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The Equilibrium between Nitric Oxide, Bromine and Nitrosyl Bromide

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Introduction

The formation of nitrosyl bromide from nitric oxide and bromine is of considerable interest because, kinetically, the reaction is one of very few third order homogeneous gas reactions. Since the reaction is readily and measurably reversible, it would be possible to predict the rate of decomposition of nitrosyl bromide if the standard free energy change as a function of the temperature were known accurately. Moreover, the reaction may find application in the study of other reversible reactions involving bromine or nitric oxide.

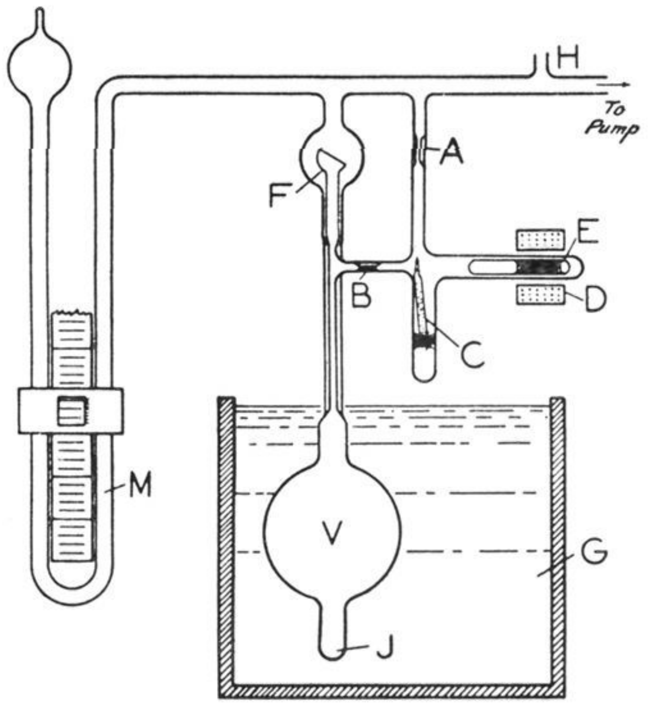

Fig. 1.—Reaction cell and auxiliary apparatus (not to scale).

The equilibrium has been studied by Trautz and Dalal,[1] but due to the manometer system which they used the results are not very accurate. Moreover, they postulate the existence of nitrosyl dibromide, $NOBr_2$, and nitrosyl tribromide, $NOBr_3$, although Dixon's[2] results with nitrosyl chloride do not indicate the existence of the corresponding chlorine compounds, which would be expected to be more stable. The experiments described in this paper were undertaken to determine accurately the equilibria in the reaction between nitric oxide and bromine to form nitrosyl bromide.

Preparation of Materials and Experimental Method

The bromine was prepared by treating a saturated solution of twice recrystallized potassium bromate and potassium bromide with c. p. concentrated sulfuric acid. The bromine was distilled from this mixture and then dried over specially purified anhydrous calcium bromide. The material was finally twice distilled from fresh portions of anhydrous calcium bromide, the middle fraction of the last distillation being that used in the experiments. At no time did the bromine come in contact with rubber or other organic matter, since an all-glass distilling system was used.

The nitric oxide used was prepared by a slight modification of the method described by Johnston and Giauque,[3] and was of high purity.

A preliminary series of equilibrium measurements was made using a reaction vessel of about 300 cc. capacity heated in an electric furnace, but the apparatus described below was finally adopted in order to decrease the errors due to external volume and temperature gradient.

The apparatus is shown diagrammatically in Fig. 1. V is a Pyrex reaction vessel of 1054.7 cc. capacity at 22°. G is a thermostat containing either water or molten hydrogenated cottonseed oil. The reaction vessel was connected to a Pyrex glass click-gage F and to the side-arm B by means of capillary tubing. A weighed amount of bromine to be used in a run was held in a tube C having an easily breakable tip. E is a glass enclosed iron hammer, and D a solenoid for operating it.

Several equilibrium measurements were made at different temperatures with each filling of the reaction vessel. In carrying out such a series of measurements the reaction vessel was first heated and evacuated for several hours. A convenient pressure of nitric oxide was then admitted at H and the system sealed off at A. The pressure of nitric oxide in the reaction vessel was determined by use of the click-gage and manometer M. By means of liquid air the nitric oxide was condensed in the tube J; the bromine bulb was then broken with the magnetic hammer and the bromine also allowed to condense in J. The side-arm was then sealed off at A and its volume (about 3 cc.) was determined. The pressure of nitric oxide in the reaction vessel was corrected for the small change in volume. After mixing the nitric oxide and bromine by alternately freezing and evaporating them several times, the thermostat was put in place, adjusted to some definite temperature, and pressure readings were taken until the system reached equilibrium. The thermostat was then readjusted to other temperatures and a number of measurements of equilibrium pressures at various temperatures were made, equilibrium being approached from both the low and high temperature sides. From these pressures and the known amounts of nitric oxide and bromine originally present in the reaction vessel the equilibrium con-

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[1] Trautz and Dalal, *Z. anorg. allgem. Chem.*, **110**, 1 (1920).

