difficult to restore the vessel to a condition which will give normal decomposition rates.

According to the reactions as written (steps a through g) the rate of disappearance of C_2H_5Br will be given by the expression

$$\frac{-d(C_2H_5Br)}{dt} = k_a(C_2H_5Br) + k_b(C_2H_5Br_{wall})(HBr_{wall}) + k_d\,(C_2H_5Br)(Br) \quad (1)$$

When $d(Br_2)/dt = 0$

$$k_b\,(C_2H_5Br_{wall})(HBr_{wall}) + k_c'\,(Br)^2(M) = k_c\,(Br_2)(M) \quad (2)$$

When $d(Br)/dt = 0$

$$2k_c\,(Br_2)(M) + k_e\,(C_2H_4Br) = 2k_c'\,(Br)^2(M) + k_d\,(Br)(C_2H_5Br) + k_f\,(Br)(C_2H_4) + k_g\,(Br)(C_2H_6) \quad (3)$$

When $d(C_2H_4Br)/dt = 0$

$$k_d\,(Br)(C_2H_5Br) = k_e\,(C_2H_4Br) \quad (4)$$

Adding twice (2), (3) and (4) together

$$2k_b\,(C_2H_5Br_{wall})(HBr_{wall}) = k_f\,(Br)(C_2H_4) + k_g\,(Br)(C_2H_6)$$

and

$$(Br) = \frac{2k_b\,(C_2H_5Br_{wall})(HBr_{wall})}{k_f\,(C_2H_4) + k_g\,(C_2H_6)} \quad (5)$$

Substituting this value of (Br) into (1) it is seen that

$$-\frac{d(C_2H_5Br)}{dt} = k_a\,(C_2H_5Br) + k_b\,(C_2H_5Br_{wall})(HBr_{wall}) + \frac{2k_b\,(C_2H_5Br_{wall})(HBr_{wall})\,k_d\,(C_2H_5Br)}{k_f\,(C_2H_4) + k_g\,(C_2H_6)} \quad (6)$$

It appears that the concentration of HBr on the wall is directly proportional to the concentration in the gas phase, but at high pressures of C_2H_5Br, $(C_2H_5Br_{wall})$ is constant independent of the concentration of C_2H_5Br. The rate of the reaction $C_2H_5Br_{wall} + HBr_{wall}$ is slow and it does not remove much C_2H_5Br directly. The concentration of C_2H_6 is small compared to the concentration of C_2H_4.[4] Equation 6 may then be rewritten

$$\frac{-d(C_2H_5Br)}{dt} = k_a\,(C_2H_5Br) + \text{constant}\,\frac{(HBr)}{(C_2H_4)}\,(C_2H_5Br) \quad (7)$$

The ratio of (HBr) to (C_2H_4) is constant because these two products are kept stoichiometrically equal as they increase during the course of the reaction. Equation 7 is the equation of a first-order reaction, and it accounts for the fact that this complex reaction still gives good experimentally determined first-order rate constants for the overall reaction.

The kinetics of the decomposition of ethyl bromide and the various factors which affect the rate as reported in earlier work appear now to be fairly well understood. The formation of a halogen by a reaction between the alkyl halide and the hydrogen halide produced by the reaction to give a steady-state concentration of an accelerating intermediate compound may well be a factor in the kinetics of other alkyl halides.

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[Contribution from the Chemical Engineering Division, Argonne National Laboratory]

Chemical Equilibria in the Gaseous System Bromine–Bromine Trifluoride–Bromine Monofluoride[1]

By Robert K. Steunenberg, Richard C. Vogel and Jack Fischer

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Equilibrium constants were determined for the gas-phase reaction $BrF_3 + Br_2 \rightleftarrows 3BrF$. The extent of the reaction was derived from manometric measurements at constant volume and the absorption spectra of the mixtures. Equilibrium constants obtained at different temperatures were used to calculate the standard free energy and enthalpy of formation of bromine trifluoride.

The first chemical evidence for the existence of bromine monofluoride was reported by Ruff and Menzel,[2] who recovered a highly volatile fraction from the distillation of a mixture of bromine and bromine pentafluoride. Further studies, made by Ruff and Braida,[3] indicated that the monofluoride is formed by the reactions of bromine with fluorine, bromine trifluoride and bromine pentafluoride. Pure bromine monofluoride was not isolated due to its dissociation, which was said to be nearly complete at 50°.[3]

A phase investigation in this Laboratory of the condensed system bromine–bromine trifluoride showed only the two pure components in the solid phases.[4] Liquid-vapor equilibrium measurements, however, strongly implied the formation of an intermediate species of high volatility.[5]

Brodersen and Schumacher[6] have calculated the dissociation energy of bromine monofluoride from the limit of the band spectrum, which they obtained from a mixture of bromine and fluorine. The microwave spectrum of a similar mixture has contributed further evidence for the existence of this compound.[7]

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **202**, 60 (1931).

