PART I

THE KINETICS OF THE VAPOR PHASE EXCHANGE OF RADIOACTIVE BROMINE BETWEEN TRICHLOROBROMOMETHANE AND BROMINE

PART II

THE KINETICS OF THE FORWARD AND REVERSE REACTIONS OF THE VAPOR PHASE THERMAL BROMINATION OF CHLOROFORM

PART III

A METHOD OF ESTIMATING AND MINIMIZING THE ERROR OF MEASUREMENT OF THE RATE OF A RADIOACTIVE EXCHANGE REACTION

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To

S. Norman Sullivan

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To my wife special thanks are due for preparing the figures and typing the thesis.

ABSTRACT

The rate of the homogeneous vapor phase thermal radioactive exchange reaction

$$CBrCl_3 + Br_2^* \longrightarrow \text{exchange}$$

and the rates of the forward and reverse reactions of the homogeneous vapor phase thermal bromination of chloroform

$$CHCl_3 + Br_2 \rightleftharpoons CBrCl_3 + HBr \qquad (A)$$

have been measured in the temperature range 420-455° K.

For the bromination reaction a mechanism which is consistent with all the experimental data is

$$Br_2 \rightleftharpoons 2Br \qquad (\overrightarrow{d}) \quad (\overleftarrow{5})$$

$$Br + CHCl_3 \rightleftharpoons \cdot CCl_3 + HBr \qquad (1) \quad (2)$$

$$\cdot CCl_3 + Br_2 \rightleftharpoons CBrCl_3 + Br . \qquad (3) \quad (4)$$

The rate determining steps are (1) and (4). The rate of the exchange reaction is given by $k_0(CBrCl_3)(Br)$ and the equation for the rate determining constant $k_0 = k_0(T)$ is identical to that for k_4 as a function of temperature. The exchange reaction takes place, therefore, by the reaction sequence (d), (4), and (3).

The activation energies of (1) and (4) imply that the CH bond in $CHCl_3$ is weaker than that in CH_4 by at least 6.6 kcal. and the CBr bond in $CBrCl_3$ is weaker than that in CH_3Br by at least 11 kcal. The equilibrium constant $K \equiv (CBrCl_3)(HBr)/(CHCl_3)(Br_2)$ is 1.96 at 442° K; the heat of reaction (A) is $-0.9(\pm 0.65)$ kcal.

In a single exploratory experiment, it was observed that the exchange reaction between bromine and trifluorobromomethane is much slower than that between bromine and trichlorobromomethane.

A method of estimating and minimizing the error of measurement of the rate of a radioactive exchange reaction is given.

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PART I

THE KINETICS OF THE VAPOR PHASE EXCHANGE OF RADIOACTIVE BROMINE BETWEEN (1) TRICHLOROBROMOMETHANE AND BROMINE AND (2) TRIFLUOROBROMOMETHANE AND BROMINE

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The Kinetics of the Vapor Phase Exchange of Radioactive Bromine between Trichlorobromomethane and Bromine

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(Received July 30, 1948)

The rate of exchange of radioactive bromine between trichlorobromomethane and bromine in the vapor phase in the temperature range 420–455°K has been determined. The rate is equal to $k[Br_2]^{\frac{1}{2}}[CCl_3Br]$, where $\log_{10}k(\text{moles/liter})^{-\frac{1}{2}}(\text{sec.})^{-1} = (-33{,}100(\pm 400))/(4.574T) + 12.75(\pm 0.20)$. The energy of activation for the elementary reaction between bromine atoms and trichlorobromomethane molecules is 10.3 kcal., and the frequency factor is 7.9×10^{10}. It is proposed that the reaction proceeds via the sequence: $Br^* + BrCCl_3 \rightarrow BrBr^* + -CCl_3$, and $Cl_3C- + Br_2^* \rightarrow Cl_3CBr^* + Br^*$, rather than by a Walden inversion mechanism. The observation that chloroform is formed when hydrogen bromide, bromine, and trichlorobromomethane are heated is cited as evidence for the presence of $-CCl_3$ radicals and for the reaction $Cl_3C- + HBr \rightarrow Cl_3CH + Br$. The $-CCl_3$ radical is then more stable than the $-CH_3$ radical by 10 kcal. or more.

The vapor pressures of liquid trichlorobromomethane are given by the equation: $\log_{10}p(\text{mm}) = (-8240/4.574T) + 7.64$. The exchange reaction $Br_2(g) + AgBr^* \rightarrow Br_2^*(g) + AgBr$ readily goes to completion and is the basis for a convenient semi-micro method for the preparation of radioactive elementary bromine.

INTRODUCTION

THE investigation of the kinetics and mechanism of the exchange of radioactivity between atoms and molecules may be expected to contribute to an understanding of free radical reactions in general in much the same ways that the study of exchange reactions between ions and molecules in solution has contributed to the theory of ionic displacement reactions in organic chemistry.[1]

Wilson and Dickinson[2] observed a photochemically induced exchange between bromine and trichlorobromomethane in carbon tetrachloride solution at 76°C, suggesting that the exchange reaction is between bromine atoms and trichlorobromomethane molecules. In order to avoid the complications in the interpretation of photo-chemical reactions because of non-uniform intensity of light along the light path and because of uncertainties as to the rate of recombination of bromine atoms, we have chosen to investigate the thermal vapor phase exchange between bromine and trichlorobromomethane.[3]

Hodges and Miceli[4] have very briefly reported that the exchange between bromine and carbon tetrabromide in the gas or liquid phase proceeds by a bromine atom mechanism, and that the activation energy for the elementary reaction is 0–3 kcal.

EXPERIMENTAL

(a) Preparation of Materials

The trichlorobromomethane was prepared by the reaction of carbon tetrachloride and aluminum bromide.[5] A sample boiling at 104.2°C at 745 mm was obtained by fractional distillation in an all-glass apparatus.

The vapor tensions of the substance were measured using a mercury manometer in a glass vacuum apparatus. These values, $p(0°) = 11\pm 1$ mm, $p(22°) = 35\pm 1$ mm, $p(24°) = 38\pm 1$ mm, in conjunction with the boiling point at atmospheric pressure, imply the vapor pressure equation, $\log_{10}p(\text{mm}) = (-8240)/(4.574T) + 7.64$, and a Trouton constant of 21.8. The measured density of 1.99 g/ml at 25°C agrees with the literature values.

Hydrogen bromide was prepared by the reaction of hydrogen and bromine over a heated

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* Contribution No. 1232 from the Gates and Crellin Laboratories of Chemistry.

[1] L. P. Hammett, *Physical Organic Chemistry*, (McGraw-Hill Book Company, Inc., New York, 1940), p. 164.

[2] J. N. Wilson and R. G. Dickinson, J. Am. Chem. Soc. **61**, 3519 (1939).

[3] Just at the conclusion of our experimental work we learned that Professor J. Willard and Mr. A. Miller of the University of Wisconsin were independently engaged in a study of the same problem. J. Chem. Phys. **17**, 168 (1949).

[4] J. H. Hodges and A. S. Miceli, J. Chem. Phys. **9**, 725 (1941).

[5] H. G. Vesper and G. K. Rollefson, J. Am. Chem. Soc. **56**, 1456 (1934).

platinum filament, and purified by repeated bulb to bulb distillation in vacuum.

The radioactive isotope used was the 34.5-hr. Br^{82}. It was prepared by irradiation of 12 liters of ethylene dibromide with neutrons from a 250-mc radon-beryllium source, extracted with 400 ml of water containing 20 mg of sodium bromide, and precipitated as silver bromide, which was washed and dried. Radioactive molecular bromine was obtained by the reaction: $AgBr^* + Br_2 \rightarrow AgBr + Br_2^*$. A quantity of 100–200 microliters of reagent grade bromine was distilled in vacuum into a Y-shaped vessel of *ca.* 50-ml volume containing the silver bromide. The tube was sealed off and heated to 160°C for several hours with occasional shaking. The radioactive bromine was then condensed in one arm of the tube. Under these conditions, there was 100 percent exchange of activity. Kolthoff and O'Brien[6] report 60 percent exchange between bromine vapor and freshly precipitated silver bromide at room temperature. This method of isolation on the semi-micro scale of radioactive bromine was selected and developed because of its convenience and because it was believed to be a method that was unlikely to introduce impurities, particularly the oxygen bearing impurities that are often troublesome in free radical chemistry.

(b) Procedure for the Exchange Reactions

Aliquots of Br_2^* (15–75 microliters) and trichlorobromomethane (100–300 microliters) were mixed in a test tube that could be attached to a vacuum apparatus by a ground joint. The mixture was distilled in vacuum through P_2O_5 and condensed in liquid air with constant pumping, and then distilled into an evacuated reaction vessel of known volume. The reaction vessels had been treated with hot sulfuric acid-dichromate solution, rinsed with hot water, treated with boiling nitric acid, rinsed four times with boiling, distilled water, and outgassed by flaming in vacuum. The volumes (*ca.* 80 ml) of the reaction vessels were determined by observing the weights of water required to fill them to the seal-off constriction.

The exchange reactions took place in the dark in an oil bath, the temperature being constant to ±0.07°C. Temperatures were measured with a Chromel-Alumel thermocouple and a Leeds and Northrup portable precision potentiometer with a precision of ±0.05°C. The thermocouple was calibrated against standard thermometers to an accuracy of 0.5°C.

In order to avoid possible photo-chemical exchange, reaction mixtures were stored in liquid air when not being handled. An experiment showed that there was no exchange in unheated reaction mixtures.

(c) Radio-Assay Procedure

After reaction, the bromine was extracted from the trichlorobromomethane with sodium nitrite solution. Mercurous bromide was precipitated from aliquots of the solution which contained an amount of bromide equivalent to 15 microliters of bromine. Reproducible counting samples were obtained by suction filtration of the precipitate through disks of S. and S. No. 576 filter paper mounted on a sintered glass plate. The area on which the smooth mercurous bromide mats were formed was defined with a glass tube pressed against the filter paper. In cases where analyses were run on two aliquots of the same solution, the results agreed within the statistical counting error, usually about 1 percent. The activity of the bromine before exchange was determined in the same way from solutions obtained by reducing measured volumes of the liquid radioactive bromine with sodium nitrite. That the transfer of bromine into the reaction vessels by distillation was quantitative was shown by radioactive assay of a reaction mixture which had not been heated.

(d) Chemical Analyses of Reaction Mixtures

For the semi-quantitative chemical analyses of the reaction products reported in the discussion, the components of reaction mixtures were separated and identified using a small glass column and the general type of vacuum techniques described by Stock[7] and Burg.[8]

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[6] I. M. Kolthoff and A. S. O'Brien, J. Chem. Phys. **7**, 401 (1939).

[7] A. Stock, *Hydrides of Boron and Silicon* (Cornell University Press, Ithaca, 1933).

[8] A. B. Burg, J. Am. Chem. Soc. **56**, 499 (1934).

TABLE I. Exchange reaction between Br_2 and CCl_3Br.

Expt.	$2[Br_2]$ (moles/liter) $\times 10^3$	$[CCl_3Br]$ (moles/liter) $\times 10^3$	t sec. $\times 10^{-3}$	T °K	$\frac{x}{c}$	k(expt.) (moles/liter)$^{-\frac{1}{2}}$ sec.$^{-1}$ $\times 10^5$	k(calc.) (moles/liter)$^{-\frac{1}{2}}$ sec.$^{-1}$ $\times 10^5$
1 a	6.77	33.45	194.3	419.10	0.282	2.98 ± .04	2.97
b	6.38	31.60			0.286	3.00 ± .04	
c	11.90	35.35			0.383	2.92 ± .08	
d	11.57	34.30			0.382	2.99 ± .08	
2 a	7.71	35.65	36.0	432.00	0.427	9.18 ± .14	9.63
b	6.55	11.30			0.730	10.05 ± .29	
3 a	7.30	36.05	36.1	433.80	0.346	11.30 ± .2	11.43
b	12.42	36.85			0.457	11.09 ± .2	
c	11.84	35.20			0.466	11.05 ± .3	
4 a	33.50	33.00	8.95	442.85	0.770	27.1 ±1.3	25.1
b	6.62	32.65			0.548	26.0 ± .6	
c	6.59	32.50			0.534	27.2 ± .6	
d	15.17	26.15			0.720	27.7 ± .8	
5 a	7.00	24.10	8.74	444.25	0.594	32.8 ±1.0	28.2
b	7.61	13.12			0.754	33.8 ±1.5	
6 a	7.38	36.55	17.05	445.07	0.287	31.6 ± .4	30.3
b	6.94	34.25			0.294	31.7 ± .4	
7 a	13.00	38.50	4.14	455.52	0.576	63.5 ±1.4	71.4
b	12.50	25.80			0.685	65.2 ±1.9	
c	10.15	34.95			0.535	70.1 ±1.2	
8 a	6.58	32.50	7.08	455.75	0.312	72.8 ±1.3	72.6
b	6.82	32.70			0.310	73.3 ±1.7	
c	10.37	30.75			0.436	69.5 ±1.3	
d	12.42	36.80			0.408	71.1 ±1.3	

RESULTS AND DISCUSSION

(a) Analysis of the Kinetic Data

An integrated form of the expression for the decrease of the activity of radioactive bromine due to exchange with trichlorobromomethane that is originally inactive is

$$\ln\left[\left(\frac{a}{b}+1\right)\frac{x}{c}-\frac{a}{b}\right]=-R(a,\,b)\frac{a+b}{ab}t.$$

In this relation

a = concentration of elementary bromine, in units of atoms per unit volume,
b = concentration of trichlorobromomethane,
c = initial activity of bromine,
x = activity of bromine after reaction for time t, and
$R(a, b)$ is the rate of exchange.

