[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON]

Vaporization of Chromium(III) Bromide. Evidence for Chromium(IV) Bromide

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In a bromine atmosphere $CrBr_3(s)$ has been found to vaporize as $CrBr_3(g)$, apparently in the monomeric form, and $CrBr_4(g)$. Thermodynamic properties of these species (relative to $CrBr_3(s)$) have been determined by the study of vaporization equilibria. In effusion experiments at low pressures, bromine, formed by decomposition of $CrBr_3$ to $CrBr_2$, leaves the cell simultaneously with $CrBr_3$. Steady-state bromine pressures show a marked dependence on the degree of decomposition of the sample and could not be used to characterize the decomposition equilibrium.

When solid chromium (III) bromide is heated to temperatures sufficient to establish a measurable vapor pressure, concomitant release of bromine, formed by decomposition of $CrBr_3$ to $CrBr_2$, has been found to occur. If $CrBr_3$ (s) is heated in bromine at pressures sufficient to prevent decomposition, the total pressure of chromium halide in the vapor phase is observed to vary with bromine pressure in such a manner as to indicate formation of significant amounts of $CrBr_4$ (g). Measurements have been made to characterize the equilibria

$$CrBr_3(s) = CrBr_3(g) \qquad (1)$$

and

$$CrBr_3(s) + {}^1/_2Br_2(g) = CrBr_4(g) \qquad (2)$$

using effusion, transpiration and diaphragm gage techniques. In effusion work $CrBr_3$ and bromine were collected separately in each run to provide information concerning (1) and the decomposition reaction

$$CrBr_3(s) = CrBr_2(s) + {}^1/_2Br_2(g) \qquad (3)$$

Effusion bromine pressures showed a marked dependence on the degree of decomposition, which has not as yet been fully explained, and further work will be necessary to determine the equilibrium constants for (3). Thermodynamic data for (1) and (2) have been obtained by studying these equilibria under conditions which ensured that the activity of $CrBr_3$ (s) remained near unity.

Experimental

$CrBr_3$ was prepared by reaction of chromium metal with bromine vapor (at *ca.* 200 mm. pressure) at 750°. The large platelets of $CrBr_3$, which sublimed out of the reaction zone, were further purified by a separate resublimation in 200 mm. pressure of bromine. The amount of chromium in the final product indicated a purity of at least 97.8%.

The effusion apparatus is shown in Fig. 1. The quartz cell A, 20 mm. o.d., was sealed to a quartz tube, 25 mm. o.d., connected to a stopcock D by a ball and socket joint. Fresh 0.5-g. samples of $CrBr_3(s)$, inserted at A (the small tube then sealed off), were used in each run to ensure that the activity of $CrBr_3$ remained near unity (only *ca.* 10^{-6} moles left the cell during a run). The system was evacuated to *ca.* 10^{-6} mm. pressure and a preheated furnace slid into position around the cell. The temperature was measured with several thermocouples spaced along the cell; the furnace was constructed with separate end windings which permitted the entire cell to be maintained in a temperature zone constant within ±1°. The run was stopped by removing the furnace.

$CrBr_3$, effusing from the cell, condensed in a well-defined ring B at the cool end of the furnace. The sublimate (insoluble in hot or cold, concentrated or dilute hydrochloric, nitric or sulfuric acids, aqua regia, or aqueous sodium hydroxide) was dissolved in molten sodium chlorate which oxidized the chromium to chromate; the solidified melt was subsequently dissolved in water. The chromate was then complexed with diphenylcarbazide and determined in a Beckman DU spectrophotometer, as described by Sandell.[1]

Two effusion cells with orifice areas (and Clausing factors[2]) of 5.04×10^{-3} cm.^{2} (0.85) and 10.46×10^{-3} cm.^{2} (0.921), respectively, were used. Bromine, which effused simultaneously with $CrBr_3$, was collected in trap C. Quantities were determined by transferring the sample to E, adding KI solution and measuring the liberated iodine by the dead-stop titration method.[3]