[3] O. Ruff and A. Braida, *ibid.*, **214**, 81 (1933).

[4] J. Fischer, R. K. Steunenberg and R. C. Vogel, This Journal, **76**, 1497 (1954).

[5] J. Fischer, J. Bingle and R. C. Vogel, *ibid.*, **78**, 902 (1956).

[6] P. H. Brodersen and H. J. Schumacher, *Z. Naturforsch.*, **2a**, 358 (1947); *Anal. asoc. quim argentina*, **38**, 52 (1950).

[7] D. F. Smith, M. Tidwell and D. V. P. Williams, *Phys. Rev.*, **77**, 420 (1950).

This paper reports the results of manometric and spectrophotometric equilibrium measurements which have been used to determine the enthalpy and free energy changes for the reaction

$$Br_2(g) + BrF_3(g) = 3BrF(g)$$

Experimental

Materials.—Reagent grade bromine was purified further by distilling off approximately one-fourth of the sample at room temperature to remove traces of chlorine. The remainder was distilled through phosphorus pentoxide into a 25-ml. Fluorothene (poly-chlorotrifluoroethylene) tube which was attached to the apparatus. A 10- to 15-ml. sample of liquid bromine, which was adequate for a large number of experiments, was freed of non-condensable gases by repeated freezing, evacuation and melting.

The bromine trifluoride, obtained from commercial sources, was purified by distillation in a $^1/_2$-inch nickel fractionation column 40 inches long and packed with $^1/_8$-inch nickel helices. A 10- to 15-ml. sample of distilled bromine trifluoride was transferred to a 25-ml. Fluorothene tube on the apparatus. This material was then degassed and purified further by slowly distilling off about one-fourth of the liquid at 75°.

Apparatus

Manometric System.—The system in which the experiments were performed consisted essentially of two nickel vessels, each having a volume of about 500 ml. One of these, vessel A, was used as a reaction chamber in which gaseous bromine was added to bromine trifluoride vapor. The other, vessel B, was used to determine the amount of bromine added to vessel A, as indicated by the pressure decrease in B. Both vessels were connected to a manifold system, about 5 ml. in volume, which was served by vacuum and helium sources. The Fluorothene tube containing the liquid bromine supply was attached to vessel B, and the one with the bromine trifluoride was connected to the manifold. All the vessels and connecting lines were made of nickel or Monel, and were joined by welds, silver solder or flare connectors with Teflon gaskets. Hoke No. 1103 valves were used throughout this portion of the system.

The pressure in the manifold was measured by means of a mercury manometer used in conjunction with a Booth–Cromer pressure transmitter and self-balancing electronic relay.[8] The transmitter served to isolate the system containing the reactants from the mercury manometer. The valves were arranged so that one pressure transmitter could be used for both the vessels. The precision of the pressure measurements was approximately ±0.2 mm. of mercury.

That part of the system containing the bromine and bromine trifluoride was enclosed in a thermostated, insulated box in which hot air was circulated. The temperatures were measured with copper–constantan thermocouples and a Rubicon Type B potentiometer. The thermocouples were calibrated with a standard platinum resistance thermometer.

Spectrophotometer Cells.—The spectrophotometric measurements were made over the range 2000 to 8000 Å., using a Cary Model 14 double-beam recording spectrophotometer. The cells, which had been used previously to obtain the spectrum of fluorine,[9] were machined from nickel pipe with an inside diameter of 2.2 cm. The replaceable quartz windows were held in place by brass ring nuts and sealed to the cell body with Teflon gaskets. The optical path was 10.00 cm. A $^1/_4$-inch nickel side tube was provided with a Hoke No. 1103 bellows valve and a flare connector so it could be attached to the manifold system. Asbestos-covered Nichrome wire wrapped around the nickel body of the cell served as a heater. The temperature was measured with a copper–constantan thermocouple silver-soldered to the cell wall. A similar evacuated cell was used in the reference beam.

Procedure

Manometric Measurements.—The system was first calibrated with helium in order to obtain the volume factors between vessels A and B and the manifold. After the equipment had been pretreated with bromine pentafluoride vapor, the calibrations were checked with bromine trifluoride and bromine.