This result is a consequence of the general analysis due to McKay[9] of the rate of exchange between two components in chemical equilibrium.

We have tested the hypothesis that the exchange is a reaction between bromine atoms in thermal equilibrium with bromine gas and trichlorobromomethane molecules, i.e., $R(a, b)=k\times(a/2)^{\frac{1}{2}}b$. Table I exhibits the analysis of the experiments on this basis. It is evident, particularly from experiments 2, 4, 5, that the rate constant derived in this way is essentially constant for fivefold and threefold variations in the concentrations of bromine and trichlorobromomethane, respectively.

An experiment in a vessel packed with glass beads, in which the surface area was *ca.* 12 times that in an unpacked vessel, established that the rate of reaction was not dependent on surface area; the rate constants of Table I refer to a homogeneous, gas phase reaction.

It was also established that there were no significant side reactions taking place. The following observations bear on this point:

(1) The weight of the mercurous bromide precipitate from a reaction mixture was the same within 2 percent as that from the unreacted bromine, and in agreement with the expected value. Thus, there was no consumption or formation of bromine during the reaction.

(2) A mixture of bromine and trichlorobromomethane at concentrations of 5.1×10^{-3} and 17.5×10^{-3} moles/liter, respectively, in a two-liter bulb was heated to 456°K for a time such that more than 75 percent of the trichlorobromomethane would have undergone exchange. After extraction of the bromine, the organic layer was dried and fractionally distilled in vacuum. The substance was pure trichlorobromomethane with the vapor pressures reported above; there was less than $\frac{1}{2}$ percent CCl_4 or other more volatile products and less than 1 percent of less volatile products (CCl_2Br_2, C_2Cl_6). Distillation of a known mixture showed that less than $\frac{1}{2}$ percent of carbon tetrachloride could be detected by this means.

The variation of k with temperature is described by the equation

$$\log_{10}k=(-33{,}120(\pm400))/(4.574T)+12.75(\pm0.20).$$

The values of the parameters were obtained by a least squares analysis of the data of Table I. For this treatment it was assumed that the temperatures were known with certainty. The standard deviations in k given in the table were obtained from the assumption that the error was due to statistical error of counting by using an analysis of errors in an exchange reaction that will be published separately.[10] The comparison

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[9] H. A. C. McKay, Nature **142**, 997 (1938).

[10] N. Davidson and J. H. Sullivan, to be published.

of calculated and observed rate constants indicates that other sources of error were significant.

(b) The Mechanism of the Reaction

The dependence of the rate of exchange on concentrations implies that the exchange proceeds via the sequence:

$$Br_2^* \rightleftarrows 2Br^* \quad \text{(fast)}, \tag{1}$$

$$Br^* + CCl_3Br \xrightarrow{k_0} \text{exchange}. \tag{2}$$

The bromine atoms liberated in reaction (2) are assumed to come rapidly into radioactive equilibrium with the rest of the elementary bromine. For k_0, the rate constant of the elementary reaction (2), we have $k_0 = kK_c^{-\frac{1}{2}}$, where $K_c = [Br]^2/[Br_2]$ is the equilibrium constant (in concentration units) for the dissociation of bromine.

For reaction (1), $\Delta H_{291°K} = 46{,}110$ cal.,[11] taking $\Delta C_v = 0.6$,[12] $\Delta E_{435°K} = 45{,}620$. In addition, $\Delta S_{298°K} = 25.00$ e.u.,[13] $\Delta S_{435°K} = 26.00$ e.u. For the equilibrium constant of reaction (1) in a small temperature range around 435°K, $K_p = \exp(26.00/R) \times \exp(-(45{,}620 + RT)/(RT))$ and $K_c = K_p/RT = (1/R \times 435°) \exp((26.00 - R)/(R)) \exp(-45{,}620/RT) = (10^{3.69} \times 10^{-(45,620)/(4.574T)})$. Since $k_0 = kK_c^{-\frac{1}{2}}$, $k_0 = 7.9 \times 10^{10(\pm 0.20)} \times 10^{-(10,310(\pm 400))/(4.574T)}$ moles/liter×sec. The activation energy of reaction (2) is 10,310 cal. The frequency factor corresponds to a mean collision diameter of 3.3A. This frequency factor is but slightly larger than the value of *ca.* $3 \cdot 10^{10}$, which holds for several similar reactions of bromine atoms as tabulated by Kistiakowsky and Van Artsdalen.[14]

The possible specific elementary exchange reactions are

$$Br^* + Cl_3CBr \rightarrow Br^*CCl_3 + Br \quad \text{(Walden inversion)}, \tag{2a}$$

$$Br + Br^*CCl_3 \rightarrow Br - Br^* + -CCl_3, \tag{2b1}$$

$$Cl_3C - + Br_2^* \rightarrow Cl_3CBr^* + Br^*. \tag{2b2}$$

Other possible reactions of interest here are

$$Cl_3C - + BrCCl_3 \rightarrow Cl_3CBr + -CCl_3 \quad \text{(no net effect)}, \tag{3}$$

$$Cl_3C - + Cl_3CBr \rightarrow CCl_4 + -CCl_2Br, \tag{4a}$$

$$Cl_2BrC - + Br_2 \rightarrow Cl_2CBr_2 + Br, \tag{4b}$$

$$Cl_3C - + -CCl_3 + M \rightarrow C_2Cl_6 + M, \tag{5}$$

$$Cl_3C - + Cl_3CBr \rightarrow C_2Cl_6 + Br, \tag{6}$$

$$Br + Cl_3CBr \rightarrow BrCl + -CCl_2Br, \tag{7a}$$

$$Cl_2BrC - + Br_2 \rightarrow CCl_2Br_2 + Br. \tag{7b}$$

The observation that there were no significant side reactions implies that reactions (4)–(7) are not of importance for the present research.

The heat of the Walden inversion reaction (2a) is zero, so that it is not impossible for it to have an activation energy of 10 kcals. However, there seem to be no certain examples of the Walden inversion type of reaction in the free radical reactions of organic compounds. There is no evident way of proving or disproving this mechanism except by the examination of all the other possible mechanisms.

The value of the C—H bond strength of methane of 102 kcal. determined by Kistiakowsky and Van Artsdalen (see reference 14, p. 478) implies that for the $-CH_3$ radical, $\Delta H(f)_{291°K} = 32$ kcal.[15] For the reaction of methyl bromide analogous to (2b):

$$Br + BrCH_3 = Br_2 + -CH_3, \quad \Delta H_{291°} = 21 \text{ kcal.}^{15}$$

If the reaction scheme (2b) is responsible for the exchange, the C—Br bond in trichlorobromomethane must be at least 11 kcal. weaker than the C—Br bond of methyl bromide. Nevertheless, the experiment described below strongly supports the hypothesis that the exchange proceeds via this mechanism.

Braunworth and Schumacher[16] have studied the photo-chemical bromination of chloroform. The following reactions were of importance in

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[11] F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

[12] G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), p. 80.

[13] K. K. Kelley, *The Entropies of Inorganic Substances* (1940), Bulletin 434 of the United States Department of the Interior, Bureau of Mines.

[14] G. B. Kistiakowsky and E. R. Van Artsdalen, J. Chem. Phys. **12**, 475 (1944), Table V. (The values of *A* in Table V should be multiplied by $(575)^{\frac{1}{2}}/1000$ to make them comparable to the frequency factor quoted here.)

[15] Using the values for the heats of formation of CH_4, H, Br, Br_2, and CH_3Br given in reference 11.

[16] V. V. Braunworth and H. J. Schumacher, Kolloid Zeits, **89**, 184(1939).

their discussion of the results:

	E_a(k cal.)	ΔH(k cal.)	
$Cl_3CH+Br \rightarrow Cl_3C-+HBr,$	10	4	(8a)
$Cl_3C-+HBr \rightarrow Cl_3CH+Br,$	6		(8b)
$Br+BrCCl_3 \rightarrow Br_2+-CCl_3,$	6		(2b1)
$Cl_3C-+Br_2 \rightarrow Cl_3CBr+Br.$	6	0	(2b2)

Reactions (8a) and (2b2) are the direct sequence for the bromination. Reaction (8b) accounts for the inhibition of the reaction by hydrogen bromide, and reaction (2b1) for the inhibition of the reaction by trichlorobromomethane. The temperature coefficient of the rate of reaction gives the activation energy for reaction (8a). The values for (2b) were obtained from a study of the bromine sensitized photochemical oxidation of trichlorobromomethane.[17] The inhibiting effect of hydrogen bromide corresponded to a rate constant for reaction (8b) of *ca.* $\frac{1}{10}$ that of (2b2); this ratio was independent of temperature, so that the activation energies of the two reactions must be the same. The values of ΔH were obtained as differences of activation energies, they imply that

$$CCl_3H+Br_2 \rightarrow CCl_3Br+HBr \quad \Delta H=4. \quad (9)$$

This conslusion that the bromination of chloroform is endothermic is somewhat surprising. Since the entropy of the reaction is probably quite small, it implies that the equilibrium in the reaction should lie largely to the left. Actually the reaction has been used for the synthesis of trichlorobromomethane in a sealed tube.[18]

The conclusions of Schumacher and Braunworth may not therefore be entirely correct. They contain, however, the interesting suggestion that reaction (8b) takes place at a rate comparable to that of (2b2) and that the formation of chloroform in the presence of hydrogen bromide be used to detect $-CCl_3$ radicals.

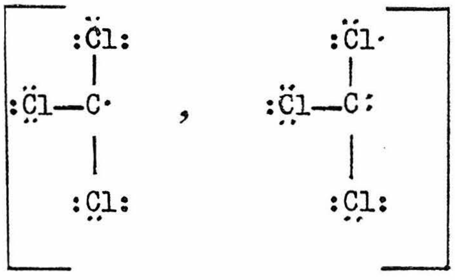

FIG. 1.

In an experiment in a two-liter flask the initial concentrations (in moles/liter) were: $[Br_2]=1.85\times10^{-3}$, $[HBr]=3.80\times10^{-2}$, $[CCl_3Br]=3.37\times10^{-2}$. The mixture was heated to 460°K for a time of about a half-time for the exchange reaction of the trichlorobromomethane with bromine. After extraction of the hydrogen bromide and bromine, the organic layer was examined in a Beckmann infra-red spectrophotometer and by vacuum distillation.

The infra-red study revealed the absorption bonds of chloroform; the optical density of the 3.3μ-CH fundamental corresponded to a mole ratio of chloroform to trichlorobromomethane of 0.10. In the vacuum distillation, the only fractions isolated were chloroform and trichlorobromomethane in a mole ratio of 0.19. The chloroform was identified by its vapor tension; its vapor density corresponded to a molecular weight of 118.4 (th. 119.4).

The observation that the rate of formation of chloroform is comparable to the rate of the exchange reaction strongly suggests that the exchange proceeds via the reaction sequence (2b) involving the $-CCl_3$ radical. We are now engaged in a precise study of the kinetics of the formation of chloroform definitely to settle this point.

It is noteworthy that as part of the recent developments in free radical chain reactions in organic chemistry, $-CCl_3$ radicals, generated either from chloroform or from trichlorobromomethane, have been used as chain carriers.[19, 20] The results of the present research suggest that the carbon bromine bond in trichlorobromomethane is weaker than the carbon bromine bond in methyl bromide. Braunworth and Schumacher's values for the activation energy and heat of reaction (8a) are much smaller than Kistiakowsky and Van Artsdalen's[14] values for

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[17] W. Franke and H. J. Schumacher, Zeits. f. physik. Chemie **B42**, 297 (1939).

[18] E. Paterno, Jahresb. Forts. Chemie **24**, 259 (1871).

[19] M. S. Kharasch, E. V. Jensen, and W. H. Urry, J. Am. Chem. Soc. 69, 1100 (1947).

[20] M. S. Kharasch, O. Reinmuth, and W. H. Urry, J. Am. Chem. Soc. 69, 1105 (1947).

the corresponding reaction of methane, *viz.*,

$$CH_4 + Br = (-CH_3) + HBr, E_A = 17.8, \Delta H = 15.8.$$

There is, therefore, evidence that the carbon hydrogen bond in chloroform is weaker than the carbon hydrogen bond in methane. If it is in general true that the C—X bond in CCl_3X is weaker than the C—X bond in CH_3X, we may say that the $-CCl_3$ radical is relatively more stable than the $-CH_3$ radical. It may be that this is because of either: (a) steric repulsion of the chlorine atoms in Cl_3CX compounds, which is partly relieved in the Cl_3C- radical because the chlorine atoms are further apart; (b) resonance stabilization involving the structures shown in Fig. 1.