[2] Dixon, *Z. physik. Chem.*, Bodenstein Festband, 679 (1931).

[3] Johnston and Giauque, This Journal, **51**, 3194 (1929).

stants for the reaction $2NO(g) + Br_2(g) = 2NOBr(g)$ were calculated for each temperature.

The temperature of the thermostat varied not over ±0.1° at temperatures up to about 200° and not over ±0.2° above that. The temperature was measured by means of calibrated mercury thermometers kept totally immersed. The mercury manometer used was 12 mm. in diameter and by means of a vernier the pressure readings were made to within ±0.1 mm.

Five separate fillings of the reaction vessel were made, three with an excess of nitric oxide and two with an excess of bromine. In Table I are presented representative results of these runs. Only every third measurement is given in the table. The equilibrium constant for the reaction $2NO(g) + Br_2(g) = 2NOBr(g)$ is given by the expression

$$K_{\text{mm.}} = \frac{4\Delta p^2}{(p^0_{NO} - 2\Delta p)^2(p^0_{Br_2} - \Delta p)}$$

where p^0_{NO} is the pressure of nitric oxide which would exist at the temperature in question if no reaction had taken place, $p^0_{Br_2}$ the corresponding pressure of bromine and Δp the difference between $p^0_{NO} + p^0_{Br_2}$ and p, the observed pressure.

TABLE I

REPRESENTATIVE RESULTS OF THE EQUILIBRIUM MEASUREMENTS[a]

T, °K.	p, mm.	$\log_{10} K_{\text{mm.}}$
At 299.4°K.:	p^0_{NO} 99.3 mm.	$p^0_{Br_2}$ 41.6 mm.
296.9	110.5	0.7452
386.5	168.6	2.779
412.1	184.2	3.272
436.7	197.4	3.545
497.1	230.2	4.575
At 298.1°K.:	p^0_{NO} 98.6 mm.	$p^0_{Br_2}$ 116.8 mm.
296.8	175.7	0.7721
392.2	264.9	2.980
433.6	298.7	3.443
473.9	332.7	4.051
492.5	346.3	4.129
At 299.9°K.:	p^0_{NO} 173.8 mm.	$p^0_{Br_2}$ 73.2 mm.
299.9	192.7	0.8333
376.3	277.6	2.535
442.2	346.1	3.556
503.4	402.6	4.188
At 297.0°K.:	p^0_{NO} 181.0 mm.	$p^0_{Br_2}$ 77.3 mm.
273.1	175.9	0.0730
290.1	193.0	.5914
320.6	206.8	.9555
323.7	231.2	1.492
349.7	262.2	2.078
373.4	290.6	2.541
409.6	332.2	3.191
441.6	365.9	3.631
476.9	401.3	4.066
497.7	421.3	4.303
At 296.3°K.:	p^0_{NO} 101.4 mm.	$p^0_{Br_2}$ 150.4 mm.
290.6	205.0	0.5555
294.8	209.3	.7378
302.1	216.0	.9050
330.2	244.8	1.651
367.4	284.9	2.431
406.9	326.2	3.110
446.4	365.8	3.688
479.5	397.3	4.123
502.9	419.0	4.421

[a] All pressure measurements are given in millimeters of mercury at 22°.

The results are shown graphically in Fig. 2, where the logarithm of the equilibrium constant is plotted against the reciprocal of the absolute temperature. The shape of the curve gives no evidence for the existence of nitrosyl dibromide or nitrosyl tribromide in the gas phase at temperatures as low as 12°, even in the presence of a large excess of bromine.

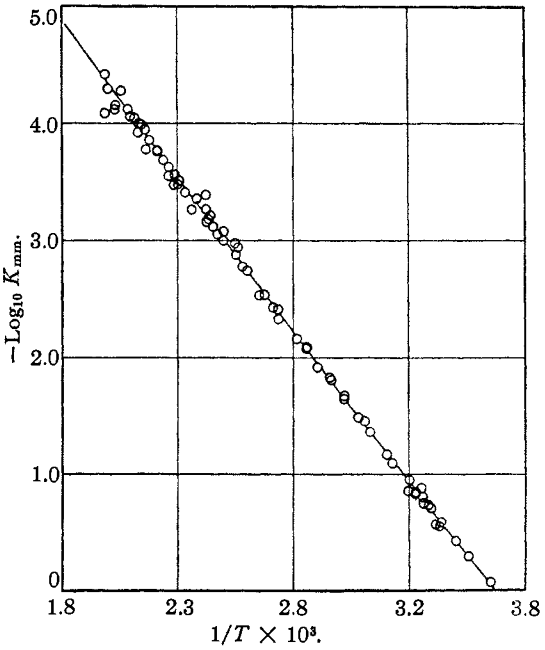

Fig. 2.

The error in the pressure measurements was ±0.1 mm., but since pressure differences are involved in the expression for the equilibrium constant, the error in this quantity may be ±4%, corresponding to an error of about 2% in log K at room temperature and less above that temperature. Because of the number of experiments made, the probable error in any equilibrium constant must be below ±2%, corresponding to an error in the heat content change accompanying the reaction of ±0.5%. The error in the free energy change calculated from the equilibrium constant at 25° is ±1%.

