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Thermodynamic Properties of Perbromyl Fluoride (BrO_3F)[1]

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Calorimetric measurements of the enthalpy of hydrolysis of BrO_3F to HF and $HBrO_4$ are reported. From these experiments the enthalpy of formation ($\Delta H_f°_{298.15}$) of $BrO_3F(l)$ was deduced to be 26.78 ± 0.25 kcal mol^{-1}. Between 188 and 292°K, the vapor pressure of BrO_3F is given by $\ln p = 17.6986 - 3048.45T^{-1}$, where p is in Torr. This equation leads to an enthalpy of vaporization, $\Delta H_{vap}°$, of 6.06 ± 0.06 kcal mol^{-1}. Thus, $\Delta H_f°_{298.15}(BrO_3F(g)) = 32.84 \pm 0.26$ kcal mol^{-1}. By means of statistical mechanics, the standard entropy of the ideal gas, $S°_{298.15}(BrO_3F(g))$, has been calculated as 71.4 ± 2 cal deg^{-1} mol^{-1}.

Introduction

The synthesis of perbromic acid and the alkali perbromates[2] led to the subsequent preparation of perbromyl fluoride, BrO_3F.[3] This compound is the acid fluoride of perbromic acid and is analogous to perchloryl fluoride, ClO_3F. However, whereas perchloryl fluoride is rather inert, perbromyl fluoride is quite reactive. Thus, BrO_3F hydrolyzes rapidly and attacks glass at room temperature,[4] whereas ClO_3F does neither.[5]

Inasmuch as the perbromates were thought until quite recently to be nonexistent, the thermodynamic properties of these compounds and their derivatives are of fundamental interest. The thermodynamics of potassium perbromate and the aqueous perbromate ion[6] have already been elucidated, and in this paper we shall deal with some of the thermodynamic properties of BrO_3F.

The present investigation had as its main goals (a) the determination of the enthalpy of formation of BrO_3F, $\Delta H_f°_{298.15}$, by calorimetric measurements of the enthalpy of hydrolysis according to

$$BrO_3F(l) + H_2O(l) \longrightarrow HF \cdot HBrO_4(aq) \qquad (1)$$

and (b) the measurement of the vapor pressure of BrO_3F and the derivation therefrom of its enthalpy of vaporization, $\Delta H_{vap}°$. It was also necessary in auxiliary experiments to determine the enthalpy of mixing of HF and $HBrO_4$, according to

$$HF(aq) + HBrO_4(aq) \longrightarrow HF \cdot HBrO_4(aq) \qquad (2)$$

Experimental Section

Preparation of Reagents.—Perbromyl fluoride was synthesized by the reaction of potassium perbromate with antimony pentafluoride in redistilled liquid hydrogen fluoride. It was freed from HF and SbF_5 by passage through pellets of sodium fluoride. The potassium perbromate used in the synthesis was prepared and purified by methods described elsewhere.[2] Examination of the BrO_3F in a Bendix time-of-flight mass spectrometer confirmed the absence of significant impurities. Perbromic acid, $HBrO_4$, was prepared according to the procedure given previously.[2] The hydrofluoric acid used in the auxiliary experiments was "Baker Analyzed" reagent grade material. It was not purified further. For the enthalpy of hydrolysis experiments, twice-distilled, air-free water was employed.

Calorimetric Equipment.—An LKB-8700 Precision calorimetric system, which included an 18-carat gold reaction vessel, was used in the investigation. The reaction vessel was equipped with a reentrant well into which was inserted the probe of a quartz-crystal thermometer. The stirrer and ampoule-holder assembly were constructed from Kel-F plastic.[7] All temperature measurements were made with a Hewlett-Packard Model 2801-A quartz crystal thermometer.