This latter type of stabilization will be more important the more readily an electron can be removed from the ligands attached to the carbon. Judging from the present research, the extent of the stabilization of the $-CCl_3$ radical is greater than 10 kcal.

ACKNOWLEDGMENT

We are indebted to Professor R. M. Badger and Mr. S. Burket for their cooperation in the infra-red analysis for chloroform.

VAPOR PHASE EXCHANGE OF RADIOACTIVE BROMINE BETWEEN TRIFLUOROBROMOMETHANE AND BROMINE

One experiment on the vapor phase exchange of radioactive bromine between trifluorobromomethane and bromine indicated that the CBr bond in this compound is much stronger than that in trichlorobromomethane. If the mechanism for the exchange is the same here as for trichlorobromomethane, we have

$$\ln\left[(a/b + 1)(x/c) - a/b\right] = -R(a,b)\left[(a + b)/ab\right]t$$

$$R(a,b) = k'(a/2)^{\frac{1}{2}}b \quad . \qquad \text{(Thesis, page 3)}$$

The data of this experiment using trifluorobromomethane are

$T = 478^{\circ}K$

$(Br_2) = \frac{1}{2}a = 6.0 \times 10^{-3}$ moles/liter

$(CBrF_3) = b = 5.0 \times 10^{-2}$ moles/liter

$t = 7.32 \times 10^{4}$ sec.

$x = 183$ counts/min.

$c = 195$ counts/min.

from which $k' = 2.6 \times 10^{-6}$ (moles/liter)$^{-\frac{1}{2}}$sec.$^{-1}$. For comparison the value of the rate constant k at 478°K for the exchange of radioactive bromine between trichlorobromomethane and bromine can be calculated from

$$k = 10^{12.75} \times 10^{-(33{,}120/4.574T)} \qquad \text{(Thesis, page 3)}$$

$$= 4.16 \times 10^{-3} \text{ (moles/liter)}^{-\frac{1}{2}}\text{sec.}^{-1} \quad . \qquad (\text{at } 478^{\circ}K)$$

If the frequency factors for the two reactions

$$CBrCl_3 + Br \xrightarrow{k_0} -CCl_3 + Br_2 \qquad E = 10.3 \text{ kcal.}$$
$$CBrF_3 + Br \xrightarrow{k_0'} -CF_3 + Br_2 \qquad E'$$

are equal, we have

$$k_0/k_0' = k/k' = 10^{(E'-E)/(4.574T)}$$
$$E' = 17.3 \text{ kcal.}$$

Because the experimental value of $x/c = 0.94$ is very close to unity, it is important to examine the precision with which x/c was measured and to appreciate the affect of an error in x/c on E'. The deviation of x/c from unity may have been due to chance alone - to the random fluctuations which occur in counting rates as a result of the statistical nature of radioactive decay. The probable error r in x/c, assumed to be due only to statistical error of counting and determined from the probable errors in the counting rates x and c, is 0.015. From the normal curve of error the probability of an error larger than $3r$ occurringin a statistical population of errors is 0.043. For x/c, $3r = 0.045$. Therefore with a probability of (1 - .043), the values of x/c and E' are

$$(0.94 - 0.045) < x/c < (0.94 + 0.045)$$
$$16 \text{ kcal.} < E' < 19 \text{ kcal.}$$

There is a small probability, 0.007, that the random fluctuations of counting produced an error larger than $4r = 0.06$ in x/c; the "true" experimental value of x/c may have been $x/c = 1$, which gives a lower limit of $k' = 0$ and does not allow any upper limit of E' to be calculated.

PART II

THE KINETICS OF THE FORWARD AND REVERSE REACTIONS OF THE HOMOGENEOUS VAPOR PHASE THERMAL BROMINATION OF CHLOROFORM

INTRODUCTION

The determination of the kinetics of the forward and reverse reactions of the vapor phase thermal bromination of chloroform

$$CHCl_3 + Br_2 \rightleftharpoons CBrCl_3 + HBr \qquad (A)$$

was undertaken a) to furnish an experimental proof of a proposed mechanism for the vapor phase exchange of radioactive bromine between trichlorobromomethane and bromine, and b) to redetermine values of activation energies obtained by Braunwarth and Schumacher(1) in a study of the kinetics of the photobromination of chloroform, and by Franke and Schumacher(2) in a study of the bromine sensitized photochemical oxidation of chloroform.

The exchange of radioactive bromine between trichlorobromomethane and bromine has been shown to proceed via the rate determining step(3),(4)

$$Br^* + CBrCl_3 \longrightarrow \text{exchange} . \qquad (B)$$

From the exchange experiments no decision could be made as to whether the exchange took place by a one step Walden inversion or by a free radical mechanism such as

$$Br + CBr^*Cl_3 \longrightarrow -CCl_3 + Br_2^* \qquad (4)$$

$$Br_2^* + -CCl_3 \longrightarrow CBrCl_3 + Br^* . \qquad (3)$$

The kinetics of reaction (A) show that the reaction in the reverse direction, <u>ie.</u> the reaction of hydrogen bromide with trichlorobromomethane, takes place <u>via</u> the sequence

$$Br + CBrCl_3 \longrightarrow -CCl_3 + Br_2 \qquad (C)$$

$$HBr + -CCl_3 \longrightarrow CHCl_3 + Br$$

In this paper the rate constants for (B) and (C) are shown to be equal and to be the same functions of the temperature. The radioactive exchange reaction must therefore take place by the free radical mechanism, reactions (4) and (3).

Activation energies reported by Braunwarth and Schumacher(1) and by Franke and Schumacher (2) give an endothermic heat of reaction for the bromination of chloroform and are at variance with the values reported here and in a previous paper(5). The activation energies determined here indicate the bromination of chloroform to be exothermic, in agreement with the observation of Schwab and Lober(6) that the equilibrium constant

$$K \equiv (HBr)(CBrCl_3)/(Br_2)(CHCl_3)$$

decreases with increased temperature. The kinetics of the thermal bromination of chloroform is satisfactorily explained by a mechanism proposed by Braunwarth and Schumacher for the photobromination.

EXPERIMENTAL

a) General experimental method

The rate constants were determined from the direct measurements of the initial and final amounts of bromine in each reaction system. One reaction system or run gave one datum, to be used in calculating the value of a rate constant.

b) Preparation of materials

The chloroform was prepared by washing Eastman Kodak white label chloroform with concentrated sulfuric acid, then dilute sodium hydroxide followed by several portions of distilled water(7).

The chloroform was dried in the dark over potassium carbonate. Fractional distillation in the dark in an all glass apparatus gave a middle fraction of about 300 ml. from a total of 700 ml.

The bromine used was Merck reagent grade, dried over phosphorus pentoxide. The hydrogen bromide and trichlorobromomethane were prepared and purified as described in a previous paper(4). All four reactants were stored in vacuum line storage bulbs kept at the temperature of acetone dry ice mixtures.

c) Procedure for the reactions

The reactants were dried, degassed, and distilled into reaction vessels in the vacuum system shown in Figure 1. In filling the reaction vessels an aliquot of either chloroform or trichlorobromomethane was distilled through a tube containing solid potassium hydroxide and phosphorus pentoxide into the tube A. A portion of this aliquot was tested for chlorine in the case of trichlorobromomethane or chlorine and phosgene in the chloroform. These tests, using starch iodide solution and barium hydroxide solution were always negative. From A, using micropipets, (50-300 microliters) calibrated to deliver chloroform, an aliquot was pipetted into the glass tube B which was attached to the vacuum line with a ground glass joint. The liquid was degassed and dried by vacuum distillation through the P_2O_5 tube and condensation in the liquid-air trap C during constant pumping.

With the bromine storage bulb at 0° C bromine vapor was allowed to fill the volume D at room temperature at the vapor tension of liquid bromine at 0° C. The vapor was degassed by distillation into the trap C during constant pumping. The bromine and halogenated methane mixture was then distilled from C into the reaction vessel of known volume. Initial concentrations of bromine in the reaction vessels were determined by filling blanks before and after filling the reaction vessels and titrating the bromine in these using a starch iodide solution and standard thiosulfate solution.

Amounts of hydrogen bromide distilled from the hydrogen bromide storage bulb were measured in the known volume E with the gas at room temperature and at a pressure measured on the constant volume mercury manometer. After distillation of the hydrogen bromide onto the bromine-halogenated methane mixtures in the reaction vessels, the vessels were sealed off at a pressure of about 10^{-4} to 10^{-5} mm. of mercury while under constant pumping.

The density of chloroform is given as a function of temperature in the International Critical Tables. The density of trichlorobromomethane is given at 15°C; densities at other temperatures were calculated assuming the density to vary with temperature as does that of carbon tetrachloride(8). Delivery volumes of the micropipets were assumed to be the same for chloroform and trichlorobromomethane. The volume E was determined by a Boyle's law comparison to a bulb, (ca. 120 ml.), the volume of which was determined by weighing the bulb filled with water on an analytical balance. In the Boyle's law comparison carbon dioxide was used as the gas and pressures were measured on the constant volume manometer. The reaction vessels had been treated with hot sulfuric acid-dichromate solution, rinsed with water, treated with boiling nitric acid, rinsed four times with hot water and outgassed by flaming in a vacuum. The volumes (ca. 80 ml.) of the reaction vessels were determined by observing the weights of water required to fill them to the seal-off constriction.

The reactions took place in the dark in an oil bath, the temperature being constant to ±0.07° C. Temperatures were measured with a Chromel-Alumel thermocouple and a Leeds and Northrup portable precision potentiometer with a precision of ±0.05° C. The thermocouple was calibrated against standard thermometers to an accuracy of 0.5° C. In order to avoid possible photochemical reactions, reaction mixtures were stored in liquid air when not being handled.

At the end of a reaction the reaction vessels were chilled in liquid air, cracked open, and the reaction mixture titrated for bromine using potassium iodide and standard 0.02 N thiosulfate solution. A comparison of the bromine content of a blank titrated immediately after distillation to that in a reaction mixture kept at liquid air temperature for 24 hours showed no reaction in the reaction mixture.

ANALYSIS OF THE KINETIC DATA

a) The rate of the forward reaction in the absence of added hydrogen bromide and trichlorobromomethane

The rate of the forward reaction

$$Br_2 + CHCl_3 \longrightarrow CBrCl_3 + HBr$$

has been found to be proportional to the chloroform concentration and to the square root of the bromine concentration; the reaction is inhibited by hydrogen bromide and the rate is satisfactorily described by the equation

$$-d(Br_2)/dt = k_f(CHCl_3)(Br_2)^{\frac{1}{2}} \frac{1}{1 + k_2(HBr)/k_3(Br_2)} \quad . \qquad (1)$$

For runs using reaction systems in which the initial concentrations of hydrogen bromide and trichlorobromomethane were zero and $(CHCl_3) \gg (Br_2)$ this equation has been integrated assuming the concentrations of chloroform, and of bromine and hydrogen bromide in the inhibition term, to be constant during the run at the average values defined below.

$$k_f = 2 \frac{(Br_2)_o^{\frac{1}{2}} - (Br_2)_f^{\frac{1}{2}}}{(CHCl_3)_a t} \left[1 + k_2(HBr)_a/k_3(Br_2)_a\right] \qquad (2)$$

where k_2/k_3 = inhibition constant

$$(CHCl_3)_a = ((CHCl_3)_o + (CHCl_3)_f)/2$$
$$(Br_2)_a = ((Br_2)_o + (Br_2)_f)/2$$
$$(HBr)_a = (HBr)_f/2 \quad .$$

Subscripts o, f, and a on the reactants refer to initial, final, and average concentrations. In these runs the decrease in the chloroform concentration during the run amounted to about only 2% of the initial values; the changes in (HBr) and (Br_2) are significant compared to the initial concentrations, of course, but since $k_2/k_3 = .040$ (see later) and for all these runs $(HBr)_f/(Br_2)_f < 0.50$, the use of average values in the inhibition term produces errors in k_f which are small compared to experimental errors.

That equations (1) and (2) describe the rate may be seen from Table I; variations four-fold in initial bromine concentrations and two-fold in initial chloroform concentrations have no effect on calculated values of k_f. From the dependence of the rate on concentrations the rate determining elementary reaction must be one between trichlorobromomethane and bromine atoms in thermal equilibrium with bromine molecules. The experimental data in these reactions are not sufficiently precise to show the dependence of the rate on the inhibition term, $\left[1 + k_2(HBr)/k_3(Br_2)\right]^{-1}$ which varied but little from 0.98 in all these runs; however, as will be shown later, the rate expression for the forward reaction in the presence of appreciable initial concentrations of hydrogen bromide is strongly dependent upon this term.

