{-1};$ where $\log_{10}k_f$ (liter/mole) sec⁻¹ = (-32,030/4.575T) + 11.15, $\log_{10}k_r = (-32,930/4.575T) + 12.70$. The mechanism of the reaction is,

> $M + Br_2 = 2Br + M$ $Cl_{3}CH+Br=Cl_{3}C-+HBr \rightarrow (1) \leftarrow (2)$ $Cl_3C - +Br_2 = CCl_3Br + Br$ \rightarrow (3) \leftarrow (4)

where $\log_{10}k_1 = (-9300/4.575T) + 9.36$, $\log_{10}k_4 = (-10,200/4.575T) + 10.91$, $(k_2/k_3) = 0.040$. The activation energies imply that the CH bond in CHCl₃ is weaker than that in CH₄ by $6+E_2$ kcal and the Cl₃C-Br bond is weaker than the H_3C-B_1 bond by $11+E_2$ kcal, where E_2 , the activation energy of reactions (2) and (3), is estimated to be ≤ 7 kcal.

The directly determined equilibrium constant for (A) agrees well with the kinetic value, $K_e = k_1 k_3 / k_2 k_4$; $\log_{10}K_e = (900/4.575T) - 0.15$. From these data, for CCl₃Br, $\Delta H^{\circ}_{f, 298} = -9.4$ kcal, $S^{\circ}_{298} = 80$ eu S° was calculated as 80 eu from electron diffraction and spectroscopic data.

The equation for k_4 is identical with that obtained in a previous study of the exchange of radioactive bromine between Br2 and CBrCl3, thus proving this free radical mechanism for the exchange reaction.

INTRODUCTION

ILLER and Willard¹ and the authors² have shown that the exchange of bromine between trichlorobromomethane and elementary bromine proceeds by the following mechanism. Bromine atoms formed by the dissociation of Br₂ attack CCl₃Br molecules to give exchange. This attack of bromine atoms could either be a Walden inversion type of reaction, Br*+Cl₃CBr→Br*CCl₃+Br; or it could involve the reaction, $Br+BrCCl_3 \rightarrow Br_2+-CCl_3$ (4) and then the reverse of (4). Evidence for the formation of $-CCl_3$ radicals by (4) was obtained,² in that, in systems containing HBr, Br₂, and CCl₃Br, chloroform was formed, presumably according to the equation,

$$Cl_3C - +HBr \rightarrow Cl_3CH + Br.$$
 (2)

The present quantitative investigation of the rates of the reactions

$$Cl_{3}CH+Br_{2} \rightleftharpoons CCl_{3}Br+HBr$$
 (A)

confirms the proposed mechanism of the exchange reaction (via 4) and provides information about the equilibrium constant for (A) and about the rates of some elementary reactions of bromine atoms and of trichloromethyl radicals.

EXPERIMENTAL

The rates of (A) were determined by measurement of the initial and final amounts of bromine in each reaction system.

Eastman Kodak white label chloroform was washed with concentrated sulfuric acid, dilute sodium hydroxide, and several portions of distilled water.³ After drying in the dark over potassium carbonate it was fractionally distilled in the dark in an all-glass apparatus to give a middle fraction of 300 ml from a total of 700 ml.

^{*} From the Ph.D. thesis by J. H. S., March, 1950; presented at the meeting of the American Chemical Society, Detroit, April, 1950.

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¹ A. A. Miller and J. E. Willard, J. Chem. Phys. 17, 168 (1949). ^{*}N. Davidson and J. H. Sullivan, J. Chem. Phys. 17, 176 (1949).

³ A. Weissberger and E. Proskauer, Organic Solvents (The Clarendon Press, Oxford, 1935), p. 153.

TABLE I. Rate of the uninhibited forward reaction.