Since the quantities of bromine and bromine trifluoride added to the system were based on pressure measurements, it was necessary to determine their densities. The Regnault method gave values of 161 g./GMV and 140.5 g./GMV, respectively, for bromine and bromine trifluoride at 75° and 90 mm. pressure. The corresponding formula weights are 159.8 and 136.9 g./mole. The high value for bromine trifluoride might be attributed to a slight dimerization, which has been observed in the case of chlorine trifluoride vapor.[10] Since the vapor densities were normal, within the accuracy of the experiments, corrections were not made for non-ideal behavior.

The reaction $Br_2(g) + BrF_3(g) = 3BrF(g)$ forms an additional mole of gas for every two moles reacted. The extent of the reaction can be determined therefore from the pressure increase at constant volume. This was done experimentally by filling vessel A and the manifold with a known pressure of bromine trifluoride. The manifold was evacuated, then opened to vessel B, which was filled with a considerably higher pressure of bromine vapor. Some of the bromine was then admitted to vessel A, the amount being determined by the pressure decrease in vessel B and the volume factors. The manifold was re-evacuated, then opened to vessel A in order to measure the total pressure of the mixture.

Spectrophotometric Measurements.—The first step in the spectrophotometric procedure was to establish the absorption spectra of bromine and bromine trifluoride in the visible and ultraviolet regions. Bromine pentafluoride was also examined briefly, although it was not used directly in this work. Prior to each set of measurements the cell was fluorinated repeatedly with bromine pentafluoride until no bromine color was produced. The cell was evacuated and equilibrated with the box temperature. It was then exposed to the gas under examination for 5 minutes, evacuated and refilled to the desired pressure of the gas. The valves were closed and the cell was transferred to the spectrophotometer. Its temperature was indicated by the thermocouple and regulated manually with a Variac transformer which supplied power to the heater. Blank determinations were made on the cell before and after each set of experiments to check on possible etching of the quartz windows.

Before equilibrium data could be obtained, new volume factors were required with the cell attached to the manifold. These were obtained by the procedure described previously. In making an equilibrium constant determination, the cell was first exposed to 50 mm. of bromine trifluoride vapor for 5 minutes at the box temperature and re-evacuated. The equilibrium mixture was then made in vessel A by the same method used for the manometric determinations, except that the final mixture was expanded into the cell before its total pressure was measured.

The cell containing the equilibrium mixture was transferred to the spectrophotometer, where the spectra of the unreacted bromine and bromine trifluoride were readily apparent. The absorptions of bromine at 4170 Å. and bromine trifluoride at 2400 Å. were used to calculate their partial pressures in the mixture. Approximately 45 minutes were required for the spectrophotometric determination of an equilibrium constant.

Results

Manometric Data.—The initial pressures of bromine and bromine trifluoride added to vessel A, a and b, respectively, were calculated from the manometer readings and the volume factors. The total pressure of the mixture, P, was measured directly. If x represents the excess pressure produced by the reaction, then

$$x = P - (a + b)$$
$$3x = P_{BrF}$$
$$a - x = P_{Br_2}$$
$$b - x = P_{BrF_3}$$

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[8] S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," SAM Laboratories, Columbia University, MDDC-803, 1947.

[9] R. K. Steunenberg and R. C. Vogel, THIS JOURNAL, **78**, 901 (1956).

[10] H. Schmitz and H. J. Schumacher, *Z. Naturforsch.*, **2a**, 363 (1947).

The equilibrium constant for the reaction, K_p, can then be expressed as

$$K_p = \frac{P^3_{BrF}}{P_{BrF_3}\,P_{Br_2}} = \frac{(3x)^3}{(a - x)(b - x)}$$

The equilibrium constants obtained from the manometric measurements were calculated by this method.

Using approximately equal initial pressures of bromine and bromine trifluoride, equilibrium constants were measured at 10-degree temperature intervals from about 55 to 105°. The data are given in Table I. It was necessary to use smaller pressures in the lower temperature range to avoid condensation of the bromine trifluoride vapor.