Table I

Rate of the Forward Reaction

Run	$(Br_2)_o$	$(CHCl_3)_o$	T	k_f	$\bar{k}_f$
	moles/liter		°K	$(\text{moles/liter})^{-\frac{1}{2}}\text{sec.}^{-1}$	
	$\times 10^3$	$\times 10^3$		$\times 10^6$	$\times 10^6$
1a	0.452	38.4	442.03	20.61	20.76
b	0.366	31.15		20.92	
2a	0.746	32.15	441.81	19.70	20.25
b	1.752	30.15		20.85	
c	1.815	31.25		20.20	
3a	1.200	15.39	441.81	19.50	19.53
b	1.087	13.97		19.23	
c	2.102	13.73		19.87	

Table I (continued)

Run	$(Br_2)_o$	$(CHCl_3)_o$	T	k_f	$\bar{k}_f$
	moles/liter		^oK	(moles/liter)$^{-\frac{1}{2}}$sec.$^{-1}$	
	$\times 10^3$	$\times 10^3$		$\times 10^6$	$\times 10^6$
6a	1.351	29.00	442.05	20.23	20.09
b	2.098	29.12		20.03	
c	2.082	28.90		20.08	
d	2.165	30.07		20.03	
8a	2.070	28.65	419.98	2.972	3.015
b	1.977	27.40		2.995	
c	1.448	30.92		3.040	
d	1.411	30.10		3.040	
e	1.358	29.00		3.025	
11a	1.994	27.70	455.06	57.7	57.8
b	1.425	30.40		58.2	
c	1.363	29.10		58.2	
12a	2.092	28.60	455.06	57.8	
b	2.028	17.77		58.4	
c	2.200	30.10		57.8	
d	1.407	29.63		57.8	
e	1.471	30.95		57.3	

b) The rate of the reverse reaction

The rate of the reverse reaction

$$CBrCl_3 + HBr \longrightarrow CHCl_3 + Br_2$$

is proportional to the trichlorobromomethane concentration, to the square root of the bromine concentration, and to an inhibition term which involves the ratio of the bromine concentration to the hydrogen bromide concentration, <u>viz</u>.

$$d(Br_2)/dt = k_r(CBrCl_3)(Br_2)^{\frac{1}{2}} \frac{1}{1 + k_3(Br_2)/k_2(HBr)} \; . \qquad (3)$$

In all the runs on the reverse reaction the initial concentrations of hydrogen bromide and of trichlorobromomethane were large compared to that of bromine. The concentrations of hydrogen bromide and of trichlorobromomethane were treated as constants in integrating equation (3) since the percentage change in these during any run was small compared to the percentage change in the bromine concentration. The integrated rate equation is then

$$k_r = \frac{(2/3)(k_3/k_2)\left[(Br_2)_f^{3/2} - (Br_2)_o^{3/2}\right] + 2(HBr)_a\left[(Br_2)_f^{\frac{1}{2}} - (Br_2)_o^{\frac{1}{2}}\right]}{(HBr)_a(CBrCl_3)_a t} \qquad (4)$$

where $(HBr)_a = ((HBr)_o + (HBr)_f)/2$

$(CBrCl_3)_a = ((CCl_3Br)_o + (CCl_3Br)_f)/2$.

At a given temperature, five or six runs were made (Table II). Using the data from these runs equation (4), containing the two unknowns k_r and k_2/k_3, was solved by the trial and error substitution of likely values of k_2/k_3. Five or six individual values of k_r (one for each run) and an average value $\overline{k_r}$ were calculated for each trial value of k_2/k_3. That value of k_2/k_3 which gave a minimum sum of the squared deviations of the individual values of k_r from their average value $\overline{k_r}$ was taken to be the correct one. The values of k_r and k_2/k_3 as determined in this way from equation (4) and given in Table II are constant for two-fold variations in bromine, hydrogen bromide, and trichlorobromomethane initial concentrations. The rate determining step is again a reaction of bromine atoms in thermal equilibrium with bromine molecules, in this case with trichlorobromomethane molecules. The value of k_2/k_3 used in calculating k_f in Table I was taken from Table II.

Table II

Rate of the Reverse Reaction

Run	$(Br_2)_0$ moles/liter x10^3	$(CBrCl_3)_0$ moles/liter x10^3	$(HBr)_0$ moles/liter x10^3	T °K	k_r $(moles/l.)^{-\frac{1}{2}}sec.^{-1}$ x10^5	$\overline{k}_r$ $(moles/l.)^{-\frac{1}{2}}sec.^{-1}$ x10^5	k_2/k_3
5a	0.532	11.48	35.90	442.07	25.50	25.48	.0403
b	0.567	12.25	38.45		25.50		
c	1.240	20.90	28.85		25.55		
d	1.395	23.50	33.05		25.20		
e	1.315	22.13	31.20		25.65		
9a	0.552	15.06	33.55	420.10	3.64	3.65	.0408
b	0.541	14.75	37.30		3.66		
c	0.570	24.30	39.10		3.64		
d	0.576	15.72	21.40		3.675		
e	1.350	22.79	36.90		3.64		
13a	1.482	24.90	36.10	455.06	75.6	75.7	.0392
b	0.567	23.50	37.65		75.8		
c	0.598	24.78	22.27		75.6		
14a	1.360	14.42	32.45		75.7		
b	0.540	13.99	19.94		76.2		
c	0.587	23.68	34.20		75.0		

c) Determination of the ratio, k_2/k_3, from the inhibition of the forward reaction by added hydrogen bromide.

Several runs were made with the forward reaction strongly inhibited by high concentrations of hydrogen bromide. The initial concentration of trichlorobromomethane and the initial rate of the reverse reaction in these runs were zero; however, because k_r is larger than k_f by a factor of about 10 and because the concentrations of hydrogen bromide were high in all these runs, the small amounts of trichlorobromomethane ($\sim 1 \times 10^{-3}$ moles/liter) produced by the forward reaction were enough to make the average rate of the reverse reaction about 10% of that of the forward reaction. With the rate of the reverse reaction now comparable to the rate of the forward reaction, the rate expression is

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

$$-k_r(CBrCl_3)(Br_2)^{\frac{1}{2}} \frac{1}{1 + k_3(Br_2)/k_2(HBr)} \; . \qquad (5)$$

By rearranging, the rate can be expressed as a function of k_f, k_2/k_3, and the ratio k_fk_3/k_rk_2,

$$-d(Br_2)/dt = \frac{k_f}{1 + k_2(HBr)/k_3(Br_2)} \Big[(CHCl_3)(Br_2)^{\frac{1}{2}} - (HBr)(CBrCl_3)/(Br_2)^{\frac{1}{2}}(k_fk_3/k_rk_2) \Big] . \qquad (6)$$

As shown later the ratio k_fk_3/k_rk_2 is the equilibrium constant of reaction (A) for a proposed mechanism that satisfies the kinetics,

$$(HBr)(CBrCl_3)/(Br_2)(CHCl_3) \equiv K = k_fk_3/k_rk_2 \; . \qquad (7)$$

Treating the high concentrations (HBr) and ($CHCl_3$) as constants equation (6) can then be integrated to give

$$k_2/k_3 = \frac{M}{(HBr)_a} \left\{ \frac{k_fNt - 2\left[(Br_2)_o^{\frac{1}{2}} - (Br_2)_f^{\frac{1}{2}}\right]}{M^{\frac{1}{2}} \log\left[\frac{(Br_2)_o^{\frac{1}{2}} - M^{\frac{1}{2}}}{(Br_2)_o^{\frac{1}{2}} + M^{\frac{1}{2}}}\right]\left[\frac{(Br_2)_f^{\frac{1}{2}} + M^{\frac{1}{2}}}{(Br_2)_f^{\frac{1}{2}} - M^{\frac{1}{2}}}\right]} - 1 \right\} \qquad (8)$$

where

$$N = \left[(CHCl_3)_aK/(HBr)_a + 1\right](HBr)_a/K$$

$$M = \left[K(CHCl_3)_a/(HBr)_a + 1\right](Br_2)_a \; .$$

The equilibrium constant K, given in Table III, has been calculated by substituting values of $\tilde{k}_f$ from Table I and values of $\bar{k}_r$ and k_2/k_3 from Table II into equation (7).

Table III

The Equilibrium Constant from the Ratio of Rate Constants

T °K	$\bar{k}_f$ (moles/l.)$^{-\frac{1}{2}}$sec.$^{-1}$ x10^6	$\bar{k}_r$ x10^5	k_2/k_3	K
420.0	3.015	3.65	.0408	2.01
442.07	20.1	25.48	.0403	1.96
455.06	57.8	75.7	.0392	1.95

Using these values of K, and the values of $\bar{k}_f$ determined from the forward reaction, equation (8) was used to calculate the values of k_2/k_3 given in Table IV. This calculation of k_2/k_3 is not an example of "begging the question". In equation (8) k_2/k_3 is sensitively dependent on k_f (a 1% error in k_f gives a 3% error in k_2/k_3) and insensitively dependent on K (a 1% error in K gives a 0.2% error in k_2/k_3).

Table IV

The Ratio k_2/k_3 from the Inhibited Forward Reaction

Run	$(Br_2)_o$	$(CHCl_3)_o$ (moles/liter)x10^3	$(HBr)_o$	T °K	$\bar{k}_f$ x10^6	k_2/k_3	$\overline{k_2/k_3}$
4a	2.175	28.25	18.85	441.68	19.87	.0356	.0334
b	2.105	27.50	9.63			.0276	
c	2.176	28.45	9.92			.0370	
7a	1.962	27.23	14.65	442.07	20.1	.0425	.0428
b	2.317	32.15	17.34			.0435	
c	2.265	31.45	17.10			.0444	
d	2.023	27.80	24.70			.0422	
e	2.247	30.90	27.45			.0416	
10a	1.252	26.96	33.35	419.98	3.015	.0385	.0390
b	2.168	30.10	37.25			.0393	
c	2.064	28.67	19.25			.0394	
d	2.041	28.35	31.20			.0387	
e	1.933	26.82	29.67			.0391	

The low values of k_2/k_3 of Run 4 are a result of poor experimental technique rather than of insufficient correspondence between the equations describing the kinetics and the actual kinetics of the reactions. In Runs 1 - 4 bromine-halogenated methane mixtures were pipetted into the tube B and then distilled; the uncertainty in the bromine concentrations in these runs is much larger than that in later runs in which the method of filling reaction vessels described under "Experimental" was used.

The values of k_2/k_3 as calculated from the inhibited forward reaction, Runs 7 and 10, agree within experimental error with those calculated from the reverse reaction (Table II).

d) Side reactions and surface effect.

Two experiments in two-liter bulbs established that there were no significant side reactions. In each experiment fractional distillation after reaction showed less than 1% of the products to be less volatile compounds (CCl_2Br_2, C_2Cl_6). These experiments are described on pages 3 and 5. The agreement of the values of k_2/k_3 determined from the forward (Table IV) with those determined from the reverse reaction (Table II), and the agreement of the directly measured equilibrium constant K (see later) with the value of K calculated from the ratio of the rate constants also indicate that there were no significant side reactions.

Experiments on both the forward and reverse reactions in vessels packed with beads with a total surface area of <u>ca.</u> 6 times that in unpacked vessels established that the rates were independent of the surface area.

DETERMINATION OF THE EQUILIBRIUM CONSTANT

The experimental determination of an equilibrium constant by a chemical analysis of reaction systems usually means the value of the constant is bracketed between two limiting values obtained from reaction systems which approach the equilibrium state from both the forward and the reverse directions. However, the equilibrium constant may also be determined from the net rate of a reaction in either direction if the forward and reverse rates are comparable. For the bromination of chloroform let A and B represent the concentrations of chloroform and trichlorobromomethane in a reaction system

$$\underset{A}{CHCl_3} + Br_2 \rightleftharpoons \underset{B}{CBrCl_3} + HBr \quad .$$

The rate of disappearance of bromine is given by

$$-d(Br_2)/dt = \frac{k_f A(Br_2)^{\frac{1}{2}}}{1 + k_2(HBr)/k_3(Br_2)} - \frac{k_r B(Br_2)^{\frac{1}{2}}}{1 + k_3(Br_2)/k_2(HBr)}$$

$$= \frac{k_f}{1 + k_2(HBr)/k_3(Br_2)} \left\{ A(Br_2)^{\frac{1}{2}} - B(HBr)/K(Br_2)^{\frac{1}{2}} \right\} \quad . \quad (9)$$

If the concentrations of chloroform and trichlorobromomethane, A and B, are large compared to the concentrations of bromine and hydrogen bromide, the percentage change in A and B during reaction is small compared to the percentage change in (Br_2) and (HBr). For such reaction systems the rate equation can be integrated treating A and B as constants. If also the initial concentrations of all the reactants are almost at their equilibrium values, the inhibition term $\left[1 + k_2(HBr)/k_3(Br_2)\right]^{-1}$ may be taken to be constant during a reaction. Using these assumptions the rate equation can be integrated to give

$$t = \frac{2K}{k_f(KA + B)}\left\{(Br_2)_o^{\frac{1}{2}} - (Br_2)_f^{\frac{1}{2}} + 1.15(Br_2)_e^{\frac{1}{2}}\log_{10}\left[\frac{(Br_2)_o^{\frac{1}{2}} - (Br_2)_e^{\frac{1}{2}}}{(Br_2)_o^{\frac{1}{2}} + (Br_2)_e^{\frac{1}{2}}}\right]\left[\frac{(Br_2)_f^{\frac{1}{2}} + (Br_2)_e^{\frac{1}{2}}}{(Br_2)_f^{\frac{1}{2}} - (Br_2)_e^{\frac{1}{2}}}\right]\right\}\left[1 + k_2(HBr)_a/k_3(Br_2)_a\right]$$

where $(Br_2)_e = B\left[(Br_2)_o + (HBr)_o\right]/\left[KA + B\right]$

or, in order to simplify calculations

$$t = \frac{2Kv^{\frac{1}{2}}}{k_f(KA + B)}\left\{(Br_2)_o^{\frac{1}{2}} - (Br_2)_f^{\frac{1}{2}} + 1.15(Br_2)_e^{\frac{1}{2}}\log_{10}\left[\frac{(Br_2)_o^{\frac{1}{2}} - (Br_2)_e^{\frac{1}{2}}}{(Br_2)_o^{\frac{1}{2}} + (Br_2)_e^{\frac{1}{2}}}\right]\left[\frac{(Br_2)_f^{\frac{1}{2}} + (Br_2)_e^{\frac{1}{2}}}{(Br_2)_f^{\frac{1}{2}} - (Br_2)_e^{\frac{1}{2}}}\right]\right\}\left[1 + k_2(HBr)_a/k_3(Br_2)_a\right]. \quad (10)$$

Here the reactants are now given not in concentrations but in moles and v is the volume of the reaction vessel in liters. The subscripts o, f, e, and a on the reactants indicate initial, final, equilibrium, and average values. The equilibrium constant, K, is in this equation an implicit function of the experimentally determinable quantities, t, k_f, k_2/k_3, and the concentrations of the reactants.

