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Thermodynamic Functions of Thionyl Bromide

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The thermochemistry of thionyl bromide was investigated at 25° C. in a conventional reaction calorimeter. The standard enthalpy of formation of the liquid is −40.2 ± 0.3 kcal. per mole and statistical thermodynamic functions are calculated for the gas.

THE CHEMISTRY of the thionyl halides (SOX_2) has been included in a recent review (*2*). The thermal stability of these compounds decreases with increasing molecular weight, and this fact is reflected in the thermodynamic and structural data available.

Experiments on the photodecomposition of thionyl bromide by Hussain and Samuel (*5*) give two estimates (*14*) for $\Delta H_f^\circ[SOBr_2, g]$, −21.8 and −27.2 kcal. per mole. The updated version (*15*) of the National Bureau of Standards Circular 500 (*10*) reports the datum $\Delta H_f^\circ[SOBr_2, g] = -17.7$ kcal. per mole. The source of this latter figure is not clear. The value reported here diverges widely from the above. A conventional reaction calorimeter has been utilized to investigate the aqueous hydrolysis of thionyl bromide at 25° C. and molecular structure and spectroscopic data were used to calculate thermodynamic functions in the gas phase.

EXPERIMENTAL

Materials. Thionyl bromide was prepared by the method of Hibbert and Pullman (*4*) which involved passing dry hydrogen bromide gas through thionyl chloride. The product distilled at 39° C./15 mm. of Hg as an orange-yellow liquid. It was redistilled at 0.1 mm. of Hg as a clear yellow liquid and stored at −20° C. Found: Br, 76.6; Calculated for $SOBr_2$: Br, 76.9%.

Calorimeter. This was of the constant-temperature-environment type fully immersed in a thermostat maintained at 25.0 ± 0.01° C. Details of construction may be found elsewhere (*1*). Thermal leakage corrections were made by the equal areas method, which is satisfactory (*8*) when a net precision of ±0.5% is required. The precision and accuracy of the equipment were assessed by two standard reactions, one exothermic and the other endothermic. For the enthalpy of neutralization of tris(hydroxymethyl)-aminomethane (THAM) in excess 0.1*M* hydrochloric acid, the mean of seven determinations was −7.15 ± 0.03 kcal. per mole at 25° C. and $n = 600$ [lit. (*3*), −7.107 ± 0.004 kcal. per mole at 25° C. and $n = 1350$]. The enthalpy of dilution of THAM is negligible. For the enthalpy of solution of potassium chloride in water, the mean of five determinations was +4.23 ± 0.02 kcal. per mole at 25° and $n = 200$ [lit. (*3*), 4.200 ± 0.009 kcal. per mole at 25° C. and $n = 200$]. n is the mole ratio of water to solute. The precision of the electrical calibration was ±0.1%. This error was an order of magnitude smaller than the error in the observed heats of hydrolysis and, hence, was ignored. The limiting feature on the accuracy of the results reported here is the purity of the thionyl bromide at reaction time. Further details of the electrical calibration procedure are given in Reference (*1*). Enthalpies are reported in terms of the defined thermochemical calorie—1 cal. = 4.1840 abs. joule.

RESULTS

Thionyl bromide hydrolyzed rapidly and quantitatively, but without undue violence, according to the following equation:

$$SOBr_2(\text{liq.}) + (n + 1)H_2O(\text{liq.}) = [SO_2 + 2HBr]nH_2O$$

Hence,

$$\Delta H_f^\circ[SOBr_2, \text{liq.}] = 2\Delta H_f^\circ[HBr, \tfrac{n}{2}H_2O] + \Delta H_f^\circ[SO_2 nH_2O] - \Delta H_f^\circ H_2O(\text{liq}) + \Delta H_{\text{mix}} - \Delta H_{\text{obsd}}$$

where ΔH_{obsd} is the observed enthalpy of hydrolysis and ΔH_{mix} is the enthalpy of mixing of the products of hydrolysis (Table I). This latter term is small and may be estimated from the data of Johnson and Sunner (*7*). These workers measure the heat of mixing of aqueous hydrobromic acid with an aqueous sulfuric acid–sulfur dioxide solution. Selecting $n = 1240$ and ignoring the effect of the sulfuric acid, Sunner and Johnson's Equation 5 may be combined with:

$$[HBr\ 5.59H_2O] + 614.4H_2O = [HBr\ 620H_2O]\ \Delta H(25^\circ) = -1.97 \text{ kcal. per mole}$$

Table I. Heat of Hydrolysis (ΔH_{obsd}) of $SOBr_2$ in Deoxygenated Water

$T = 25.0 \pm 0.1°$ C.

Wt. of Sample, G.	n	ΔH_{obsd}, Kcal. Per Mole	ΔH_f° $SOBr_2$(Liq.), Kcal. Per Mole
1.2546	1381	-29.0_4	−40.2
1.9447	891	-29.0_1	−40.1
1.3087	1322	-28.7_2	−40.5
1.2891	1344	-29.1_4	−40.1

$\Delta H_f^\circ[SOBr_2, \text{liq.}] = -40.2 \pm 0.3$[a] kcal. per mole

[a] The error for four observations is taken as the range of the observed data plus the errors on the ancillary data combined as the root of the sum of the squares.