Transpiration measurements were conducted in an apparatus similar to one described previously.[4] Anhydrous bromine vapor served as the carrier gas; its pressure in the system was controlled by immersing an excess of the liquid (in the source vessel) in either a thermostat (21.1°, P = 185 mm.), an ice-water bath (P = 69 mm.), an aniline slush bath (−5.8°, P = 49 mm.) or a bromobenzene slush bath (−30°, P = 7 mm.). The flow rate across the sample was controlled by a capillary orifice placed between the sample tube and a bromine collecting trap cooled in liquid oxygen. Quantities of bromine flowing over the sample in a given run were determined (after collecting the material) by iodimetric methods; the pressure was measured directly with a diaphragm gage. At each pressure the effect of flow rate (varied from 3 to 70 ml./min.) on the quantity of chromium halide transported was determined at 593°. The apparent vapor pressure *vs.* flow rate curves were typical in shape, high at low flow rates, independent of flow rate at intermediate values, a tending to lower pressures at the highest flow rates. A flow rate of 30 ml./min. was selected as satisfactory.[5]

Results and Discussion

Effusion pressures of $CrBr_3$ and most of the transpiration data measured in this work, together with transpiration data at higher temperatures (nitrogen gas as a carrier) reported by Wagner and Stein,[6] are shown in Fig. 2. Our effusion data are in good agreement with the results of Wagner and Stein when the vaporizing species is assumed to be principally monomeric $CrBr_3$, the lowest solid line. The dotted and dashed lines, respectively, show how these two sets of data would compare if vaporization were assumed to occur as a dimer in both cases; the agreement is less satisfactory on the dimer basis although such a comparison is not sufficiently sensitive to preclude the presence of a small amount of dimer. Figure 2 also demonstrates that effusion pressures of $CrBr_3$ are independent of the orifice area in the low temperature range, suggesting that the steady-state pressures in both cells are virtually equilibrium values. A slight fall-off from the apparent equilibrium curve is evident at the highest temperatures in the cell with the larger orifice.

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(1) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, Chapter 14.

(2) P. Clausing, *Ann. Physik*, **12**, 961 (1932).

(3) C. W. Foulk and A. T. Bawden, THIS JOURNAL, **48**, 2045 (1926).

(4) N. W. Gregory and R. O. MacLaren, *J. Phys. Chem.*, **59**, 110 (1955).

(5) For a more detailed description of these and other experiments, see the Doctoral Thesis of Rodney Jerome Sime, University of Washington, 1959.

(6) C. Wagner and V. Stein, *Z. physik. Chem.*, **192**, 129 (1942).

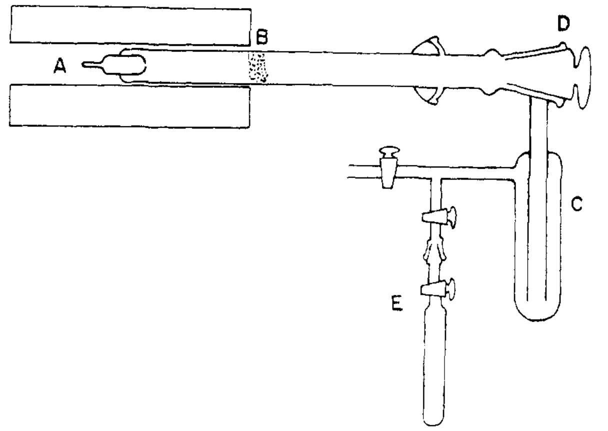

Fig. 1.—Knudsen effusion apparatus.