	(1)			,	7 / 4 3
(Br2)0	(Br2)((mole/liter)	(CHCla)0	Т	<i>Rf</i> (mole/lite	Rf(AV) er) $r sec^{-1}$
×10 ³	×10 ³	×10 ³	°K	X	105
0.452	0.238	38.4	442.03	20.61	20.76
0.366	0.203	31.15		20.92	
0.746	0.379	32.15	441.81	19.70	19.88
1.752	1.161	30.15		20.85	
1.815	1.211	31.25		20.20	
1.200	0.829	15.39		19.50	
1.087	0.770	13.97		19.23	
2.102	1.653	13.73		19.87	
1.351	0.598	29.00	442.05	20.23	20.09
2.098	1.127	29.12		20.03	
2.082	1.120	28.90		20.08	
2.165	1.151	30.07		20.03	
2.070	1.462	28.65	419.98	2.972	3.015
1.977	1.403	27.40		2.995	
1.448	0.901	30.92		3.040	
1.411	0.882	30.10		3.040	
1.358	0.861	29.00		3.025	
1.994	1.174	27.70	455.06	57.7	57.8
1.425	0.689	30.40		58.2	
1.363	0.672	29.10		58.2	
2.092	1.240	28.60		57.8	
2.028	1.476	17.77		58.4	
2.200	1.285	30.10		57.8	
1.407	0.707	29.63		57.8	
1.471	0.734	30.95		57.3	

Merck reagent grade bromine was dried over phosphorus pentoxide. Hydrogen bromide and trichlorobromomethane were prepared as described previously.²

The reactants, after degassing, were distilled into storage vessels attached to a vacuum line and kept in the dark at the temperature of dry ice. Apiezon grease was used as a stopcock lubricant. To prepare a reaction mixture, chloroform or trichlorobromomethane was distilled through a tube containing potassium hydroxide pellets and phosphorus pentoxide. Portions of the condensate were tested for oxidizing matter with starch iodide solution, and in the case of chloroform, for phosgene with barium hydroxide solution. The tests were always negative. Using a micropipet (50-300 microliters) that had been calibrated to deliver with chloroform, a measured volume of the liquid was then added to a glass tube that could be attached to the vacuum apparatus with a ground joint. The chloroform or trichlorobromomethane was distilled through P₂O₅ and condensed at liquid air temperature in a U-tube with constant pumping, and then distilled in a closed system into the evacuated reaction cell. Bromine was measured as a gas at the vapor pressure of the liquid at 0°C in vessels of known volume. Hydrogen bromide was measured in a system of known volume using a mercury manometer. For each substance, some of the stored material was always pumped out before taking the sample to be used. After the reactants were condensed in the reaction vessel, it was sealed at a pressure of 10⁻⁴-10⁻⁵ mm of mercury while under constant pumping. The cleaning of the reaction vessels (*ca.* 80 ml) and details of the temperature measurements have already been described.²

At the end of a reaction, the vessels were chilled in liquid air and cracked open; the bromine content was measured by addition of excess aqueous potassiuin iodide and titration with standard 0.02N thiosulfate solution. The bromine content of unreacted samples was (to ± 1 percent) that expected from the amount of bromine taken as a gas, and there was no change in the amount of bromine in a sample stored at liquid air temperature for 24 hours.

RESULTS

The rate law for the forward reaction of (A) has been found to be

$$\frac{-d(Br_2)/dt = k_f (CHCl_3)(Br_2)^{\frac{1}{2}}}{\times [1 + k_2 (HBr)/k_3 (Br_2)]^{-1}}.$$
 (R1)

For the reverse reaction, the rate law is

$$\frac{d(\mathrm{Br}_2)/dt = k_r(\mathrm{CCl}_3\mathrm{Br})(\mathrm{Br}_2)^{\frac{1}{2}}}{\times [1 + k_3(\mathrm{Br}_2)/k_2(\mathrm{HBr})]^{-1}}.$$
 (R2)

Equation (R1), for example, shows that the forward reaction is inhibited by hydrogen bromide. The term $[1+k_2(\text{HBr})/k_3(\text{Br}_2)]^{-1}$ and the similar term in (R2) will be referred to as "inhibition terms." The evidence for these expressions is given in the following sections.