Reaction systems were prepared in which the concentrations of the reactants fulfilled the conditions under which the differential rate equation (9) was integrated. After reaction times of 6 - 10 hours these were analyzed for bromine. The values of K given in Table V were calculated from equation (10) by trial and error - by substituting likely values of K until the equation was satisfied. The time, t, is a sensitive function of K; a change of 1 part in 200 in K produces a change in t of 10 minutes in 385 (Run 1), and a change of 50 minutes in 640 (Run 2). In Table V a comparison of the value of $K_f \equiv (HBr)_f(CBrCl_3)_f/(Br_2)_f(CHCl_3)_f$ for each run with the values of K and $K_o \equiv (HBr)_o(CBrCl_3)_o/(Br_2)_o(CHCl_3)_o$ for the same run shows that the concentrations of the reactants changed very little from their initial values over a 6 - 10 hour reaction time; the systems were, therefore, close to their equilibrium states.

The average value of K in Table V is 1.95 which agrees well with the value calculated from the ratio of rate constants, K = 1.96 at 442.07°K (Table III).

Table V

Measurement of the Equilibrium Constant at One Temperature

$T = 442.07^{\circ}K$

$\bar{k}_f = 20.1 \times 10^{-6}$

Run	v	$CHCl_3$	$CBrCl_3$	$(HBr)_o$	$(Br_2)_o$	$(Br_2)_f$	K_o	K_f	K
	liters	millimoles							
15a	.0753	2.257	.908	.657	.1057	.1113	2.50	2.33	2.05
b	.0754	2.257	.908	.657	.1057	.1128	2.50	2.29	1.97
c	.0767	2.257	.908	.552	.1057	.1072	2.10	2.07	1.99
d	.0783	2.257	.908	.555	.1057	.1079	2.10	2.06	1.96
e	.0781	2.257	.908	.596	.1057	.1097	2.27	2.15	1.98
16a	.0847	1.505	.593	.506	.1055	.1058	1.89	1.885	1.87
b	.0832	1.505	.593	.521	.1055	.1063	1.95	1.93	1.89
c	.0868	1.505	.593	.541	.1055	.1066	2.02	1.99	1.95
d	.0841	1.505	.593	.561	.1055	.1085	2.10	2.02	1.89
e	.0833	1.505	.593	.418	.1055	.1002	1.57	1.68	1.89

TEMPERATURE DEPENDENCE OF RATE CONSTANTS

The variations of k_f and k_r with temperature are described by the equations

$$\log_{10}k_f = -\frac{32{,}030(\pm 300)}{4.574T} + 11.15(\pm 0.15)$$

$$\log_{10}k_r = -\frac{32{,}930(\pm 300)}{4.574T} + 12.70(\pm 0.15) \quad .$$

The parameters in these equations were determined graphically by plotting $\overline{k}_f$ and $\overline{k}_r$ against 1/T on an extended scale. Probable errors, r, of $\overline{k}_f$ and $\overline{k}_r$ at the extremal temperatures were calculated from the individual values of k_f and k_r at these temperatures. The errors in the parameters are those resulting from the assumption of errors of 0.1°C in each of the extremal temperatures and errors of 2r in $\overline{k}_f$ and $\overline{k}_r$ - these errors taken as to give a maximum error in the activation energies.

The temperature dependence of the inhibition constant, k_2/k_3, is too small to be determined from the precision of the results. The trends shown in Tables II and IV are in opposite directions. The data in the tables indicates that over the temperature range 420-455°C $k_2/k_3 = .040 \pm .002$.

MECHANISM OF THE REACTION

A mechanism for reaction (A), consistent with the dependence of the forward and reverse rates on concentrations, is one similar to that proposed by Braunwarth and Schumacher(1) for the photobromination of chloroform.

$$\mathrm{M} + \mathrm{Br_2} \longrightarrow 2\mathrm{Br} + \mathrm{M} \qquad (d)$$

$$\mathrm{Br} + \mathrm{CHCl_3} \longrightarrow \mathrm{HBr} + {-\mathrm{CCl_3}} \qquad (1)$$

$$\mathrm{HBr} + {-\mathrm{CCl_3}} \longrightarrow \mathrm{CHCl_3} + \mathrm{Br} \qquad (2)$$

$$\mathrm{Br_2} + {-\mathrm{CCl_3}} \longrightarrow \mathrm{CBrCl_3} + \mathrm{Br} \qquad (3)$$

$$\mathrm{Br} + \mathrm{CBrCl_3} \longrightarrow \mathrm{Br_2} + {-\mathrm{CCl_3}} \qquad (4)$$

$$\mathrm{M} + 2\mathrm{Br} \longrightarrow \mathrm{Br_2} + \mathrm{M} \qquad (5)$$

Reaction (2) accounts for the inhibition of the forward reaction by hydrogen bromide; reaction (3) shows the reverse reaction to be inhibited by bromine. The inhibition terms $(1 + k_2(\mathrm{HBr})/k_3(\mathrm{Br_2}))^{-1}$ and $(1 + k_3(\mathrm{Br_2})/k_2(\mathrm{HBr}))^{-1}$ are the fractions of $-\mathrm{CCl_3}$ radicals which are reacting at any time to give trichlorobromomethane and chloroform respectively. Application of the method of stationary states to this mechanism results in the general rate equation (5) which is in agreement with all the experimental data;

$$-d(\mathrm{Br_2})/dt = k_1(\mathrm{CHCl_3})(\mathrm{Br})\,\frac{1}{1 + k_2(\mathrm{HBr})/k_3(\mathrm{Br_2})} - k_4(\mathrm{CBrCl_3})(\mathrm{Br})\,\frac{1}{1 + k_3(\mathrm{Br_2})/k_2(\mathrm{HBr})} \qquad (5)$$

where the rate constants for the elementary reactions are

$$k_1 = k_f\,K_c^{-\frac{1}{2}}$$

$$k_4 = k_r\,K_c^{-\frac{1}{2}}$$

and $K_c = k_d/k_5 = (\mathrm{Br})^2/(\mathrm{Br_2})$.

Setting the rate equal to zero in equation (5) yields
$K \equiv (\mathrm{HBr})(\mathrm{CBrCl_3})/(\mathrm{Br_2})(\mathrm{CHCl_3}) = k_1k_3/k_2k_4$.

For reaction (d) $\Delta H_{291^oK} = 46{,}110$ cal;(9) taking $\Delta C_v = 0.6$,(10) $\Delta E_{435^oK} = 45{,}620$. In addition, $\Delta S_{298^oK} = 25.00$ e.u.,(11) $\Delta S_{435^oK} = 26.00$ e.u. For the equilibrium constant of reaction (d) in a small temperature range around 435°K,

$$K_p = e^{26.00/R}\, e^{-(45{,}620 + RT)/RT}$$

$$K_c = K_p/RT$$

$$= (1/435R)e^{(26.00-R)/R}\, e^{-45{,}620/RT}$$

$$= 10^{3.69}\, 10^{-45{,}620/RT} .$$

Since $k_1 = k_f K_c^{-\frac{1}{2}}$ and $k_4 = k_r K_c^{-\frac{1}{2}}$,

$$k_1 = 10^{9.31(\pm 0.15)}\, 10^{-(9{,}220(\pm 300))/4.574T}$$

and $$k_4 = 10^{10.86(\pm 0.15)}\, 10^{-(10{,}120(\pm 300))/4.574T} .$$

The activation energies of reactions (1) and (4) are

$$E_1 = 9{,}220(\pm 300) \text{ kcal.}$$

$$E_4 = 10{,}120(\pm 300) \text{ kcal.}$$

The frequency factor of reaction (1) is smaller by a factor of 10 than those tabulated by Kistiakowsky and Van Artsdalen (12) for similar reactions of bromine atoms with methane and methyl bromide. Corresponding to the frequency factors given, the mean collision diameters, s, calculated from

$$k = s^2 \left[8\pi kT(m_1 + m_2)/m_1 m_2 \right]^{\frac{1}{2}} e^{-E/RT}$$

are $s_1 = 0.5$Å, $s_4 = 3.1$Å . A plausible explanation of the low frequency factor for (1) is a steric hindrance effect caused by the large chlorine atoms on chloroform; unfortunately, frequency factors or collision diameters for any similar reaction

$$CHY_3 + X \longrightarrow -CY_3 + HX \qquad \text{(Y, X are halogens)}$$

are not recorded in the literature for comparison.

The equation for k_4 as a function of temperature is identical within experimental error to that determined for k_0 and T in the exchange of radioactive bromine between bromine and trichlorobromomethane (page 4),

$$Br^* + CBrCl_3 \longrightarrow \text{exchange}$$

$$\log_{10}k_0 = -10{,}310(\pm 400)/4.574T + 10.9(\pm 0.20) \ .$$

Reaction (4) is therefore the rate determining step in the radioactive exchange reaction which must take place _via_ the sequence (d), (4), and (3).

DISCUSSION

Kistiakowsky and Van Artsdalen$^{(12)}$ have determined the CH bond strength in methane to be 102 kcal. This implies that for the $-CH_3$ radical $\Delta H(f)_{291^oK} = 32$ kcal.$^{(13)}$ For reactions of methane and methyl bromide analogous to reactions (1) and (4):

	E(act.)	ΔH_{291^oK}
$Br + CH_4 \longrightarrow -CH_3 + HBr$	17.8	15.8 kcal.
$Br + CH_3Br \longrightarrow -CH_3 + Br_2$		21 kcal.

The activation energies for the elementary reactions

$$Br + CHCl_3 \longrightarrow HBr + -CCl_3 \qquad E_1 = 9.2 \text{ kcal.}$$

$$Br + CBrCl_3 \longrightarrow Br_2 + -CCl_3 \qquad E_4 = 10.1 \text{ kcal.}$$

indicate therefore that the CH bond in $CHCl_3$ is weaker than the CH bond in CH_4 by at least 6.6 kcal. and that the CBr bond in

$CBrCl_3$ is weaker than the CBr bond in CH_3Br by at least 11 kcal.

These results are in disagreement with those reported by Braunwarth and Schumacher$^{(1)}$ from a study of the photochemical bromination of chloroform.

	E(act.) kcal.	ΔH kcal.	
$Br + CHCl_3 \longrightarrow HBr + {-CCl_3}$	10	4	(1)
$HBr + {-CCl_3} \longrightarrow CHCl_3 + Br$	6		(2)
$Br_2 + {-CCl_3} \longrightarrow CBrCl_3 + Br$	6	0	(3)
$Br + CBrCl_3 \longrightarrow Br_2 + {-CCl_3}$	6		(4)

The activation energies for (3) and (4) were obtained by these authors from the kinetics of the bromine sensitized photochemical oxidation of trichlorobromomethane.$^{(2)}$ In the bromination of chloroform the ratio $k_2/k_3 = 0.14$ was independent of temperature, so that the activation energies of (2) and (3) must be equal. The values of ΔH were obtained as differences of activation energies and imply that

$$CHCl_3 + Br_2 \longrightarrow CBrCl_3 + HBr \qquad \Delta H = 4 \text{ kcal.}$$

In this work, the activation energies E_1 and E_4, the temperature independence of k_2/k_3, and the errors in E_1, E_4, and k_2/k_3 give

$$\Delta H = E_1 - E_4$$
$$= -0.9(\pm\ 0.65) \text{ kcal.}$$

where the probable error $0.65 = 10^{-3}(300^2 + 300^2 + 500^2)^{\frac{1}{2}}$. The difference between the results reported here and those of Braunwarth and Schumacher lies mainly in the values of the activation energy for reaction (4). The overall reaction from which E_4 was obtained by Franke and Schumacher$^{(2)}$ is complex and it may be that the mechanism from which E_3 and E_4 were determined is incorrect. Schwab and Lober,(6) in a study of the carbon catalyzed thermal bromination of chloroform have shown the reaction to be exothermic; the equilibrium constant decreases as the temperature is increased.