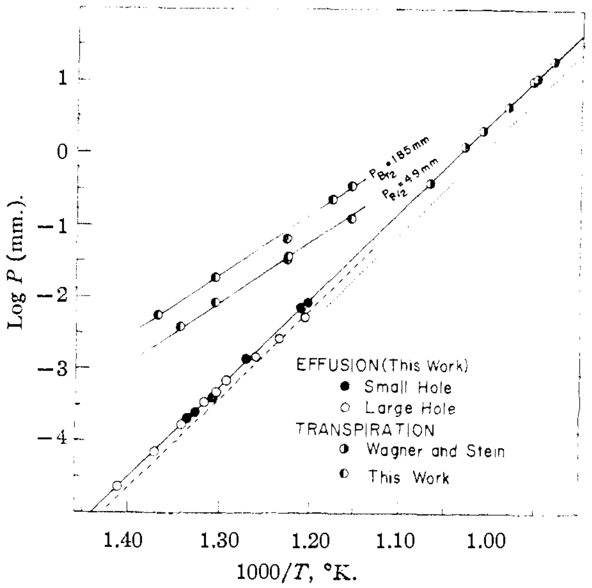

Fig. 2.—Chromium bromide vapor pressures over $CrBr_3$(s).

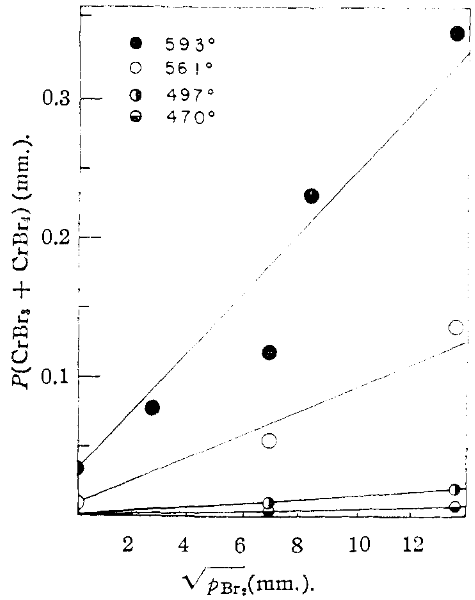

Fig. 3.—Br_2-$CrBr_3$ + $CrBr_4$ isotherms.

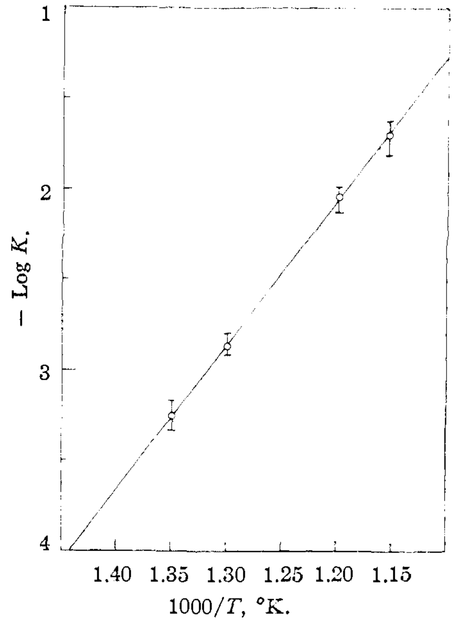

Fig. 4.—Equilibrium constant for $CrBr_3(s) + {}^1/_2Br_2(g) = CrBr_4(g)$.

The equation of the solid line (equilibrium 1)) based on the effusion work is: $\log P_{mm.} = -12380\ T^{-1} + 12.82$, which corresponds to $\Delta F^0 = \Delta H^0 - T\Delta S^0 = 56610 - 44.50T$ (std. state one at.) for the temperature range 708 to 1068°K.

As shown in Fig. 2, the total pressure of chromium halide over $CrBr_3$ at higher bromine pressures, determined by the transpiration method with bromine as the carrier gas, is much larger than obtained in our effusion work or than is indicated by the transpiration work of Wagner and Stein.[6] The chromium halide pressure varied with the bromine pressure in such a way as to indicate the formation of $CrBr_4$(g). At bromine pressures of 183 and 49 mm. the total pressure of chromium halide was determined from 457 to 593°, shown in Fig. 2. At the highest temperature and bromine pressure, the chromium halide vapor is about 90% $CrBr_4$. Measurements at 69 and 7 mm. bromine pressure were also made at 593° (not shown in Fig. 2). In effusion experiments the bromine pressures are so small that $CrBr_4$ is of negligible importance.