(a) The Uninhibited Forward Reaction

For runs in which the initial concentrations of hydrogen bromide and trichlorobromomethane were zero and $(CHCl_3)\gg(Br_2)$, Eq. (R1) has been integrated assuming the concentrations of chloroform, and of bromine and hydrogen bromide in the inhibition term, to be constant at the average values defined by equations like $(CHCl_3)_a$ = [$(CHCl_3)_0$ +($CHCl_3)_t$]/2. Subscripts 0, *t*, and *a* on the reactants refer to initial, final, and average concentrations. The integral of (R1) then is

$$k_{f} = 2 \frac{(\text{Br}_{2})_{a}^{\dagger} - (\text{Br}_{2})_{t}^{\dagger}}{(\text{CHCl}_{3})_{a}t} [1 + k_{2}(\text{HBr})_{a}/k_{3}(\text{Br}_{2})_{a}]. \quad (\text{R3})$$

For these runs, the change in $(CHCl_3)$ was only about two percent; the fractional changes in (HBr) and (Br_2) are of course larger, but since $k_2/k_3=0.040$ (see later) and for all these runs $(HBr)_t/(Br_2)_t<0.5$, the use of average values in the inhibition term produces errors in k_f which are small compared to experimental error.

As shown in Table I, fourfold variations in $(Br_2)_0$ and twofold variations in $(CHCl_3)_0$ have no effect on the calculated values of k_f . The inhibition term was close to 0.98 for all the runs.

(b) The Reverse Reaction

For the measurements of the rate of (A) in the reverse direction, the initial concentrations of hydrogen bromide and of trichlorobromomethane were large compared to

1	4	4
-	T	-

that of bromine. However it was not possible to achieve the condition $[k_3(Br_2)/k_2(HBr)] \ll 1$; it was therefore necessary to evaluate simultaneously k_r and k_2/k_3 from the results of several runs at a fixed temperature. Assuming (CCl_3Br) and (HBr) to be constant at their average values, an integrated form of (R2) is

$$k_{r} = \frac{(2/3)(k_{3}/k_{2})[(\mathrm{Br}_{2})_{i}^{\dagger} - (\mathrm{Br}_{2})_{0}^{\dagger}] + 2(\mathrm{HBr})_{a}[(\mathrm{Br}_{2})_{i}^{\dagger} - (\mathrm{Br}_{2})_{0}^{\dagger}]}{(\mathrm{HBr})_{a}(\mathrm{CCl_{3}Br})_{a}t}.$$
 (R4)

The results are given in Table II. For a series of runs at a given temperature, trial and error numerical methods were used to select that value of k_2/k_3 which gave the most consistent set of values of k_r , that is, which minimized the mean square deviation of the calculated k_r 's from their average value.

(c) The Inhibited Forward Reaction

The constant, k_2/k_3 , can be evaluated from measurements of the inhibition of the forward reaction by hydrogen bromide as well as from the rate of the reverse reaction. First we note that the rate laws (R1) and (R2) are mutually consistent in that they predict an equilibrium constant for reaction (A) of the correct functional form.

$$K_s = \frac{k_f k_3}{k_2 k_r} = \frac{(\text{CCl}_3\text{Br})(\text{HBr})}{(\text{CCl}_3\text{H})(\text{Br}_2)}.$$
 (R5)

For the experiments of this section, there was no added trichlorobromomethane, and the initial concentrations of chloroform and hydrogen bromide were large compared to that of bromine. Because k_r is larger than k_f by a factor of about 10 and because the concentrations of hydrogen bromide were large, the small amounts of trichlorobromomethane ($\sim 1 \times 10^{-3}$ mole/liter) produced by the forward reaction were enough to make the average rate of the reverse reaction about 10 percent of the forward reaction. By using (R5) and the total rate law obtained by combining (R1) and (R2), and by treating (HBr) and (CHCl₃) as constant during the course of the reactions, one obtains

$$\frac{k_{2}}{k_{3}} = \frac{M}{(\mathrm{HBr})_{a}} \left\{ \frac{k_{f}Nt - 2[(\mathrm{Br}_{2})_{0}^{\frac{1}{2}} - (\mathrm{Br}_{2})_{t}^{\frac{1}{2}}]}{M^{\frac{1}{2}}\log\left[\frac{(\mathrm{Br}_{2})_{0}^{\frac{1}{2}} - M^{\frac{1}{2}}}{(\mathrm{Br}_{2})_{0}^{\frac{1}{2}} + M^{\frac{1}{2}}}\right] \left[\frac{(\mathrm{Br}_{2})_{t}^{\frac{1}{2}} + M^{\frac{1}{2}}}{(\mathrm{Br}_{2})_{t}^{\frac{1}{2}} - M^{\frac{1}{2}}}\right] \right]$$
(R6)

where

$$M \equiv (Br_2)_a + K_e (CHCl_3)_a (Br_2)_a / (HBr)_a,$$

$$N \equiv (CHCl_3)_a + (HBr)_a / K_e.$$

This relation and values of K_e and k_f from Tables I and II were used to calculate the values of k_2/k_3 given in Table III. In (R6), k_2/k_3 is sensitively dependent on k_f (a one percent error in k_f gives a three percent error in

TABLE II. Rate of the reverse reaction.