TABLE I

MANOMETRIC EQUILIBRIUM DATA

Temp., °C.	Initial pressure, mm.		Total pressure, mm.	K_p, mm.
	Br_2	BrF_3		
55.6	20.2	20.7	53.1	720
57.1	20.0	20.4	52.0	570
65.0	30.0	30.1	78.6	1280
65.2	30.3	30.2	79.0	1240
65.4	30.0	30.4	78.8	1210
74.4	50.0	50.0	129.8	1750
74.5	49.9	49.9	129.1	1600
84.8	49.8	50.0	131.1	2400
84.8	50.0	49.9	131.3	2430
96.7	50.0	50.0	134.8	4920
96.7	50.0	50.0	134.9	5040
96.7	50.0	50.1	134.8	4790
107.1	50.0	50.0	137.2	8480
107.1	50.0	50.1	137.3	8420
107.1	50.0	50.3	137.1	7560

Spectrophotometric Data.—The spectrophotometer scans were made over the range 2000 to 8000 Å. at 75°. The bromine absorption lies in the visible region, while bromine trifluoride absorbs strongly in the ultraviolet. Bromine pentafluoride showed substantially the same absorption as the trifluoride. Observations at various pressures indicated conformance with Beer's law, and temperature changes from 50 to 100° had no discernible influence on the spectra.

The partial pressures of bromine, $(a - x)$, and bromine trifluoride, $(b - x)$, were determined from the spectra of the equilibrium mixtures at 4170 and 2400 Å., respectively. The partial pressure of bromine monofluoride, $3x$, was obtained by the difference

$$3x = P - [(a - x) + (b - x)]$$

The equilibrium constants were then calculated as before.

The first series of spectrophotometric determinations was made at 75°, using various ratios of the reactants and total initial pressures $(a + b)$ of about 100 mm. In other measurements at 75°, the initial pressures were varied from 50 to 150 mm. The average equilibrium constant from these data at 75° was 2.2 atm., with a mean deviation of 0.5 atm. Similar determinations were made at 10-degree intervals from 55 to 105°. In a few cases the initial ratios and pressures of the reactants were varied at temperatures other than 75°. The usable pressure range was restricted somewhat by the vapor pressure of bromine trifluoride at the lower temperatures.

The atomic ratio of fluorine to bromine in the product was one of the criteria used to characterize it as bromine monofluoride. The manometric calculations were based on the assumption that an equivalent amount, x, of each of the reactants was consumed. The spectral data, however, give the amounts of each reactant consumed, x_a and x_b. Since the initial pressures, a and b, are known, and the quantities $(a - x_a)$ and $(b - x_b)$ are given directly by the spectra, x_a and x_b are readily calculated. The F:Br ratio, n, of the product is then

$$n = \frac{3x_a}{x_a + 2x_b}$$

The average value of this ratio for all the spectrophotometric experiments was $n = 0.99$ with a standard deviation of 0.12.

An absorption spectrum due to bromine monofluoride was first noticed as a fine structure which appeared on the shoulder of the bromine peak in the vicinity of 5000 Å. A few experiments were performed in an attempt to obtain the pure bromine monofluoride spectrum. The cell, containing an equilibrium mixture, was placed in the spectrophotometer in the usual manner. The reference cell was then filled with bromine vapor to a pressure equivalent to its partial pressure in the mixture. This resulted in a characteristic spectrum for bromine monofluoride. Accurate molar absorptivity measurements were not possible, since the bromine absorption is an order of magnitude stronger than that of bromine monofluoride. The wave lengths of the peaks in the fine structure, however, corresponded within the experimental accuracy of ± 5 Å. to the lines in the band spectrum reported by Brodersen and Schumacher.[6] Qualitatively, it appears as if bromine monofluoride has only a slight color, similar to that of bromine, but far less intense.

Discussion

When gaseous bromine and bromine trifluoride were mixed, the total pressure of the mixture rose substantially over the sum of the initial pressures of the reactants added to the system. The only reasonable reaction that would result in an increase in the total number of moles of gas present was the production of bromine monofluoride. This fact, along with reasonably consistent equilibrium data for this reaction and a fluorine-to-bromine ratio of unity in the product was considered to be ample evidence that the correct stoichiometry had been chosen. A further indication was given by the presence of the bromine monofluoride spectrum in the equilibrium mixture. During all the measurements, the final equilibrium pressure was reached immediately, indicating that the rate of the reaction is rapid.

The manometric equilibrium measurements were of a higher precision than was obtained by the spectrophotometric method, but additional information was provided by the latter. Both the manometric and the spectrophotometric data were subjected separately to a least squares treatment, giving the following equations for the temperature dependence

$$\log_{10} K_{p,\ atm} = -\frac{2597.06}{T} + 7.83262 \text{ (manometric data)}$$

$$\log_{10} K_{p,\ atm} = -\frac{2816.10}{T} + 8.41011 \text{ (spectrophotometric data)}$$

Thermodynamic data were calculated at 298.16°K. by extrapolating the temperature dependence equations for the equilibrium 30° below the temperature range of the measurements. At 298.16°K.