In solution calorimetric studies, the sample, before dissolution or reaction, is customarily contained in a glass ampoule. Occasionally, when the sample reacts with glass, ampoules constructed of Kel-F have been used.[8] In the present investigation, because of the significant reactivity of perbromyl fluoride toward even Kel-F and Teflon, it was necessary to use platinum for the ampoule material. These ampoules were essentially hollow cylinders of approximately 0.6 ml internal volume, with one end closed by means of a 5-mil thick platinum window welded to the walls. A platinum filling tube ($^1/_8$-in. o.d.) was welded to the other end of the ampoule. Preliminary experiments had shown that 5-mil platinum windows could be readily pierced by the vertical spike on the base of the reaction vessel. Two experiments were performed to determine the enthalpy of breaking of the ampoule windows, ΔH_{break}. The platinum ampoules, identical with those used in the enthalpy of hydrolysis experiments, contained water in order to obviate the correction for the enthalpy of vaporization of water into the ampoule. The measured enthalpies of breaking were 0.249 and 0.241 cal, and a mean value of 0.245 cal was taken for ΔH_{break}.

Calorimetric Procedures and Measurements.—Each ampoule used in the experiments with BrO_3F was cleaned by heating to a bright red color in a flame. It was then attached to a Monel vacuum line *via* the filling tube and checked for leaks. When a satisfactory vacuum was established, a predetermined volume of BrO_3F gas was condensed into the ampoule by cooling with liquid nitrogen. Upon completion of the transfer, the filling tube was crimped closed. About 30 min later, after thermal equilibration, the ampoule and its contents were weighed accurately, attached to the ampoule-holder assembly, and placed in the calorimeter vessel along with 99.345 g of water. After the forerating period, the platinum window was pierced and rapid hydrolysis ensued. In order to ensure that the solution in the reaction vessel was at a uniform concentration, the stirrer assembly was raised and lowered several times, about 2 min after the commencement of hydrolysis. When the run was completed, the product solution was siphoned off for analysis, and the ampoule was removed, dried thoroughly, and weighed.

In another set of experiments, Kel-F ampoules containing 47.3% aqueous hydrofluoric acid were broken in a solution of $HBrO_4$ in order to measure the enthalpy of mixing according to reaction 2. The procedure followed was similar to that used for the BrO_3F runs.

The mean energy equivalent of the calorimetric system, $\bar{\varepsilon}(\text{calor})$, was determined by electrical calibrations performed before and after each measurement of the enthalpy of reaction.

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

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[7] P. A. G. O'Hare, G. K. Johnson, and E. H. Appelman, *ibid.*, **9**, 332 (1970).

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TABLE I
VAPOR PRESSURE OF PERBROMYL FLUORIDE AS A FUNCTION OF TEMPERATURE

T, °K	p, Torr	
	Measd	Calcd[a]
188.05	5 ± 1.5	4.4
193.55	7 ± 1.5	7.0
205.75	16 ± 1.5	17.9
216.25	35 ± 1.5	36.7
227.75	72 ± 1.6	74.7
237.05	125 ± 1.6	126.3
250.45	253 ± 2.0	251.3
261.30	424 ± 2.5	416.6
273.15	689 ± 3.5	691
282.62	994 ± 4.4	1004
291.85	1418 ± 5.5	1413

[a] By means of eq 3.

The calibrations were made at the same temperatures as the enthalpy measurements.

Postreaction Analysis.—In order to characterize as thoroughly as possible the products of reaction, a number of analyses were performed on the hydrolysates from the calorimetric experiments. These analyses were for total acid, total oxidizing power, Br_2 + HOBr, BrO_3^-, HBr, and trace metals.

The solutions were analyzed for total acid by titration with sodium hydroxide, which had been standardized against potassium acid phthalate. The total oxidizing power of the solutions was determined by iodometric titration after reduction with 12 *M* HBr.[2] Primary standard grade potassium iodate was used to standardize the thiosulfate used for the iodometric titration.

After reduction with 0.3 *M* Br^- at about pH 2, the combined oxidizing power of Br_2 + HOBr in the solution was determined colorimetrically as Br_3^-. The combined oxidizing power of Br_2 + HOBr + BrO_3^- was determined similarly, except that the reductant used was 0.4 *M* HBr.