(Br ₂) ₀	$(Br_2)_i$	(CBrCl ₃)	0 (HBr)0	T	k, (mole	kr (Av)	k_2/k_3
×10 ³	×10 ³	×10 ³	$\times 10^3$	°K	×10 ⁵	×10 ⁵	000
0.552	2.030	15.06	33.55	420.10	3.64	3.64	0.0408
0.541	2.067	14.75	37.30		3.66		
0.570	3.105	24.30	39.10		3.64		
0.576	1.822	15.72	21.40		3.675		
1.350	3.630	22.79	36.90		3.64		
0.532	1.843	11.48	35.90	442.07	25.50	25.48	0.0403
0.567	2.012	12.25	38.45		25.50		
1 240	3.295	20.90	28.85		25.55		
1.395	3.825	23.50	33.05		25.20		
1.315	3.585	22.13	31.20		25.65		
1 482	4 068	24.90	36.10	455.06	75.6	75.7	0.0392
0 567	3 155	23.50	37.65	100100	75.8		
0.508	2 640	24 78	22 27		75.6		
1 360	2.010	14 42	32.45		75 7		
0.540	1 660	13 00	10 04		76.2		
0.540	3 003	23.68	34.20		75.0		

 k_2/k_3) and insensitively dependent on K_e (a one percent error in K_e gives a 0.2 percent error in k_2/k_3); therefore this determination of k_2/k_3 from the forward reaction is reasonably independent of the determination of k_2/k_3 from the reverse reaction. It is seen that the values of k_2/k_3 obtained in this study of the inhibited forward reaction are in good agreement with those calculated from the reverse reaction.

(d) The Equilibrium Constant, K_e

Table IV summarizes the average values of k_f and k_r ; and of the equilibrium constant, K_e , calculated from (R5) using $k_2/k_3 = 0.040$, independent of temperature.

Гавle III. The ra	tio of k_2/k_3	from the i	nhibited for	rward reaction.
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(Br ₂) ₀	(Br2) <i>t</i> (mole/li	(CHCla) ter) X10 ³	(HBr)₀	°K [™] K	kf (Av) ×10 ^{\$}	k2/k3	k2/k3 (Av)
1.962 2.317 2.265 2.023 2.247	$\begin{array}{r} 1.372 \\ 1.577 \\ 1.550 \\ 1.498 \\ 1.638 \end{array}$	27.23 32.15 31.45 27.80 30.90	14.65 17.34 17.10 24.70 27.45	442.07	20.1	0.0425 0.0435 0.0444 0.0422 0.0416	0.0428
1.252 2.168 2.064 2.041 1.933	0.915 1.566 1.365 1.459 1.395	26.96 30.10 28.67 28.35 26.82	33.35 37.25 19.25 31.20 29.67	419.98	3.015	0.0385 0.0393 0.0394 0.0387 0.0391	0.0390

т	kj (mole,	k_r	
°K	×10 ⁶	×105	K.
420.0	3.015	3.65	2.06
422.07	20.1	25.48	1.97
445.06	57.8	75.7	1.91

TABLE IV. Values of k_f , k_r , and K_e .

TABLE V. Measurement of the equilibrium constant at 442.07°K.