PHOTOMETRIC DETERMINATION OF THE BROMINATION RATE

An attempt was made to follow the rate of bromination of chloroform photometrically. A thermostated and heavily insulated cylindrical oven, 6" in inner diameter and about 12" long, was constructed. To reduce temperature gradients a variable speed blower circulated air within the oven. Five reaction absorption cells, 1 cm. in diameter and 10 cms. long, were held parallel to the axis of the oven on a rotatable rack. The rack, movable from outside the oven, could be rotated to bring each reaction cell into alignment with optically polished windows in the ends of the oven (Figure 2). Light tight shutters kept the interior of the oven dark except when measurements were taken.

The light source was an AH4 mercury arc lamp; Corning glass filters #5120, #403, and #3484 isolated the 5460Å mercury line (Figure 3), which gave convenient optical densities with the bromine concentrations used. The relative light transmittances in Figure 3 were measured on a Beckmann spectrophotometer using a band width of 1.75Å. A variable slit was used to adjust the intensity of the light beam. Relative (small) light intensities were measured by a photomultiplier tube, the output from which was determined by measuring the potential drop across a .1 megohm wire wound resistor with a student potentiometer. The optical path was completely enclosed and was defined from the slit to the photomultiplier tube housing by diaphragms.

According to Urmston and Badger, (14) "a very appreciable fraction of the bromine molecules excited by light in the visible region of discrete absorption dissociate without collision by other molecules". In order to be free of any complications due to photochemical dissociation of bromine molecules the average concentration of photochemically produced bromine atoms had to be negligible compared to the concentration of bromine atoms in thermal equilibrium with bromine molecules.

Based on the results of Rabinowitch and Lehman(15) on the rate of recombination of bromine atoms, a calculation of the permissible upper limit of the light intensity indicated that it would be necessary to use a sensitive photomultiplier tube to measure light intensities. Using an RCA 929 PMT, a light beam through the reaction cell could generate a current output of about 10 - 50 times the PMT dark current without appreciably distrubing the <u>average</u> bromine atom concentration — if the pressure within the cell were about one atmosphere. Although the Br concentration might increase by one-fifth its value during a measurement of the optical density of the reaction system, a calculation showed the recombination rate to be high enough to bring the concentration down to within one or two percent of the thermal value within a few minutes. Since the measurement of an optical density took only a minute, the time average value of the bromine atom concentration over a period of an hour could be confined to within one or two percent of the thermal value if but a few measurements were taken on the cell.

Rabinowitch and Lehman showed that bromine atoms combine only on ternary collisions; the rate of recombination is proportional to the total pressure. To work with pressures appreciably lower than one atmosphere in the reaction cells appreared to be experimentally unfeasible. With a pressure of one-tenth atmosphere the half life of the bromine atoms would be greater by a factor of 10; in order to keep the bromine atom concentration near the thermal equilibrium value the light beam intensity would have to be reduced to a value near the limiting sensitivity of the photomultiplier tube.

Preliminary measurements on the apparatus indicated that the precision of the results which would be obtained in determining rate constants and activation energies of the order of 30 kcal. would be smaller than that desirable. The temperature difference between any two reaction cells in the furnace was about 1°C and variable. The resulting uncertainty in determining an over-all activation energy of about 30 kcal. would be about 1.5 kcal.; in the activation energy of interest here, a difference of two large values, $E \sim (33-23)$ kcal., this would be an undesirably large percentage error.

To be independent of slow changes with time in the mercury arc intensity or phototube sensitivity, relative light intensities were measured. The output from the PMT for a reaction cell in the light path was compared to that obtained with nothing in the light path immediately before and after the cell measurement. The optical densities of the cell windows were known and optical densities of reaction mixtures could be determined in this way with a precision of about one percent, but with difficulty.

The current output of a photomultiplier tube is strongly dependent on the position of the light beam on the photosensitive cathode. Although this position-sensitivity was considerably reduced by placing tracing paper light-diffusing screens in front of both the AH4 lamp and the PMT, the variations of the PMT output produced by the mercury arc wavering in its quartz envelope made the measurement of even relative intensities difficult. Because of fluctuations in the position and the intensity of the mercury arc only average values of optical densities were precise to one percent, these obtained by averaging three or four measurements taken over a tedious ten minute period. Each separate measurement of an optical density — blank, reaction cell, blank — took three minutes. A 6 volt tungsten filament lamp powered by a storage battery gave a beam of constant intensity, but a band width which would allow Beer's law to be used could not be isolated by filters (Figure 3).

Because of the temperature gradients in the oven and the fluctuations in the mercury arc this method of following the reaction was discarded in favor of the less elegant but more accurate method described under "Experimental".

APPENDIX

DETERMINATION OF THE CHAIN BREAKING STEP BY THE METHOD OF STATIONARY STATES

In the chain reaction mechanism

$$Br_2 + M \longrightarrow 2Br + M \qquad (d)$$

$$CHCl_3 + Br \longrightarrow -CCl_3 + HBr \qquad (1)$$

$$-CCl_3 + HBr \longrightarrow CHCl_3 + Br \qquad (2)$$

$$-CCl_3 + Br_2 \longrightarrow CBrCl_3 + Br \qquad (3)$$

$$CBrCl_3 + Br \longrightarrow -CCl_3 + Br_2 \qquad (4)$$

the following reactions are possible chain breaking steps

$$2Br + M \longrightarrow Br_2 + M \qquad (5)$$

$$2\ -CCl_3 + M \longrightarrow C_2Cl_6 + M \qquad (6)$$

$$2\ -CCl_3 \longrightarrow C_2Cl_6 \qquad (7)$$

$$-CCl_3 + Br + M \longrightarrow CBrCl_3 + M \qquad (8)$$

Each of these chain breaking steps when combined with the chain forming mechanism, (d) through (4), gives a separate complete reaction mechanism. Four different rate equations for the overall reaction are derived by the application of the method of stationary states to each of these four hypothetical reaction mechanisms (below). Three of these rate equations, based on (6), (7), and (8) as the chain breaking steps. do not agree with the rate equation derived from the experimental data; but that derived by the method of stationary states assuming (5) as the chain breaking step <u>is</u> the experimental rate equation on page 19.

Because the numbers of vibrational degrees of freedom in hexachloroethane and trichlorobromomethane are larger than that in bromine, the free radical recombination rate constants k_6 and k_8 should be larger than k_5; the recombination reaction of $-CCl_3$ radicals may actually be the fast bimolecular reaction (7). However, the rates of (6), (7), and (8) must be small compared to that of the dominant chain breaking step (5), since only (5) gives a rate equation consistent with the experimental data. The stationary state concentration of $-CCl_3$ radicals must, therefore, be small compared to the stationary state concentration of bromine atoms.

I. If the reaction mechanism is

$$\begin{array}{lllllll}
 & & & & & \rightarrow & \leftarrow \\
Br_2 & + M & \longrightarrow & 2Br & + M & (d) & \\
CHCl_3 & + Br & \rightleftarrows & -CCl_3 & + HBr & (1) & (2) \\
-CCl_3 & + Br_2 & \rightleftarrows & CBrCl_3 & + Br & (3) & (4) \\
2Br & + M & \longrightarrow & Br_2 & + M & (5) &
\end{array}$$

then (letting $R \equiv -CCl_3$) the stationary state concentration of bromine atoms is given by

$$d(Br)/dt = 0 = 2k_d(Br_2)(M) - 2k_5(Br)^2(M) - k_1(RH)(Br)$$
$$- k_4(RBr)(Br) + k_2(R)(HBr) + k_3(R)(Br_2) .$$

Let the last four terms = A. Then,

$$d(Br)/dt = 0 = 2k_d(Br_2)(M) - 2k_5(Br)^2(M) + A$$

$$d(R)/dt = 0 = -A$$

from which $(Br) = \sqrt{K_c(Br_2)}$

$$(R) = (Br)\,\frac{k_1(RH) + k_4(RBr)}{k_2(HBr) + k_3(Br_2)} .$$

The rate in the forward direction is

$$-d(Br_2)/dt = k_3(Br_2)(R) - k_4(RBr)(Br)$$

$$= k_3(Br_2)(Br)\,\frac{k_1(RH) + k_4(RBr)}{k_2(HBr) + k_3(Br_2)} - k_4(Br)(RBr)\ .$$

After substitution of $(Br) = \sqrt{K_c(Br_2)}$ and a rearrangement of terms,

$$-d(Br_2)/dt = \frac{k_1K_c^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}(RH)}{1 + k_2(HBr)/k_3(Br_2)} - \frac{k_4K_c^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}(RBr)}{1 + k_3(Br_2)/k_2(HBr)}\ .$$

This is the experimental rate equation (5) on page 19 with $k_f = k_1K_c^{\frac{1}{2}}$ and $k_r = k_4K_c^{\frac{1}{2}}$. Therefore the mechanism above is in complete agreement with the experimental data. Reactions (6), (7), and (8) lead to a kinetics very different from that experimentally observed, as shown below. This fact, taken with the assumption that the rate constants for (6) and (8) are at least as large as k_5, indicates that reaction (5) is the dominant chain breaking step only because the stationary state concentration of $\cdot CCl_3$ radicals is lower than that of the bromine atoms.

The chain lengths for both the forward and reverse reactions can be calculated. For the forward reaction,

$$\text{chain length} \equiv \frac{d(RBr)/dt}{d(Br)/dt}$$

$$= \frac{k_1(RH)(Br)}{2k_d(Br_2)(M)}\ \frac{1}{1 + k_2(HBr)/k_3(Br_2)}\ .$$

In measuring the rates in the forward direction $k_2(HBr)/k_3(Br_2) << 1$. Since $2k_d(Br_2)(M) = 2k_5(Br)^2(M)$,

$$\text{chain length} = \frac{k_1(RH)}{2k_5(M)\sqrt{K_c(Br_2)}} .$$

The bromine atom recombination rate constant k_5 was measured by Rabinowitch and Lehman with helium as M; $k_5 = 3 \times 10^9$ (moles/liter)$^{-2}$sec.$^{-1}$.(15) For chloroform or bromine as M, the work of Hilferding and Steiner indicates that k_5 would be greater by a factor of about 10; $k_5 = 3 \times 10^{10}$.(16) Using this and the following experimental values typical of the measurements made

$(M) = 20 \times 10^{-3}$ moles/liter

$(RH) = 20 \times 10^{-3}$

$(Br_2) = 2 \times 10^{-3}$

$k_1 = 5 \times 10^4$ (moles/liter)$^{-1}$sec.$^{-1}$ (435°K)

$K_c = 6.3 \times 10^{-20}$ moles/liter (435°K)

we have

$$\text{chain length (forward direction)} = 7.5 \times 10^4 .$$

The chain in the reverse direction is longer because $k_4 \sim 10k_1$.

$$\text{chain length} \equiv \frac{d(RH)/dt}{d(Br)/dt}$$

$$= \frac{k_4(RBr)}{2k_5(M)\sqrt{K_c(Br_2)}} \quad \frac{1}{1 + k_3(Br_2)/k_2(HBr)} .$$

Typical experimental concentrations which were used and measured values of the rate constants are

$(M) = 40 \times 10^{-3}$ moles/liter

$(RBr) = 20 \times 10^{-3}$

$(HBr) = 20 \times 10^{-3}$

$(Br_2) = 1 \times 10^{-3}$

$k_4 = 6 \times 10^{5}$ (moles/liter)$^{-1}$sec.$^{-1}$ (435°K)

$K_c = 6.3 \times 10^{-20}$ moles/liter (435°K)

$k_3/k_2 = 25$

from which chain length (reverse direction) $= 3 \times 10^{5}$.