$\log_{10} K_{p,\ atm} = -0.87767$ (manometric)
$\log_{10} K_{p,\ atm} = -1.03482$ (spectrophotometric)

From

$\Delta F = -RT\, 2.303 \log K_{p,\ atm}$
$\Delta F = -1200$ cal./mole (manometric)
$\Delta F = -1400$ cal./mole (spectrophotometric)

The standard error of $\log K_{p,\ atm}$ for the manometric data was ± 0.0575, while that for the spectrophotometric data was ± 0.129. The corresponding standard errors for ΔF were therefore ± 78 and ± 176 cal./mole.

$\Delta F = -1200 \pm 80$ cal./mole (manometric)
$\Delta F = -1400 \pm 180$ cal./mole (spectrophotometric)

From the slopes of the least squares lines and their standard deviations, the enthalpy change accompanying the reaction was

$\Delta H = 11{,}900 \pm 500$ cal./mole (manometric)
$\Delta H = 12{,}900 \pm 700$ cal./mole (spectrophotometric)

Using the more accurate manometric data, and taking the gases at 1 atm. and 298.16°K. as the standard state, the results may be summarized as

$Br_2(g) + BrF_3(g) = 3BrF(g)$
$\Delta H° = 11.9 \pm 0.5$ kcal./mole
$\Delta F° = -1.2 \pm 0.08$ kcal./mole

From these data it was possible to calculate the enthalpy and free energy of formation of bromine trifluoride, quantities which were not available previously. Thermodynamic data were available in the literature[11] for the reaction

$^1/_2Br_2(g) + {}^1/_2F_2(g) = BrF(g)$
$\Delta H°_{298.16} = -18.4 \pm 0.5$ kcal./mole
$\Delta F°_{298.16} = -18.7$ kcal./mole

The standard state chosen for this calculation was the ideal gases at 1 atm. The values, obtained from spectroscopic data on the dissociation of bromine monofluoride,[6] were based on the assumption that the fluorine was in the excited state and the bromine was not.[11]

Using the more conventional standard states, the standard enthalpy and free energy of formation of bromine trifluoride were calculated for 1 atm. pressure and 298.16°K. The vapor pressure and enthalpy of vaporization of bromine trifluoride were obtained from the data of Oliver and Grisard.[12]

$^1/_2Br_2(l) + {}^3/_2F_2(g) = BrF_3(l)$
$\Delta H°_{BrF_3} = -75$ kcal./mole
$\Delta F°_{BrF_3} = -57$ kcal./mole

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[11] W. H. Evans, T. R. Munson and D. D. Wagman, *J. Research Natl. Bur. Standards*, **55**, 147 (1955).

[12] G. D. Oliver and J. W. Grisard, THIS JOURNAL, **74**, 2705 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Decomposition of Carbon Dioxide in a Radiofrequency Arc[1]

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A kinetic study has been made of the chemical processes that govern the decomposition of gaseous carbon dioxide in a 3 Mc. electric discharge in a flow system. Factorial experiments showed the following parameters to be of prime importance in controlling the decomposition into CO and O_2: pressure, flow rate and current. An analysis based on available thermodynamic, kinetic and spectroscopic information indicated the likely elementary chemical steps and experimental results were compared with theory through a simple hydrodynamic model. This kinetic scheme requires the reverse reaction between CO and oxygen atoms as well as the recombination of oxygen atoms as a terminating step. The former reaction explains the inertness of CO_2 in static radiation systems. The experimental flow rate dependence can be explained within experimental error and a semiquantitative interpretation of pressure and current effects is given.

Introduction

During the past few years, a series of investigations have been carried out by the senior authors on the chemical effects in gaseous radio frequency electric discharges which included studies on fixation of nitrogen,[2] formation of hydrazine,[3] and irradiation of CO_2–H_2O mixtures.[4] In the work reported herein, the decomposition of carbon dioxide was selected as a representative and a sufficiently simple chemical system whose study could serve as a model for a deeper understanding of the controlling physical and chemical processes in electric discharges with respect to more complex molecular systems.

A radiofrequency discharge in the range of approximately 3 megacycles was used. A flow apparatus was selected to facilitate chemical analysis

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[2] Wm. S. Partridge, R. B. Parlin and B. J. Zwolinski, *Ind. Eng. Chem.*, **46**, 1468 (1954).

[3] W. H. Andersen, Ph.D. thesis, University of Utah, 1952.

[4] K. A. Wilde, B. J. Zwolinski and R. B. Parlin, *Science*, **118**, 43 (1953).