Equilibrium constants for reaction 2 were determined by plotting the total pressure of chromium halide *vs.* the square root of the bromine pressure at temperatures of 470, 497, 561 and 593° (Fig. 3). Lines shown are of the form $P(CrBr_4 + CrBr_3) = K_2(P_{Br_2})^{1/2} + K_1$. The slope of each line gives K_2 and the intercept K_1 at each temperature; K_1 was actually determined with better accuracy from the effusion data. In Fig. 4, the logarithm of K_2 is plotted against the reciprocal of the absolute temperature. The line drawn corresponds to the equation $\log K_2 = 7970T^{-1} + 7.52$ (P in mm.). Hence the standard (atm.) free energy equation for reaction 2 is: $\Delta F^0 = 36{,}400 - 27.8T$ (for the temperature interval 706 to 866°K.). The uncertainty in ΔH^0 is about two kcal.

Steady-state bromine pressures in the effusion cells (Fig. 5) were calculated from the amounts of

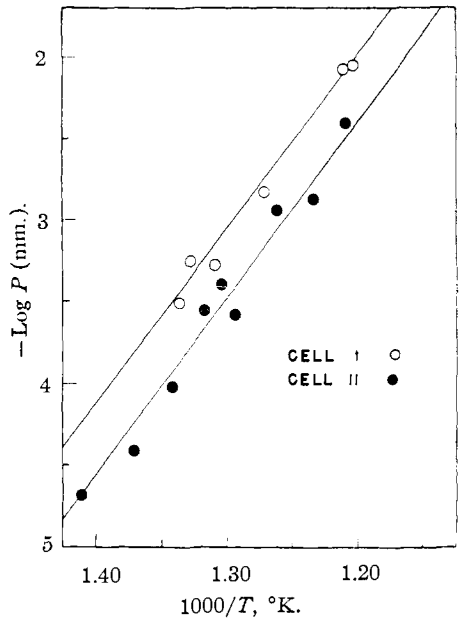

Fig. 5.—Bromine pressure over chromic bromide; effusion technique.

bromine collected in each of the runs for which $CrBr_3$ pressures were determined. The bromine pressures are much less consistent than the corresponding data for $CrBr_3$ (Fig. 2) taken from identical runs. A marked effect of orifice area is apparent in Fig. 5 but is not observed in Fig. 2. This suggests that the accommodation coefficients are quite different for the two processes. Reaction 3 is believed responsible for the release of bromine; complete decomposition of $CrBr_3$ to $CrBr_2$ at higher temperatures in vacuum systems has been observed in separate experiments. The vapor pressure of $CrBr_2$ is only about 1% of that of $CrBr_3$ in the temperature range of the present work and hence need not be considered.[5]

One series of effusion experiments was conducted in which decomposition (and vaporization) of a single sample of $CrBr_3$ was allowed to continue in successive runs until the residual material was about 30% decomposed. A continuous and marked fall-off of bromine pressures was observed, with the last measured value only 4% of those in the corresponding cell in Fig. 5. The scatter of data in Fig. 5 is undoubtedly associated in large part with this dependence on the degree of decomposition of the sample, since the runs shown in Fig. 5 were not conducted in such a way as to ensure the same final degree of decomposition in all cases. However the difference in the results from the cells with different orifice diameters cannot be attributed to the degree of decomposition, since a number of runs in cell 2 resulted in a smaller degree of decomposition than some of those in cell 1; the lower values in cell 2 are believed to result from a small accommodation coefficient for decomposition reaction. $CrBr_3$ pressures could not be conveniently followed in this long series of measurements; the vaporized material was allowed to accumulate outside the furnace. At the end, however, a rough measurement of the $CrBr_3$ vapor pressure, found to be *ca.* 40% of those in Fig. 2, was obtained by moving the furnace so the final sample could be collected separately.