No correction was made for the small volume of the click-gage and capillary tubing which were out of the thermostat and at approximately room temperature. This volume was about one cubic centimeter and the correction due to this dead space would make a negligible difference in log K below 450°K. but may be as much as -1% at temperatures around 500°K.

When the results of the experiments are combined with specific heat data, the following expression for the standard change in heat content and free energy accompanying the reaction $2NO\ (g) + Br_2(g) = 2NOBr(g)$ are obtained

$$\begin{aligned} &NO(g),^4 && C_p = 7.922 - 0.00441\,T + 6.30 \times 10^{-6}T^2 \\ &Br_2(g),^5 && C_p = 7.710 + 0.00415\,T - 3.7 \times 10^{-6}T^2 \\ &NOBr(g),^6 && C_p = 5.07 + 0.0163\,T - 12.9 \times 10^{-6}T^2 \end{aligned}$$

Whence

$$\begin{aligned} \Delta C_p &= -13.41 + 0.0372\,T - 34.7 \times 10^{-6}T^2 \\ \Delta H^0 &= -8780 - 13.14\,T + 0.0186T^2 - 11.6 \times 10^{-6}T^3 \\ \Delta F^0 &= -8780 + 30.88\,T \log_{10}T - 51.26T \\ &\qquad - 0.0186T^2 + 5.8 \times 10^{-6}T^3 \end{aligned}$$

These expressions are valid in the temperature range 250–600°K.

Directly from the experimental curve and independent of specific heat data, we obtain

$$\begin{aligned} \Delta H^0_{298.1} &= -11{,}430 \pm 60 \text{ cal.} \\ \Delta F^0_{298.1} &= -2790 \pm 30 \text{ cal.} \\ \Delta S^0_{298.1} &= -29.0 \pm 0.3 \text{ cal./deg.} \end{aligned}$$

This last value, combined with the known entropies of bromine[7] and nitric oxide,[4] gives for the standard virtual entropy of NOBr, $S^0_{298.1} = 65.2 \pm 0.3$ cal./deg. When the free energy change for the reaction studied is combined with that for the formation of nitric oxide, 20,650 cal.,[8] the standard free energy of formation of nitrosyl bromide gas from the elements in their standard states at 25° becomes 19,260 cal.

Summary

The equilibrium in the reaction $2NO(g) + Br_2(g) = NOBr(g)$ has been measured in the temperature range from 273.1 to 520°K. From the results of the measurements the following thermodynamic equations have been derived for the reaction

$$\begin{aligned} \Delta H^0 &= -8780 - 13.41\,T + 0.0186\,T^2 - 11.6 \times 10^{-6}T^3 \\ \Delta F^0 &= -8780 + 30.88\,T \log_{10} T - 51.26\,T \\ &\qquad - 0.0186\,T^2 + 5.8 \times 10^{-6}T^3 \end{aligned}$$

At 25° the free energy of formation of NOBr(g) from the elements is 19,260 cal. The virtual entropy of NOBr(g) at 25° and one atmosphere is 65.2 ± 0.3 cal./deg.

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[4] Constructed from the data of Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933).

[5] Constructed from the data of Gordon and Barnes, *J. Chem. Phys.*, **1**, 694 (1933).

[6] In the absence of experimental data for nitrosyl bromide the equation given by Eastman, Bureau of Mines, Technical Paper, 1929, for the specific heat of sulfur dioxide was used.

[7] Brown, *Phys. Rev.*, **42**, 355 (1932).

[8] Giauque and Clayton, THIS JOURNAL, **55**, 4875 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constants of Benzoic Acid and of the Three Monochlorobenzoic Acids, at 25°, from Conductance Measurements[1]

BY BLAIR SAXTON AND HARRY F. MEIER

The ionization constants were determined by the method and technique described in an earlier paper[2] except for the following changes.

All measurements were made with the bridge described by Dike.[3]

A "flask cell" similar to cell B but constructed entirely of silica with the exception of two small Jena G 20–silica graded seals, used in inserting the electrode supports, was used in measuring the conductances of the acids. Cell B was used in measuring the conductances of the sodium salts of the acids. Purified nitrogen, saturated with water vapor, was substituted for air in the removal of carbon dioxide. The water was from the Barnstead "Conductivity Water Still." When distilled directly into the silica cell and "aerated" with nitrogen its specific conductance was slightly lower than 1×10^{-7} mhos. Since a considerable amount of the work had been completed before the publication of the new measurements on potassium chloride by Jones and Bradshaw,[4] the results here reported are based upon the older measurements on the 0.01 demal solution given by Parker and Parker.[5] As pointed out in our previous paper,[4] both standards will give the same value of the ionization constant. The cell constant for the silica cell, C, is 1.0559.

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[1] This paper contains material which represents part of the dissertation submitted by Harry F. Meier to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[2] Saxton and Langer, THIS JOURNAL, **55**, 3638 (1933).

[3] Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[4] Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

[5] Parker and Parker, *ibid.*, **46**, 312 (1924).