TABLE II
CALORIMETRIC RESULTS FOR THE HYDROLYSIS OF $BrO_3F(l)$[a]

m', g	0.49953	0.46206	0.45950	0.46326	0.47200
x,[b] mol	1622	1753	1763	1748	1716
$\bar{\epsilon}$(calor), cal deg^{-1}	105.363	105.343	105.304	105.211	105.250
Δt_c, deg	1.03867	0.96254	0.96507	0.96850	0.98820
$\bar{\epsilon}$(calor)($-\Delta t_c$), cal	−109.437	−101.397	−101.626	−101.897	−104.008
ΔH_{break}, cal	0.245	0.245	0.245	0.245	0.245
ΔH_{vap}, cal	0.190	0.190	0.190	0.184	0.178
ΔH_{diln},[c] cal	−0.048	0.009	0.016	0.009	−0.003
ΔH_r, cal g^{-1}	−218.31	−218.48	−220.18	−219.01	−219.47
ΔH_r, kcal mol^{-1}	−32.07	−32.09	−32.34	−32.17	−32.24

Av $\Delta H_r = -32.18 \pm 0.05$[d] kcal mol^{-1}

[a] For the reaction $BrO_3F(l) + xH_2O \rightarrow HF \cdot HBrO_4 \cdot (x - 1)H_2O$. [b] The calorimeter contained 99.345 g of water. [c] This term is the enthalpy of dilution of the product solution from $x - 1$ H_2O to 1724 H_2O. [d] Standard deviation of the mean.

Trace metals were detected by emission spectrography, and Br^- was determined nephelometrically as AgBr.

Analytical Results and Interpretation.—The total acid found was in excellent agreement with the amount required by eq 1. The total oxidizing power was also in reasonable agreement, but tended to be somewhat low (by 0.1–1.0%). Typically, the quantities of Br_2 + HOBr and of BrO_3^- were about 0.2–0.3 and 3–6 μmol, respectively, per experiment. We have found, however, that the reaction vessel is itself capable of reacting with substantial amounts of aqueous Br_2. Hence the observed quantities of Br_2 + HOBr must be regarded as lower limits. About 200–400 μg of silver was usually found per experiment, although about 800 μg was found in the third experiment (Table II). The silver was presumably leached out of the reaction vessel. Bromide was never found to exceed the detection limit of about 100 μg per experiment.

Even though several plausible mechanisms can be postulated for the production of Br_2, HOBr, and BrO_3^- and for the release of the silver, it is not possible from the available chemical evidence to identify uniquely the reactions involved. However, the thermal corrections corresponding to each of the plausible processes were calculated, and it appears that if an uncertainty of 1 cal g^{-1} is assigned to the measured heat of hydrolysis in addition to the standard deviation, ample allowance is thereby made for any likely side reactions.

Vapor Pressure Measurements.—The vapor pressure of BrO_3F at various temperatures was measured in a well-fluorinated Monel vessel. Pressures were determined with a Monel Bourdon gauge having a resolution of approximately ±1 Torr. This gauge was calibrated against a Texas Instrument Co. high-precision quartz Bourdon gauge which, in turn, was calibrated against a dead-weight gauge. Temperatures were measured with an iron–constantan thermocouple, which was calibrated by comparison with a platinum resistance thermometer.

Results

In Table I are given the vapor pressures of BrO_3F at various temperatures. The vapor pressure *vs.* temperature data were weighted according to the uncertainties given in the table and were fitted by the method of least squares to the equation

$$\ln p = 17.6986 - 3048.45/T \qquad (3)$$

in which p, the vapor pressure, is in Torr, and T is in degrees Kelvin. The enthalpy of vaporization, $\Delta H_{vap}°$, deduced by means of the Clausius–Clapeyron equation, is 6.06 ± 0.06 kcal mol^{-1}. The uncertainty is *twice* the calculated external standard deviation.

Calorimetric data for the hydrolysis of $BrO_3F(l)$ according to eq 1 are given in Table II. Symbols used in this table have been explained either in the present text or in previous communications from this Laboratory.[6,7] The correction denoted by ΔH_{vap} is for the saturation of the vapor space of the ampoule and was calculated from the density of the liquid, the enthalpy of vaporization, and eq 3. The density of the liquid was measured in a Teflon pycnometer and found to be about 2.2 g cm^{-3} at 20°. For the conversion of ΔH_r from a gram to a molar basis, the molecular weight of BrO_3F was taken to be 146.9006.