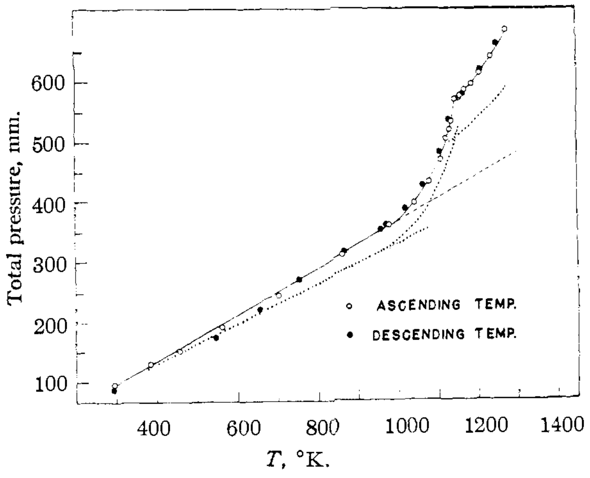

Fig. 6.—Total pressure above $CrBr_3 + Br_2$ mixture.

Effects of the type described in the preceding paragraph would be expected if $CrBr_3$ and $CrBr_2$ form a continuous series of solid solutions over this composition interval; however the pressure–composition relationship did not correlate well with Raoult's law and it should be noted that a marked decrease in the accommodation coefficients as the crystal surfaces become depleted in bromine could cause a similar effect. Further work will be necessary before the correct explanation can be given; it is apparent from the present findings that effusion bromine pressures cannot be used to determine the thermodynamic relationship of solid $CrBr_2$ and $CrBr_3$.

In view of the change of the bromine pressure with the degree of decomposition of the sample it is somewhat difficult to estimate the partial pressure of bromine which was present in Wagner and Stein's transpiration experiments. However, assuming pressures expected from our effusion results (Fig. 5) and equilibrium constants based on those evaluated for reaction (2), it appears that $CrBr_4$ was not present at significant concentrations in their experiments.

In an attempt to make an over-all check on the interpretation of data presented in this study, the total pressure developed in a quartz diaphragm gage,[4] in which was placed initially 3.22×10^{-5} mole of $CrBr_3$ and 96.5 mm. pressure of bromine at 21° (gage volume 17.1 ml.), was measured as a function of temperature and is shown in Fig. 6. The dotted line represents the total pressure expected from the perfect gas law and the equilibrium constants for reactions 1 and 2 (uncorrected for ΔC_p effects), including the effect of dissociation of bromine molecules at the highest temperatures. The marked break in the curve near 1145°K. indicates complete vaporization of the chromium bromide.

Two troublesome experimental difficulties were encountered: after cooling, the null point of the gage appeared to have shifted slightly and a small residual gas pressure (at Dry Ice temperature) was observed. The latter is believed due to hydrogen bromide, formed by reaction of the sample with a small amount of adsorbed water in the system (although the system was flamed strongly under high vacuum before bromine was admitted). If one assumes the number of moles of HBr formed by such a reaction is indicated by the increase in total pressure over that expected from the initial pressure of bromine at 700° (973°K.), and that this amount remains constant at higher temperatures, then the measured total pressures, corrected for the contribution from HBr, correspond well with the calculated curve. Even though these experimental difficulties seriously limit the effectiveness of this experiment, the results offer some support to the validity of the interpretation.

Data available concerning $CrCl_4$ may be compared with our results. The heat and entropy changes for the reaction

$$CrX_3(s) + {}^1/_2X_2(g) = CrX_4(g)$$

at 800°K. are 28.0 and 36.4 kcal. and 25.4 and 27.8 e.u., respectively, for X = Cl[7] and X = Br. These entropy changes appear reasonable although a quantitative estimate of the entropy of CrX_4 (g) molecules is difficult to make without spectroscopic data because of the large contribution of vibrational states at this high temperature.

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(7) H. A. Doerner, Bureau of Mines Bulletin, 577, 1937.