$sec \times 10^{-4}$	(CHCla)	(CBrCla) mole/lite	(HBr) r)×10 ³	0 (Br2)0	(Br2);	K ₀	K:	K.
2.31 2.31 3.858 3.858	30.0 28.8 17.77 18.07	12.06 11.60 7.00 7.12	8.72 7.09 5.97 5.02	1.404 1.350 1.246 1.267	1.478 1.378 1.249 1.203	2.50 2.10 1.89 1.57	2.33 2.06 1.885 1.68	2.05 1.96 1.87 1.89
							Average	1.94

An attempt was made to check the "kinetic" equilibrium constant by a direct measurement of the equilibrium at 442°K. Systems close to equilibrium change their composition very slowly and these studies served only to indicate limits for K_e . A representative selection of the data is given in Table V. The quantities K_0 and K_t are the initial and final values of the function, $K = (HBr)(CBrCl_3)/(Br_2)(CHCl_3).$

It is evident that the K's are tending towards a value close to 1.97, the value of K_e indicated by the kinetic data. (A defect in the experiments is that there was only one case in which K_0 was chosen substantially smaller than 1.97, so that an increase in the K function was observed.) The K_e column in Table V lists values of the equilibrium constant calculated from the change in K(from K_0 to K_t) in time t. To do this, the rate equation was integrated, assuming a constant value for the term $[1+k_2(\text{HBr})/k_3(\text{Br}_2)]$, and K_e evaluated in terms of K_0 , K_t , t, k_f , and k_2/k_3 . The rather complicated expressions used are given elsewhere.* It may be said that the value of K_e obtained by observing small changes in systems close to equilibrium is in satisfactory agreement with the K_e obtained by rate measurements on systems far from equilibrium.

(e) Side Reactions and Surface Effects

Experiments on both the forward and reverse reactions in vessels packed with glass beads with a total surface area of ca. six times that in unpacked vessels established that the rates were independent of the surface area.

It is to be recalled that we previously reported² the formation of CHCl₃, but of no CCl₄, C₂Cl₆, CCl₂Br₂, or other products when a mixture of Br2, HBr, and CCl3Br was heated to 460°K for a time somewhat longer than that used typically in the present measurements. This and the general consistency of the kinetic results indicate that only reaction (A) was of importance for the present study.

(f) Numerical Results

The parameters of the equations

$$\log_{10}k_f$$
 (liter/mole)[†] sec⁻¹

$$=\frac{-32,030(\pm 300)}{4.575T}+11.15(\pm 0.15), \quad (R7)$$

$$\log_{10}k_r = \frac{-32,930(\pm 300)}{4.575T} + 12.70(\pm 0.15) \quad (R8)$$

were determined graphically from plots of $\log k_f$ (Av) and $\log k_r$ (Av) against 1/T. Probable errors r, of k_f (Av) and k_r (Av) at the extreme temperatures, were calculated from the individual value of k_1 and k_2 at these temperatures. The errors in the parameters are those resulting from the assumption of errors of 0.1°C in each of the extreme temperatures and errors of 2r in k_f (Av) and k_r (Av)—the errors taken so as to give a maximum error in the activation energies.

The data in Tables II and III indicate that over the temperature range 420-455°K, $k_2/k_3 = 0.040 \pm 0.002$. The corresponding, kinetically derived equation for the equilibrium constant, K_e , of the reaction (A) is

$$\log_{10} K_e = \frac{900(\pm 600)}{4.575T} - 0.15(\pm 0.30).$$
 (R9)

DISCUSSION

(a) The Thermodynamics of Reaction (A)

Equation (R9) implies that, for (A), $\Delta H^{\circ}_{440^{\circ}}$ $= -0.90(\pm 0.6)$ kcal, and $\Delta S^{\circ}_{440} = -0.70(\pm 1.4)$ eu. From tabulated values of heat capacities, ${}^{4}\Delta C^{\circ}_{p, 298^{\circ}}$ = 3.23. Assuming this as an average value of ΔC_p over the temperature range 298°-440°, $\Delta H^{\circ}_{298^{\circ}} = -1.4$ kcal, $\Delta S^{\circ}_{298} = -2.0$ eu. For the hitherto unreported quantities, the heat of formation and entropy of trichlorobromomethane one calculates, $\Delta H^{\circ}_{f, 298^{\circ}} = -9.4$ kcal, and $S^{\circ}_{298} = 80.1(\pm 1.4)$ eu. Comparison of various thermochemical compilations^{4, 5} suggests that an uncertainty in the heat of formation of chloroform (taken as -24.0 in the above calculations) as well as the uncertainty of ΔH for (A) contributes to the uncertainty for the heat of formation of CCl₃Br. Using the molecular structure given by Pfeiffer⁶ from electron diffraction measurements (C-Cl=1.76A, C-Br=1.91A,

⁴Selected Values of Chemical Thermodynamic Properties (Natl. Bur. of Standards, Washington, D. C.):

Br2 and Br, Series I, Table 11-1, June 30, 1948; Series III,

June 30, 1948.