(*15*) to obtain:

$$|\mathrm{HBr}\ 620\ \mathrm{H_2O}| + |0.264\ \mathrm{SO_2} + 1466.8\ \mathrm{H_2O}| =$$

$$|\mathrm{HBr} + 0.264\ \mathrm{SO_2} + 2086.8\ \mathrm{H_2O}|\ \Delta H(25^\circ) = +0.38 \text{ kcal. per mole}$$

Hence, $\Delta H_{\text{mix}} = 0.4 \pm 0.2$ kcal. per mole, where the assigned limits of error are assumed to include the uncertainty in ignoring the effect of the sulfuric acid on the mixing and the different relative stoichiometry in Johnson and Sunner's final thermodynamic state and that used here.

The calorimetric liquid was freshly boiled distilled water, through which a stream of nitrogen was passed prior to calorimetry. The air space in the calorimeter was flushed with oxygen-free nitrogen before loading. Under these conditions, the concentration of sulfate formed by oxidation was negligible.

The ancillary thermodynamic data were:

$$\Delta H_f^\circ|\mathrm{SO_2}\cdot 2500\mathrm{H_2O}|(7) = -80.33 \pm 0.26 \text{ kcal. per mole.}$$

$$\Delta H_f^\circ|\mathrm{HBr}\cdot 3000\mathrm{H_2O}|(13) = -29.05 \pm 0.09 \text{ kcal. per mole.}$$

$$\Delta H_f^\circ|\mathrm{H_2O}, \text{liq.}|(15) = -68.315 \text{ kcal. per mole.}$$

The heats of dilution of aqueous SO_2 and HBr were taken from Wagman *et al.* (*15*). The first two data differ marginally from those given in (*15*)—i.e., −79.776 and −28.994 kcal. per mole. Mayes and Partington (*9*) quote vapor pressure data for $SOBr_2$ (range 45° to 138° C.) over the pressure range 22 to 773 mm. of Hg. The results can be represented by

$$\log_{10} P_{\text{mm}} = -\frac{2218}{T(^\circ\text{K.})} + 8.273$$

from which a figure for the latent heat of vaporization (assumed at the mean temperature) was derived.

$$\Delta H(\text{liq.} \rightarrow \text{g., } 91^\circ \text{C.}) = 10.1 \text{ kcal. per mole.}$$

Using Watson's equation (*6, 16*) this datum was converted to 25° C. and was assigned an error of ±0.5 kcal.

$$\Delta H(\text{liq.} \rightarrow \text{g., } 25^\circ \text{C.}) = 11.0 \pm 0.5 \text{ kcal. per mole.}$$

and

$$\Delta H_f^\circ|\mathrm{SOBr_2}, g| = -29.2 \pm 0.6 \text{ kcal. per mole.}$$

This latter datum diverges considerably from the figure quoted in the updated (*15*) N.B.S. Circ. 500—i.e., −17.7 kcal. per mole.

The molecular structure of thionyl bromide is available from an electron diffraction study (*12*). The data are: r(S—O) = 1.45A. (assumed), r(S—Br) = 2.27 ± 0.02A., $\mathrm{Br\hat{S}Br} = 96 \pm 2^\circ$, and $\mathrm{O\hat{S}Br} = 108 \pm 3^\circ$. Stammreich *et al.* (*11*) quote the following fundamental vibrational frequencies: 1211, 405, 267, 120, 379, and 223 cm.$^{-1}$. Using these data, and a rigid-rotator, simple harmonic oscillator assumption, the statistical thermodynamic functions for the assumed perfect gas at 1 atm. were calculated. The computation was performed on a digital computer and the results are given in Table II. To estimate the error in these data, the bond lengths were varied within the experimental limits and a similar procedure applied to the bond angles and vibrational frequencies. The error in r(S—O) was assumed to be ±0.02A. and the error in the frequencies was taken as ±2 cm.$^{-1}$ for the highest, ±5 cm.$^{-1}$ for the lowest, and ±3 cm.$^{-1}$ for the remainder. The calculation was repeated with the adjusted data and the maximum errors of 298.15° K. are, $C_p^\circ = 16.66 \pm 0.03$, $(H_T^\circ - H_0^\circ)/T = 12.88 \pm 0.05$, $-(G_T^\circ - H_0^\circ)/T = 66.66 \pm 0.14$ and $S^\circ = 79.54 \pm 0.15$ cal. deg.$^{-1}$ mole^{-1}.

Table II. Thermodynamic Functions for Thionyl Bromide—Perfect Gas at 1 Atm.

T, °K.	C_p°	$\frac{H_T^\circ - H_0^\circ}{T}$	$-\left[\frac{G_T^\circ - H_0^\circ}{T}\right]$	S°
	Cal. Per Deg. Per Mole			
100	11.52	9.21	54.75	63.96
200	15.07	11.37	61.82	73.20
273.15	16.34	12.55	65.55	78.10
298.15	16.66	12.88	66.66	79.55
300	16.68	12.90	66.74	79.65
400	17.60	13.97	70.61	84.58
500	18.20	14.76	73.82	88.58
600	18.60	15.37	76.57	91.94
700	18.88	15.85	78.97	94.83
800	19.08	16.25	81.12	97.36
900	19.23	16.57	83.05	99.62
1000	19.34	16.84	84.81	101.65

$I_A I_B I_C = 1.7636 \times 10^{-112}$ g.^{3} cm.^{6}

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