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The Reaction of Nitrogen(II) Oxide with Diethylamine

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The reaction between diethylamine and nitric oxide in ether solution and in the pure amine is described. Infrared and nuclear magnetic resonance spectroscopy indicate that the structure of the product is $Et_2NH_2^+Et_2NN_2O_2^-$. The sodium salt, $Na^+Et_2NN_2O_2^-$ was prepared. A reaction mechanism in which NO behaves as a Lewis acid is proposed to explain this reaction and the one with sulfite ion leading to the formation of $O_3SN_2O_2^{=}$.

Introduction

The nature of the reaction between sulfite ion and nitric oxide in basic aqueous solution has been a controversial subject.[2] The structure of the product was eventually established by X-ray diffraction[3] and infrared spectroscopy[4] but the reaction type has not yet been classified. We propose that this reaction and several others reported in the literature furnish evidence that nitric oxide can behave as an electron pair acceptor. In order to establish this reaction mode we are undertaking an investigation of the reactions of nitric oxide with a series of Lewis bases. Reaction conditions for preparing, and evidence for establishing the structure of $Et_2NH_2^+Et_2NN_2O^-$ are presented in this article. A general mechanism is tentatively proposed to classify both the amine and sulfite reactions.

Experimental

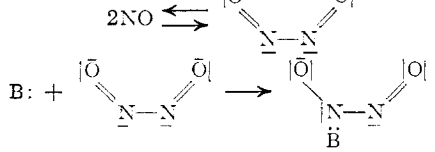
Eastman Kodak "White Label" anhydrous diethylamine (100 ml.) is dissolved in 150 ml. of diethyl ether (Merck, Reagent grade) contained in a dry, three-necked flask. Similar results are obtained from amine freshly distilled from BaO. The relative amounts of amine and ether are not critical. Two of the three necks serve as inlet and outlet, respectively, and the third accommodates a sealed stirrer. The flask is incorporated into a closed system and flushed with nitrogen to remove oxygen. The amine–ether solution is cooled to −78° and nitric oxide gas is slowly added. The commercial grade nitric oxide employed is purified by bubbling through 10 *M* sodium hydroxide and dried by passing through columns containing sodium hydroxide pellets. The product precipitates from solution as the reaction proceeds with stirring for a period of 15 hours. Upon filtration and washing with ether, 10.7 g. of crude product representing a yield of 11% was obtained.

Infrared spectra were obtained with a Perkin–Elmer model 21 infrared spectrometer with sodium chloride optics. The instrument was calibrated using water vapor absorption and the appropriate corrections applied to the reported spectra. The magnetic susceptibility was measured with a modified Curie magnetic balance. Nuclear magnetic resonance spectra were obtained using a Varian high resolution nuclear magnetic resonance spectrometer and associated magnet. Spectra were obtained using a 40 mc. probe.

Results and Discussion

In contrast to the abundance of literature concerning reactions of nitric oxide to produce the nitrosyl ion, there is very little evidence to indicate that nitric oxide is capable of behaving as an electron pair acceptor. The reaction with sulfite ion represents one possible example. The phase diagram for the binary system dimethyl ether–nitric oxide[5] indicates the formation of the compound $(CH_3)_2ON_2O_2$. The proposed existence of the acid $H_2N_2O_3$[6] and the preparation of salts of this acid[7] are further examples.

The following mechanism, consistent with the above observations and with those to be reported on the diethylamine-nitric oxide reaction, is tentatively proposed:



where B is an electron pair donor.

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[1] Abstracted in part from the Senior Thesis of F. E. Paulik, University of Illinois, 1957. Presented at the Fall (1959) Meeting of the American Chemical Society.

[2] J. Pelouz, *Ann. Pharm.*, **15**, 240 (1835); E. Weitz and F. Achterberg, *Ber.*, **66B**, 1718 (1933); F. Raschig, *Ann.*, **241**, 232 (1887); E. Divers and T. Haga, *J. Chem. Soc.*, **67**, 452 (1895); **69**, 1610 (1896); A. Hantzsch, *Ber.*, **27**, 3264 (1894).

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