June 30, 1948. HBr, Series I, Table 11–2, June 30, 1948. CHCl₃, Series I, Table 23–7, June 30, 1949. CCl₄, Series I, Table 23-7, June 30, 1949. CCl₄Br, Series I, Table 23-10, March 31, 1948. Cl, Series I, Table 10-1, June 30, 1948. H, Series I, Table 8-1, June 30, 1947.

⁵ F. R. Bichowsky and F. D. Rossini, The Thermochemistry of the Chemical Substances (Rheinhold Publishing Corporation, New York, 1936), p. 241.

⁶ H. G. Pfeiffer, Ph.D. thesis, California Institute of Technology, 1948

 $\angle Cl - C - Br = 110^{\circ}$), and the vibrational frequency assignment made by Simanouti⁷ (A_1 , 710, 418, 243 cm⁻¹; E, 765, 289, 187 cm⁻¹), one computes for the entropy of CCl₃Br, $S_{ROT} = 27.1$, $S_{VIB} = 10.9$, and $S^{\circ}_{298^{\circ}} = 79.8$ eu. The vibrational entropy was calculated using the harmonic oscillator approximation. The agreement with the measured entropy is excellent.

(b) The Mechanism of the Reaction

A mechanism for reaction (A) that is consistent with the rate laws is similar to the one proposed by Braunwarth and Schumacher⁸ for the photo-bromination of chloroform.

$$Br_2 + M \rightarrow 2Br + M,$$
 (d)

$$2Br + M \rightarrow Br_2 + M, \qquad (r_1)$$

$$Cl_{3}CH+Br\rightarrow Cl_{3}C-+HBr,$$
 (1)

$$l_3C - + HBr \rightarrow Cl_3CH + Br,$$
 (2)

$$Cl_3C - +Br_2 \rightarrow Cl_3CBr + Br,$$
 (3)

$$Cl_{3}CBr+Br\rightarrow Cl_{3}C-+Br_{2}.$$
 (4)

Apart from (4) which is the elementary reaction responsible for the reversal of (A), the mechanism is like that involved in the bromination of hydrogen or methane. So long as (r_1) is the only important chain terminating reaction, the equilibrium concentration of bromine atoms is maintained,

С

$$(\mathrm{Br}) = \left[K_c(\mathrm{Br}_2) \right]^{\frac{1}{2}} \tag{R10}$$

where $K_c(=k_d/k_{r_1})$ is the equilibrium constant, in concentration units, for the dissociation of bromine.

The rate laws derived from this mechanism are (R1) and (R2), and the rate constants for the elementary reactions (1) and (4) are given by $k_1 = k_f K_c^{-\frac{1}{2}}$ and $k_4 = k_r K_c^{-1}$. In a small temperature range around 440°K, $K_c = (RT)^{-1}K$

$$= (RT)^{-1} \exp[(\Delta S - R)/R] \exp(-\Delta E/RT).$$

Using the thermodynamic data for bromine,⁴ one obtains

$$\log_{10}k_1 (\text{liter/mole sec}) = \frac{-9300(\pm 300)}{4.575T} + 9.36, (R11)$$

$$\log_{10}k_4 = \frac{-10,200(\pm 300)}{4.575T} + 10.91.$$
(R12)

As previously remarked,³ the frequency factor for (4) $(8.1 \times 10^{10} \text{ liter/mole sec})$ is of the order of magnitude of the collision number. The ratio of the frequency factors of (4) and (1) is 35. The ratio of the frequency factors of (3) and (2) is 25. In general the frequency factor for a reaction in which a radical picks off a

bromine atom from a molecule will be greater than the frequency factor for removal of a hydrogen atom because of the greater dimensions of the activated complex in the former case.

Reactions (3) and (4) provide a mechanism for the exchange of labelled bromine between trichlorobromomethane and bromine. The equations (R8) and (R12) are, within experimental error, identical with the corresponding results, obtained by us,² for the exchange rate constants, thus demonstrating that reactions (3) and (4) are indeed the path for the exchange.