The calculation of $\Delta H_f°_{298.15}(BrO_3F(l))$ is outlined in Table III. As mentioned previously, the enthalpy of mixing of HF with $HBrO_4$ was determined in separate experiments; because this enthalpy, ΔH_2 in Table III, is rather small, we decided not to present a detailed tabulation of the experimental data.

Discussion

In the present investigation, a value of 26.78 ± 0.25 kcal mol^{-1} has been determined for the standard enthalpy of formation of $BrO_3F(l)$. Some additional thermodynamic properties of perbromyl fluoride are given in Table IV. $S°_{298}(BrO_3F(g))$ was calculated by means of the standard formulas of statistical mechanics.[9] In this computation, vibrational frequencies were taken from the study by Claassen and Appelman,[4] and the structural data, *viz.*, l(Br–O) = 1.55 Å, l(Br–F) = 1.72 Å, ∠OBrO = 116°, and ∠OBrF = 100°, were estimated by analogy with ClO_3F.[10] The sym-

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TABLE III

CALCULATION OF $\Delta H_f{}^\circ{}_{298.15}(\mathrm{BrO_3F(l)})$[a,b]

1.	$\mathrm{HBrO_4 \cdot HF \cdot 1724H_2O \rightarrow BrO_3F(l) + 1725H_2O(l)}$	$\Delta H_1 = 32.18 \pm 0.18$ kcal mol^{-1} [c]
2.	$\mathrm{HBrO_4 \cdot 1723H_2O + HF \cdot 1.237H_2O \rightarrow HF \cdot HBrO_4 \cdot 1724.237H_2O}$	$\Delta H_2 = -0.80 \pm 0.05$ kcal mol^{-1} [c]
3.	$\mathrm{0.5F_2(g) + 0.5H_2(g) + 1.237H_2O(l) \rightarrow HF \cdot 1.237H_2O}$	$\Delta H_3 = -76.17 \pm 0.06$ kcal mol^{-1} [d]
4.	$\mathrm{0.5Br_2(l) + 2O_2(g) + \infty H_2O(l) \rightarrow BrO_4^- \cdot \infty H_2O}$	$\Delta H_4 = 3.19 \pm 0.15$ kcal mol^{-1} [e]
5.	$\mathrm{BrO_4^- \cdot \infty H_2O + 0.5H_2(g) \rightarrow (H^+ + BrO_4^-) \cdot \infty H_2O}$	$\Delta H_5 = 0 \pm 0$ kcal mol^{-1} [f]
6.	$\mathrm{(H^+ + BrO_4^-) \cdot \infty H_2O \rightarrow HBrO_4 \cdot 1723H_2O + (\infty - 1723)H_2O(l)}$	$\Delta H_6 = 0.06 \pm 0.05$ kcal mol^{-1} [g]
7.	$\mathrm{H_2O(l) \rightarrow H_2(g) + 0.5O_2(g)}$	$\Delta H_7 = 68.32 \pm 0.02$ kcal mol^{-1} [f]
8.	$\mathrm{0.5Br_2(l) + 0.5F_2(g) + 1.5O_2(g) \rightarrow BrO_3F(l)}$	$\Delta H_f{}^\circ{}_{298.15}[\mathrm{BrO_3F(l)}] = 26.78 \pm 0.25$ kcal mol^{-1}

[a] Species in this table are in the aqueous state, unless designated otherwise. [b] Uncertainties are twice the overall standard deviation. [c] Measured in present investigation. [d] Reference 8. [e] Reference 6. [f] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand.* (*U. S.*), *Tech. Note*, **No. 270-3** (1968). [g] Estimated value based on similarity to other perhalates: V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," Report NSRDS-NBS-2, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1965.