II. If the reaction mechanism is

$$\begin{array}{lclcc} & & & \longrightarrow & \longleftarrow \\ Br_2 + M & \longrightarrow & 2Br + M & (d) & \\ CHCl_3 + Br & \Longleftrightarrow & -CCl_3 + HBr & (1) & (2) \\ -CCl_3 + Br_2 & \Longleftrightarrow & CBrCl_3 + Br & (3) & (4) \\ 2\,-CCl_3 + M & \longrightarrow & C_2Cl_6 + M & (6) & \end{array}$$

then, letting $R \equiv -CCl_3$ and $A = k_2(R)(HBr) + k_3(R)(Br_2) - k_1(RH)(Br) - k_4(RBr)(Br)$, the stationary state concentrations of bromine atoms and $-CCl_3$ radicals are given by

$$d(Br)/dt = 2k_d(Br_2)(M) + A = 0$$

$$d(R)/dt = -2k_6(R)^2(M) - A = 0$$

from which $(R) = (k_d/k_6)^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}$

$$(Br) = \frac{2k_d(Br_2)(M) + (k_d/k_6)^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}\left[k_2(HBr) + k_3(Br_2)\right]}{k_1(RH) + k_4(RBr)} .$$

The rate in the forward direction is

$$-d(Br_2)/dt = d(RBr)/dt = k_3(Br_2)(R) - k_4(RBr)(Br).$$

After substitution of the expressions for (R) and (Br) the rate is $-d(Br_2)/dt = k_3(k_d/k_6)^{\frac{1}{2}}(Br_2)^{3/2}$

$$- k_4(RBr)\frac{2k_d(Br_2)(M) + (k_d/k_6)^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}\left[k_2(HBr) + k_3(Br_2)\right]}{k_1(RH) + k_4(RBr)} .$$

When the reverse reaction can be neglected, ie, the initial concentration of trichlorobromomethane is zero, the rate of the forward reaction is

$$-d(Br_2)/dt = k_3(k_d/k_6)^{\frac{1}{2}}(Br_2)^{3/2} .$$

The rate of the forward reaction is negligible compared to the reverse rate when (RBr) $>>$ (RH) and (HBr) $>>$ (Br_2). The reverse rate is then given by

$$d(Br_2)/dt = k_2(k_d/k_6)^{\frac{1}{2}}(HBr)(Br_2)^{\frac{1}{2}} .$$

These rate equations are very different from those derived from the experimental data, and indicate that reaction (6) is unimportant compared to reaction (5) as a chain breaking step. As stated previously, it is very probable that $k_6 \gtrsim k_5$; if $k_6 \geq k_5$, the reason that the rate of (6) is small compared to the rate of (5) must be that $(R)/(Br) < 1$.

III. If the recombination of $-CCl_3$ radicals takes place by the bimolecular reaction (7), a mechanism based on this reaction as the sole chain breaking step yields the following rate equations which are similar to those derived in II.

$$-d(Br_2)/dt = k_3(k_d/k_7)^{\frac{1}{2}}(M)^{\frac{1}{2}}(Br_2)^{\frac{3}{2}} \qquad \text{(forward rate)}$$

$$d(Br_2)/dt = k_2(k_d/k_7)^{\frac{1}{2}}(M)^{\frac{1}{2}}(HBr)(Br_2)^{\frac{1}{2}} \qquad \text{(reverse rate)}$$

The lack of agreement between these equations and the experimental data indicates that (7) is not an important chain breaking step in the actual reaction mechanism.

If reaction (7) were the sole chain breaking step, the amount of hexachloroethane produced in a typical five hour reaction run would be negligible and unobservable.

$$\begin{aligned} d(C_2Cl_6)/dt &= k_7(R)^2 \\ &= k_7(k_d/k_7)(Br_2)(M) \\ &= k_5K_c(Br_2)(M) \\ C_2Cl_6 &\sim k_5K_c(Br_2)(M) \text{ x } t \text{ x } v \\ &\sim 1.3 \text{ x } 10^{-10} \text{ moles produced.} \end{aligned}$$

IV. If the reaction mechanism is

$$\begin{array}{lcll} & & & \rightarrow \quad \leftarrow \\ Br_2 + M & \longrightarrow & 2Br + M & (d) \\ CHCl_3 + Br & \rightleftharpoons & -CCl_3 + HBr & (1) \quad (2) \\ -CCl_3 + Br_2 & \rightleftharpoons & CBrCl_3 + Br & (3) \quad (4) \\ -CCl_3 + Br + M & \longrightarrow & CBrCl_3 + M & (8) \end{array}$$

the stationary state concentrations of bromine atoms and $-CCl_3$ radicals, letting $R \equiv -CCl_3$, are given by

$$d(Br)/dt = 2k_d(M)(Br_2) + k_2(R)(HBr) + k_3(R)(Br_2) - k_1(RH)(Br) - k_4(RBr)(Br) - k_8(R)(Br)(M) = 0$$

$$d(R)/dt = - k_2(R)(HBr) - k_3(R)(Br_2) + k_1(RH)(Br) + k_4(RBr)(Br) - k_8(R)(Br)(M) = 0$$

from which

$$(R) = (k_d/k_8)(Br_2)/(Br) \; .$$

The bromine atom concentration (Br) is obtained as a function of the measurable concentrations by substituting this expression for (R) into $d(R)/dt = 0$. After a rearrangement of terms,

$$d(R)/dt = 0 = \left[k_1(RH) + k_4(RBr)\right](Br)^2 - k_d(Br_2)(M)(Br)$$

$$- \left[k_2(HBr) + k_3(Br_2)\right](k_d/k_8)(Br_2) = 0 \; .$$

Letting $k_1(RH) + k_4(RBr) = D$, and $k_2(HBr) + k_3(Br_2) = E$,

$$(Br) = \frac{k_d(Br_2)(M) + \sqrt{k_2{}^2(Br_2)^2(M)^2 + 4ED(k_d/k_8)(Br_2)}}{2D}$$

$$= \frac{k_d(Br_2)(M)}{2D}\left\{1 + \sqrt{1 + \frac{4ED}{k_d k_8(Br_2)(M)^2}}\right\} \; .$$

The fraction under the square root sign is $\gg$ 1; using the values of the concentrations given on page 37 and the following values of the rate constants

$k_d = K_c k_5 = 2 \times 10^{-9}$ (moles/liter)$^{-2}$sec.$^{-1}$

$k_3 \sim 10^6$ (moles/liter)$^{-1}$sec.$^{-1}$

$k_8 \sim 3 \times 10^{10}$ (moles/liter)$^{-2}$sec.$^{-1}$

$k_1 = 5 \times 10^4$ (moles/liter)$^{-1}$sec.$^{-1}$

$k_4 = 6 \times 10^5$ (moles/liter)$^{-1}$sec.$^{-1}$

$k_2/k_3 = .04$

the value of the fraction is about 10^{11} . The bromine atom concentration is therefore

$$(Br) = \frac{k_d(Br_2)(M)}{2D} \times \frac{2(ED)^{\frac{1}{2}}}{(k_d k_8)^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}(M)}$$

$$= (k_d/k_8)^{\frac{1}{2}}(E/D)^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}$$

$$= (k_d/k_8)^{\frac{1}{2}}\left\{\frac{k_2(HBr) + k_3(Br_2)}{k_1(RH) + k_4(RBr)}\right\}^{1/2}(Br_2)^{\frac{1}{2}} \; .$$

The rate in the forward direction is

$$-d(Br_2)/dt = k_3(Br_2)(R) - k_4(RBr)(Br) \ .$$

When the initial concentration of trichlorobromomethane is zero the reverse rate is negligible compared to the forward rate which is

$$\begin{aligned}-d(Br_2)/dt &= k_3(Br_2)(R)\\ &= k_3(Br_2)(k_d/k_8)(Br_2)/(Br)\\ &= k_3(k_d/k_8)^{\frac{1}{2}} \left\{\frac{k_1(RH)}{k_2(HBr) \quad k_3(Br_2)}\right\}^{1/2} (Br_2)^{3/2}\\ &= \frac{k_3(k_d/k_8)^{\frac{1}{2}}k_1^{\frac{1}{2}}(RH)^{\frac{1}{2}}(Br_2)^2}{(1 + k_2(HBr)/k_3(Br_2))^{\frac{1}{2}}} \ .\end{aligned}$$

When (RBr) >> (RH) and (HBr) >> (Br_2) the rate of the reverse reaction is

$$\begin{aligned}d(Br_2)/dt &= k_4(RBr)(Br)\\ &= k_4(RBr)(k_d/k_8)^{\frac{1}{2}} \left\{\frac{k_2(HBr) + k_3(Br_2)}{k_1(RH) + k_4(RBr)}\right\}^{1/2} (Br_2)^{\frac{1}{2}}\\ &= (k_4k_d/k_8)^{\frac{1}{2}}(RBr)^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}(k_2(HBr) + k_3(Br_2))^{\frac{1}{2}} \ .\end{aligned}$$

Since these equations are inconsistent with the experimental data, reaction (8) is not an important chain breaking step.

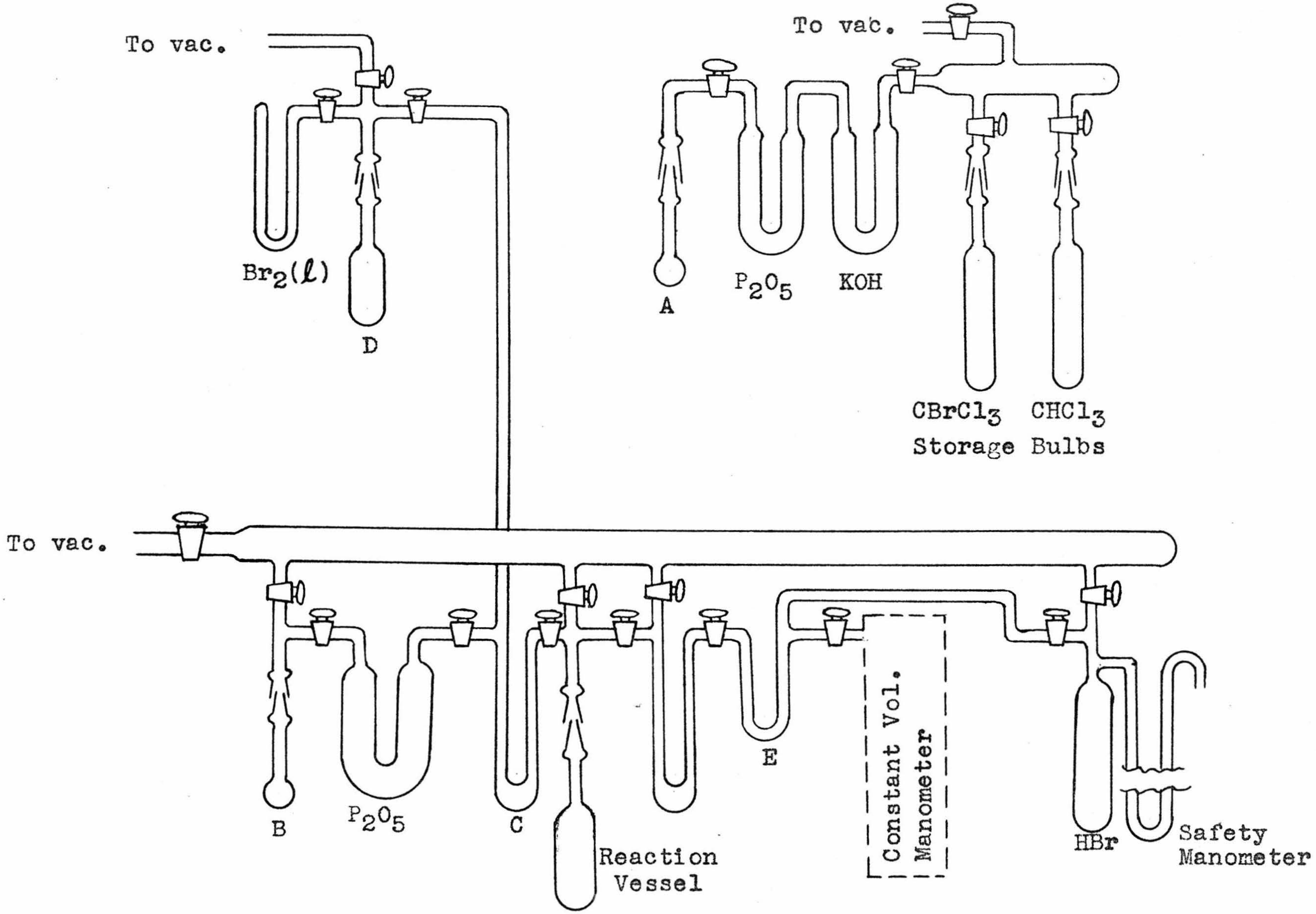

Figure 1. Apparatus for filling reaction vessels.

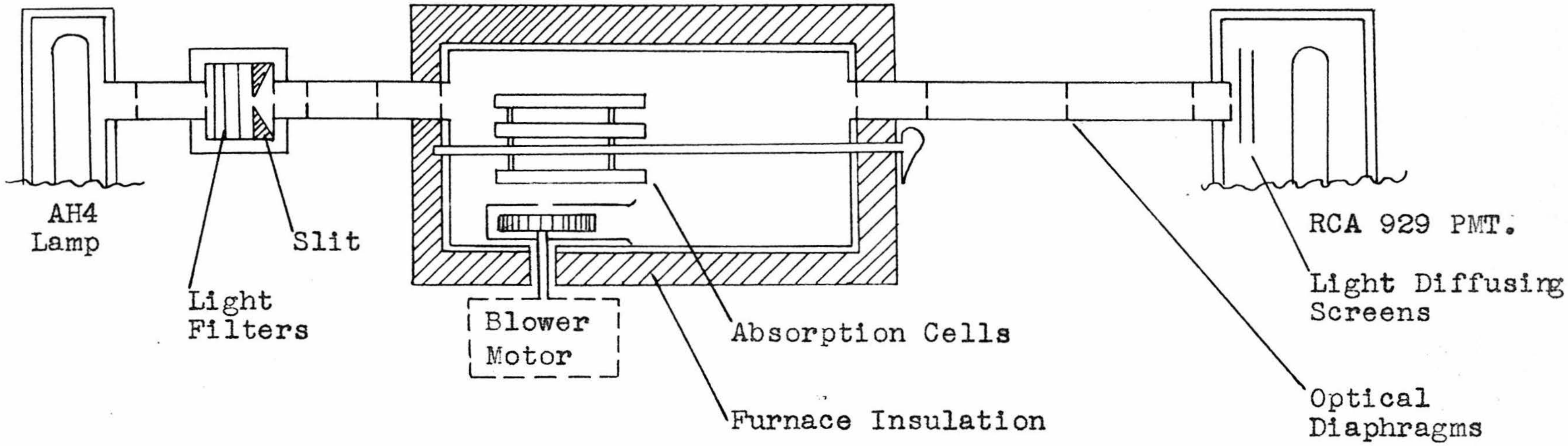

Figure 2. Optical path in apparatus for photometric determination of bromination rates.