Braunwarth and Schumacher, on the basis of their study⁸ of the photo-bromination of chloroform at 110° to 130° , report that the activation energy for (1) is 10 kcal and that $k_2/k_3 = 0.14$, independent of temperature. The value of the activation energy for (1) agrees with the result obtained by us, but the values of k_2/k_3 are not in good agreement. Activation energies for both (4) and (3)were assigned as 6 kcal on the basis of a study of the bromine sensitized photo-chemical oxidation of trichlorobromomethane. We have already pointed out² that these assignments imply the implausible value of ΔH for (A) of 4 kcal.

(c) Activation Energies and Bond Strengths

If we let the positive number E_2 be the activation energy for reactions (2) and (3),⁹ then at 440°, $\Delta H(1)$ = 9.3 – E_2 , and $\Delta H(4) = 10.2 - E_2$ kcal. The difference in ΔC_p 's for (1) and (4) is taken as 3.2 cal mole deg⁻¹, but the individual values are not known. Purely for the sake of numerical consistency with the thermochemical calculations of Sec. (a), we revise these ΔH 's slightly and take at 298°, $\Delta H^{\circ}(1) = 9.0 - E_2$, and $\Delta H^{\circ}(4) = 10.4 - E_2$ kcal. The heat of formation of the $-CCl_3$ radical is then $20.4 - E_2$. Then:

$$CCl_{3}H \rightarrow -CCl_{3}+H, \quad \Delta H = 96.5-E_{2}, \\ CCl_{3}Br \rightarrow -CCl_{3}+Br, \quad \Delta H = 56.5-E_{2}, \\ CCl_{4} \rightarrow -CCl_{3}+Cl, \quad \Delta H = 74.9-E_{2}. \end{cases}$$

It is indicated in the next section that probably $E_2 < 7$ kcal. For comparison, these values and the values of some bond dissociation energies, D(RY) (that is, ΔH_{298} for the reaction, $RY \rightarrow R+Y$), as compiled by Roberts and Skinner¹⁰ are exhibited in Table VI.

It is seen that the Cl₃C-Br bond is at least 11 kcal weaker than the H_3C-Br bond, that the Cl_3C-H bond is at least 6 kcal weaker than the H_3C-H bond, and that the Cl₃C-Cl bond is at least 6 kcal weaker than H_3C-Cl bond. The situation is just the reverse for the comparison of the t-Bu-radical with the $-CH_3$

⁷ T. Simanouti, J. Chem. Phys. **17**, 245 (1949). ⁸ V. V. Braunwarth and H. J. Schumacher, Kolloid Z. **89**, 184 (1939).

⁹ From the relation $k_2/k_3=0.040\pm0.002$ over the temperature range 420° to 455°, it follows that $E_2-E_3=0\pm1$ kcal. It may be recalled that, for the corresponding reactions of the methyl radical, Kistiakowsky and Van Artsdalen (reference 12) give $\dot{E}_2 - E_3 = 2$ kcal, and for the corresponding hydrogen atom reactions, $E_2 - E_3 = 0.06$ kcal, and $E_2 = 1.0$ kcal [M. Bodenstein and S. C. Lind, Z. physik. Chem. **119**, 123 (1926); M. Bodenstein and G. Jung., *ibid*.

 <sup>121, 127 (1926)].
 &</sup>lt;sup>10</sup> J. S. Roberts and H. A. Skinner, Trans Faraday Soc. 45, 339 (1949).

TABLE VI. D(R-Y) values (kcal).

radical; in this case there is a marked weakening of the C-H bond and a less marked weakening of the C-Br bond.

One would expect that by introducing free radicals into a mixture of isobutane and trichlorobromomethane one could initiate the chain reaction,

$$Cl_{3}C - +t - BuH \rightarrow Cl_{3}CH + t - Bu -,$$

$$t - Bu - + BrCCl_{3} \rightarrow t - BuBr + - CCl_{3},$$

in which each step is exothermic, resulting in an exchange of hydrogen and bromine between the two radicals. West and Schmerling¹¹ have observed the corresponding exchange of chlorine and hydrogen atoms between carbontetrachloride and various hydrocarbons.