TABLE IV

THERMODYNAMIC PROPERTIES OF PERBROMYL FLUORIDE AT 298.15°K

	S°, cal deg^{-1} mol^{-1}	$\Delta S_f{}^\circ$,[a] cal deg^{-1} mol^{-1}	$\Delta H_f{}^\circ$, kcal mol^{-1}	$\Delta G_f{}^\circ$, kcal mol^{-1}
$\mathrm{BrO_3F(l)}$	49.4 ± 3	-66.5 ± 3	26.78 ± 0.25	46.61 ± 0.92
$\mathrm{BrO_3F(g)}$	71.4 ± 2	-44.5 ± 3	32.84 ± 0.26	46.11 ± 0.92

[a] $S^\circ{}_{298}$ values for $\mathrm{Br_2(l)}$, $\mathrm{O_2(g)}$, and $\mathrm{F_2(g)}$ were taken from the "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1960–1965.

metry number was taken to be 3, in accordance with the tetrahedral C_{3v} symmetry deduced from the spectral studies.[4] The ground-state quantum weight was assumed to be unity. $S^\circ{}_{298}(\mathrm{BrO_3F(l)})$ was taken to be equal to $S^\circ{}_{298}(\mathrm{BrO_3F(g)}) - \Delta H_{\mathrm{vap}}{}^\circ/T_{\mathrm{B}}$. From eq 3, T_{B} the normal boiling point, was calculated to be 275.5°K.

The hydrolyses of $\mathrm{BrO_3F}$ and $\mathrm{ClO_3F}$ may be written

$$\mathrm{BrO_3F(g) + H_2O(l) \longrightarrow BrO_4^-(aq) + HF(aq) + H^+(aq)} \quad (4)$$

$$\mathrm{ClO_3F(g) + H_2O(l) \longrightarrow ClO_4^-(aq) + HF(aq) + H^+(aq)} \quad (5)$$

Based on the appropriate $\Delta G_f{}^\circ$ values[6,11,12] we find the Gibbs free energy of reaction 4 to be 4.3 kcal mol^{-1} more negative than that of reaction 5. Hence, $\mathrm{BrO_3F}$ is slightly less stable with respect to perbromate ion than is $\mathrm{ClO_3F}$ with respect to perchlorate ion. This difference helps to explain the high reactivity of $\mathrm{BrO_3F}$ with such substances as water and glass, although purely kinetic effects are doubtless also involved.

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Anomalous Reactions of Triphenylchlorosilane with Metal Carbonyl Anions

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Silyl halides react in an anomalous fashion with most metal carbonyl anions to give disiloxanes. The metal carbonyl anion may rearrange to polynuclear anions, abstract hydrogen from the solvent or other sources, be oxidized to the dimer or higher oligomers, or be halogenated by the silyl halide. Increasing the nucleophilicity of the metal carbonyl anion by phosphine substitution was thought to be a possible mechanism for suppressing the anomalous reaction, but only tricarbonyltriphenylphosphinecobaltate(1−) gives a normal substitution product. Germanium and tin halides give smooth substitution reactions except when bulky substituents on the anion cause severe steric hindrance.

Introduction

In connection with our research efforts aimed at stabilizing p_π–p_π bonds[1] between carbon and its congeners, we desired a means of attaching silicon, bearing reactive functional groups, to a transition metal carbonyl moiety. In the past 10 years or so, a large number of compounds containing bonds between a transition metal and silicon, germanium, or tin have been reported. The methods used to prepare these compounds are rather varied, as the following examples illustrate:[2] (A) reaction of a silyl metallic with a metal halide[3,4]

$$\mathrm{Ph_3SiLi + Cp_2ZrCl_2 \longrightarrow Cp_2Zr(Cl)SiPh_3} \quad (1)$$

(B) reaction of a silylamine with a metal hydride[3]

$$\mathrm{Me_3SiNMe_2 + CpMo(CO)_3H \longrightarrow CpMo(CO)_3SiMe_3 + HNMe_2} \quad (2)$$

(C) reaction of group IV hydrides with transition metal compounds[5,6]

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(2) The following abbreviations will be used throughout the text: Cp, π-$\mathrm{C_5H_5}$; Ph, $\mathrm{C_6H_5}$; Me, $\mathrm{CH_3}$; THF, tetrahydrofuran.

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