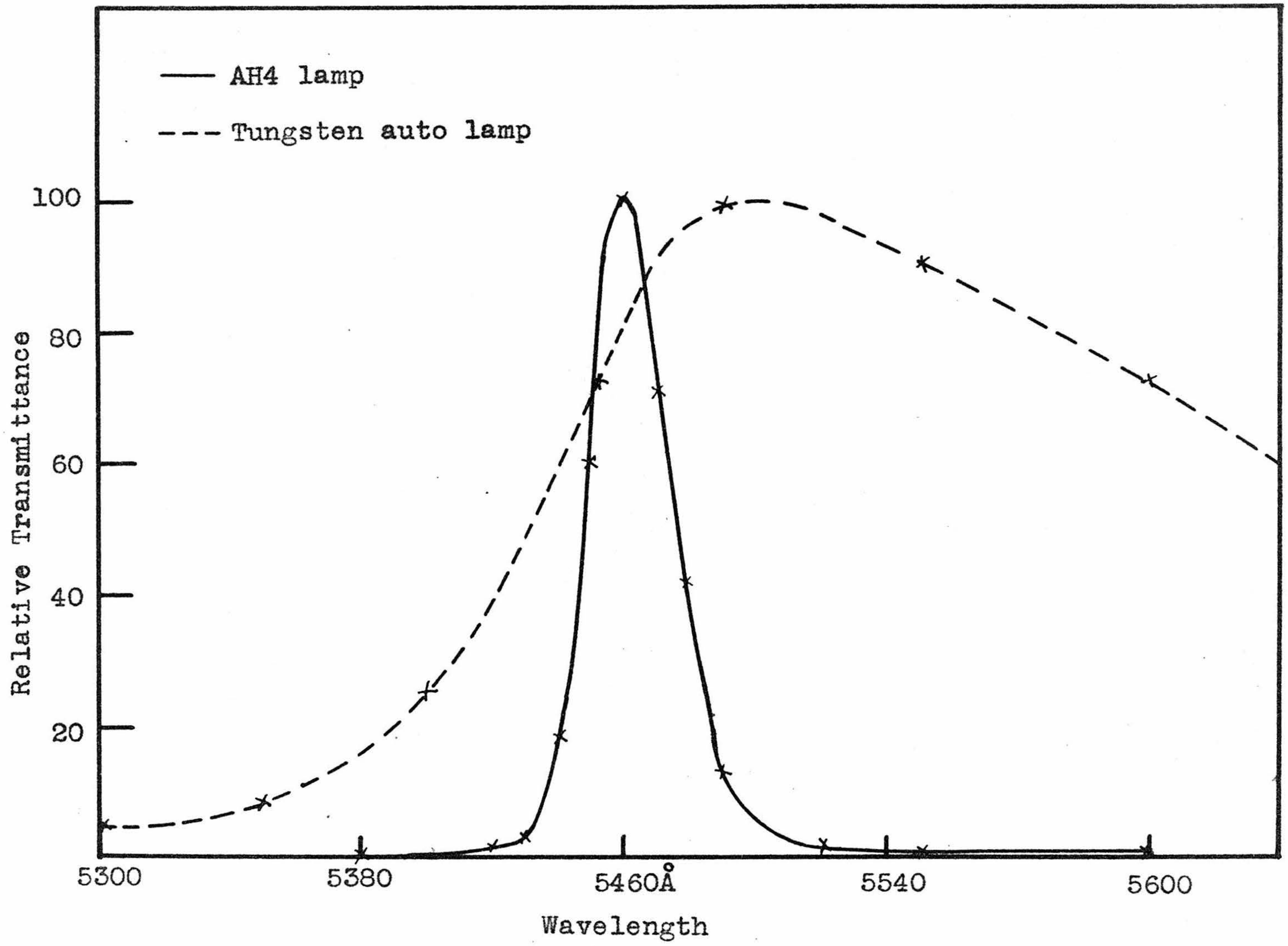

Figure 3. Isolation of the 5460A Hg line by #5120, #403, and #3484 Corning glass filters.

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PART III

A METHOD OF ESTIMATING AND MINIMIZING THE ERROR OF MEASUREMENT OF THE RATE OF A RADIOACTIVE EXCHANGE REACTION

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A Method of Estimating and Minimizing the Error of Measurement of the Rate of a Radioactive Exchange Reaction

By Norman Davidson and John H. Sullivan

It has been explicitly pointed out by several authors that for a radio-active exchange reaction between two components in chemical equilibrium, the activity of either component varies in a simple exponential manner with time.[1,2] We present here, as a consequence of this analysis, a method for: (a) the estimation of the error, due to the error of radioassay, in the rate constant for the exchange reaction, as a function of the extent of exchange; (b) the selection of the optimum degree of exchange to minimize this error.[3]

For the case where the rate is measured by the decrease in the activity of the component that initially contained all the activity, the integrated rate expression is

$$\ln\left[\left(\frac{a}{b}+1\right)\frac{x}{c}-\frac{a}{b}\right] = -R(a,b)\,\frac{a+b}{ab}\,t \qquad (1)$$

In this relation: a is concentration of component A that initially contained all the activity; b is concentration of initially inactive component B; c is initial activity of A; x is activity of A at time t and $R(a, b)$ is the rate of exchange

For very short times of reaction x will be almost the same as c and the error in the rate large For long times of reaction, the components will be almost in equilibrium with respect to the distribution of activity which will then change but little with time. It is often the case that the errors in a, b, t are small compared to the errors of radioassay in x and c. Set $z = x/c$ and $s = R((a + b)/ab)t$. The variable s is dimensionless and proportional to two factors: (1) Rt, the total number of concentration units (*i. e.*. atoms/cc. or moles/liter) that have undergone mutual exchange, and (2) the term $(a + b)/ab$ (Displayed in the form $s = Rt/b + Rt/a$, it is evident that s is the sum of the number of exchanges per atom of a, and the number of exchanges per atom of b). Then

$$-\frac{\mathrm{d}\ln s}{\mathrm{d}\ln z} = \frac{1+(a/b)\exp(s)}{s} = E(a/b,s) \qquad (2)$$

The relation $\sigma_s = |\mathrm{d}s/\mathrm{d}z|\sigma_z$ holds for the standard deviations, σ_s and σ_z, of s and z, because of the assumption that the error in s is due entirely to the error in z.[4] Then

$$\frac{\sigma_s}{s} \times \frac{z}{\sigma_z} = -\frac{\mathrm{d}\ln s}{\mathrm{d}\ln z} = E(a/b,s) \qquad (3)$$

For $\sigma_z, (\sigma_z/z)^2 = (\sigma_x/x)^2 + (\sigma_c/c)^2$; the standard deviations of the activities may be due to statistical counting errors or may be manipulative errors determined by reproducibility tests. It is often the case that the fractional error in $x, (\sigma_x/x)$, is a constant; this is roughly true, for example, if the error is principally a counting error and one counts all samples to the same number of counts, or if the error is a manipulative error in preparing chemically identical samples for radioassay. For such cases, the minimum of E locates the point for minimum error in s (and hence in the rate function R). Knowing the value of s corresponding to the minimum value of E and using a preliminary value of R, the optimum t may be chosen.

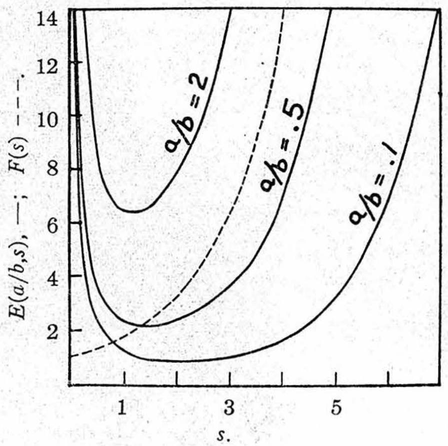

Fig. 1.—Error functions for exchange reactions.

The minimum of the error function, E, may be found by solution of the equation: $s - 1 = (b/a)\exp(-s)$. It will generally be more useful to construct a family of curves like those in the figure so that the error in s will be known for any s (or z). Estimates of the standard deviation in s obtained in this way are useful, for example as weighting factors in averaging data or in least squares treatments of data on the variation of rate of exchange with temperature or ionic strength. For such applications, the function E is useful even when the fractional error of radioassay is not constant. For these cases, knowing σ_x as a function of x and hence (for given a and b) as a function of s, one could construct the function, $E(s)\sigma_x(s)/x(s)$, and thus select the point of minimum error. For the usual case where σ_x/x does not change too rapidly with x, it may be sufficient to select by inspection a point in the region of the minimum of the $E(s)$ curve without making the more elaborate calculations required to select the optimum point.

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[1] McKay, *Nature*, **142**, 997 (1938).

[2] Duffield and Calvin, This Journal, **68**. 557 (1946).

[3] Roseveare *ibid.*, **53**, 1651 (1931) has applied similar arguments to the problem of estimating and minimizing the error in the rate constants for chemical reactions.

[4] See, for example, Margenau and Murphy The Mathematics of Physics and Chemistry," D Van Nostrand Co., New York, N. Y., 1943 p 498.

PROPOSITIONS

1. A consideration of the relative rates of possible chain breaking steps in the thermal bromination of chloroform leads to the following values of rate constants and activation energies for reactions (2) and (3)

$$HBr + \cdot CCl_3 \longrightarrow CHCl_3 + Br \qquad (2)$$

$$Br_2 + \cdot CCl_3 \longrightarrow CBrCl_3 + Br \qquad (3)$$

$$k_2 > 5 \times 10^6 \qquad E_{act.} < 5 \text{ kcal.}$$

$$k_3 > 10^8 \qquad E_{act.} < 5 \text{ kcal.}$$

2. On the basis of the activation energies given above for reactions (2) and (3) the CH bond in $CHCl_3$ is at least 6.6 and at most 11.6 kcal. weaker than the CH bond in CH_4, and the CBr bond in $CBrCl_3$ is at least 11 and at most 16 kcal. weaker than the CBr bond in CH_3Br.(1)

3. The photochemical rearrangement of N-chloroacetanilide in the solid state observed by Porter and Wilbur(2) and the thermal rearrangement of liquid benzoylchloroaminobenzene observed by Chattaway and Orton(3) are not satisfactory proof of a direct intramolecular interchange of atoms.(4) A photochemical rearrangement of these compounds occurring in a dilute inert solution solidified as a glass would be proof of an intramolecular process.

4. The marked decrease in the resistance of a palladium oxide film caused by proton recoil might be utilized as a simple neutron spectrometer by interposing various thicknesses of a non-hydrogenous material between the source of recoil protons and the oxide film.(5)

5. In the investigation of the kinetics of the phosphorus tribromide catalyzed conversion of white phosphorus into red the large solvation effects during precipitation of the red phosphorus could be considerably diminished by studying the rate in a solution of the tribromide and white phosphorus in an inert solvent. A dependence of the rate on the phosphorus tribromide concentration might be obtained in this way.(6)

6. Additional evidence for the weak bonding of O_2 molecules to form O_4 could be given by an attempted exchange reaction between O_2^{18} and O_2^{16} .

7. In a study of a chain reaction, the absence in a reaction system of a compound which would be formed in a particular chain breaking step is sometimes taken as an indication that this chain breaking step is not present.(7) This reasoning is fallacious; the amounts of such compounds may be unobservable.(8) A more sensitive indication of the chain breaking mechanism is the overall rate equation.

8. In a thermal halogenation reaction a square root dependence of the rate on the halogen concentration does not necessarily indicate the rate determining step involves halogen atoms in thermal equilibrium with halogen molecules. A steady state concentration of halogen atoms appreciably less than the equilibrium value may give the same rate equation.

9. Investigations of the photolysis of formaldehyde indicate that two primary steps,

$$HCHO + hv \longrightarrow CO + H_2$$

$$HCHO + hv \longrightarrow CHO + H$$

may take place in the decomposition to carbon monoxide and hydrogen.(9) The relative importance of these two steps can be determined by the photolysis of a mixture of DCDO and HCHO.

10. Athletics for the graduate student would be unobtrusively, effectively, and cheaply encouraged by the athletics department of Cal. Tech. if school purchased athletic equipment were assigned to the various divisions for graduate student and faculty use. I believe the ready availability of this equipment would be of considerable benefit to the health, general well being, and the social life of the graduate students at Cal. Tech.

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