It should be noted that many of the comparisons of bond strengths that can be made using Table VI or an extension thereof are dependent on the rather uncertain values of the heats of formation of the organic halides. The comparison of the Cl_3C-H and H_3C-H bond strengths is not subject to this difficulty but is essentially a comparison of the energy of activation of (1) with the activation energy for the corresponding reaction

$$CH_4+Br\rightarrow H_3C-+HBr.^{12}$$

(d) The Activation Energies of Reactions (2) and (3)

It is of interest to investigate what information about the rates of reactions (2) and (3) or about E_2 , the activation energy for both of these reactions, is given by the present research. For simplicity, consider the uninhibited forward reaction

$$Br_2 + M \rightarrow 2Br + M$$
, (d)

$$Cl_{3}CH+Br\rightarrow Cl_{3}C-+HBr,$$
 (1)

$$Cl_3C - +Br_2 \rightarrow Cl_3CBr + Br$$
 (3)

¹¹ J. P. West and L. Schmerling, J. Am. Chem. Soc. 72, 3525 (1950).
 ¹² G. B. Kistiakowsky and E. R. Van Artsdalen, J. Chem. Phys.

12, 474 (1944).

and the conceivable chain terminating reactions

$$2Br+M\rightarrow Br_2+M,$$
 (r₁)

$$Cl_3C - +Br + M(?) \rightarrow Cl_3CBr + M,$$
 (r₂)

$$\operatorname{Cl}_{3}C - + \operatorname{Cl}_{3}C - + M(?) \rightarrow C_{2}\operatorname{Cl}_{6} + M.$$
 (r₃)

Rabinowitch and Wood have measured the rates of (r_1) .¹³ From their data we estimate that for M = chloroform, $k_{r_1} = 1.5 \times 10^{10}$ (liter²/mole² sec) at room temperature. (The quantity k_{r_1} is one-half the rate constant of Rabinowitch and Wood.) Knowing the equilibrium constant for the dissociation of bromine, one can then calculate $k_d = K_c k_{r_1}$. Assuming¹⁴ that k_{r_1} is independent of temperature, k_d (liter/mole sec)=7×10¹³ × exp(-45,300/RT).

The rate of homogeneous dissociation of bromine at 440° when $(Br_2) = 0.001$ mole/liter and $(M) = (CHCl_3)$ =0.03 is calculated to be 6×10^{-14} mole/liter sec. The rate of formation of CCl₃Br according to Table I is 2×10^{-8} mole/liter sec. There is probably also some heterogeneous dissociation of bromine molecules, but the above calculation strongly suggests that every bromine atom created by (d) initiates a large number of cycles of the chain reactions (1) and (3) before one of the radical recombinations (r) occurs. Under these conditions of long chain length, if (r_2) or (r_3) were the important chain terminating reactions, the rate equation would be $d(\text{CCl}_{3}\text{Br})/dt = (k_{1}k_{3}k_{d}/k_{r_{2}})^{\frac{1}{2}}(\text{Cl}_{3}\text{CH})^{\frac{1}{2}}(\text{Br}_{2})$ $k_3(k_d/k_{r_2})^{\frac{1}{2}}(\mathrm{Br}_2)^{\frac{3}{2}}$ respectively (assuming that or $M = CHCl_3$, rather than (R1).

Since these equations do not fit the facts, (r_2) and (r_3) are not important and (r_1) is. However, it is probable that k_{r_2} and k_{r_3} are as large as k_{r_1} ; or, if these reactions are not subject to three body restrictions, effectively larger. Therefore the steady-state concentration of trichloromethyl radicals must be less than the steady-state concentration of bromine atoms; otherwise (r_2) or (r_3) would contribute to the kinetics. When the chain length is large, $(Cl_3C-)/(Br)=k_1(Cl_3CH)/k_3(Br_2)$. We suppose that this ratio, $(Cl_3C-)/(Br), \leq 0.1$. Then using the typical conditions, $(Br_2)=0.001$, $(Cl_3CH)=0.03$, $k_3/k_1\geq 300$. However, as noted previously, the frequency factor for (3) may well be *ca*. 30 times the frequency factor for (1). Therefore, $\exp(E_1-E_2/RT)\geq 10$; $E_2\leq 7$ kcal.

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¹³ E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. 32, 907 (1936).

¹⁴O. K. Rice, J. Chem. Phys. 9, 258 (1941), has pointed out the possibility of this calculation and interpreted the high value of the frequency factor for this bimolecular reaction.