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Solubility of Antimony Oxyhalides in Water

Toshiaki KISHIKAWA and Taizo YOSHIDA

Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University, Kurokami-cho, Kumamoto

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The hydrolytic behavior[2] of a neutron-irradiated antimony tribromide has indicated the presence of free bromine(^{82m}Br) at the end of the irradiation. Such a bromine atom must be the result of hydrolysis, of a solubility equilibrium of the hydrolyzed product, or of the Szilard-Chalmers process.[3] The present paper will deal with the hydrolytic behavior of antimony trihalides (chloride, bromide, and iodide), a study conducted by means of a radiotracer technique, X-ray diffractional identification, and X-ray spectrochemical analysis, and with the radiometric determination of the solubilities of the hydrolyzed products.

If water is added to antimony trihalides, various oxyhalides can be obtained, depending on the amount of water added and on the amount of free acid in the solution.[4] When 1 mol of antimony trihalide is treated with 8 mol of water, antimony monooxyhalide is formed (1). When 27 mol of water are used, the oxyhalide shown in Eq. (2) is formed:[4a]

$$SbX_3 + H_2O \rightarrow SbOX + 2HX \qquad (1)$$

$$4SbX_3 + 5H_2O \rightarrow Sb_4O_5X_2 + 10HX \qquad (2)$$

Experimental

Stoichiometric Determination of the Composition of Antimony Oxyhalides. Antimony oxybromide was chosen as a sample of the oxyhalides.

Materials. Radiobromine (^{82}Br) produced[5] from neutron-irradiated ammonium bromide, the radiochemical purity of which had been tested by measuring its gamma-spectrum and half-life, was introduced, after it has passed through a dehydrating agent ($CaCl_2$), into a cooled trap containing antimony powder suspended in carbon disulfide. After the reaction (performed at room temperature) had been completed, the excess antimony powder was filtered off, and then the solvent was evaporated. Antimony tribromide (^{82}Br) was thus obtained.

Procedure. About 36 mg of antimony tribromide (^{82}Br) were treated with 1 m*l* of water[6] in a small test tube. After thorough shaking for 3 min, the contents were centrifuged for 5 min (2000 rpm). Then the centrifugate was pipetted out and the residue was washed with water. The radioactivities of both the centrifugate plus washings and the residue were counted by using an NaI(Tl) well-crystal scintillation detector and a scaler.

X-Ray Diffraction. *Sample Preparation.* The antimony trihalides (Cl, Br, and I) were obtained commercially or were prepared by methods similar to that described above. Each of them was dissolved in carbon disulfide. Hydrolysis was done by thorough shaking from a two-phase mixture of the carbon disulfide solution and water in the same $SbBr_3/H_2O$ proportions as have been described above. After aging, the precipitate was filtered out and dried in a desiccator until use. The precipitate was finely powdered by means of a spatula.

Measurement. Powder X-ray diffraction patterns of the samples were recorded with a Tokyo Shibaura Electric, Model ADX-103, X-Ray Diffractometer. Mn-filtered Fe$K\alpha$ radiation at 35 kV and 7 mA was used. A G-M counter was used as an X-ray detector. The intensities reported are described in terms of peak heights above the background, so scaled that the most intense line is given a value of 100.

X-Ray Spectrochemical Analysis. *Sample Preparation.* An addition technique was carried out. As additives, Wako Pure Chemicals' antimony powder and ammonium halides (Br and I) were used. Each additive was homogeneously mixed in the oxyhalide by the use of a mortar and a pestle.

Measurement. The instrument used for the X-ray specter measurements was a Tokyo Shibaura Electric, Model AFX-103, Spectrometer. A Toshiba AF-50W-type tungsten target tube operated at 35 kV and 25 mA was used. A LiF plane-crystal and an NaI(Tl) crystal were used for diffracting the fluorescent spectrum and for the X-ray detection respectively. The peak measurements of the elements were corrected for the background near the peak to provide the net peak-intensity values. The position of each $K\alpha$ peak was located approximately by scanning the spectrum of the element and was then

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1) Part V on Hot-Atom Chemistry of Bromine. Presented at the Joint Local Meeting of Chugoku-Shikoku and Kyushu Branches of the Chemical Society of Japan, Tokushima, November 1968.

2) T. Kishikawa, Y. Aratono and C. Shinomiya, This Bulletin, **43**, 1276 (1970).

3) L. Szilard and T. A. Chalmers, *Nature*, **134**, 462 (1934).

4) a) C. Lea and J. K. Wood, *J. Chem. Soc.*, **125**, 137 (1934). b) V. von Richiter, *Ber.*, **4**, 408 (1871). c) G. Peason, *Trans. Roy. Soc.* (London), **81**, 323 (1891). d) J. Davy, *ibid.*, **102**, 190 (1912). e) J. M. van Benmelen, P. A. Meerburg and U. H. Noodt, *Z. Anorg. Allg. Chem*, **33**, 272 (1803); J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 9, Longmans, London (1929), Chapter 52.

5) F. Weygand, H. Grisevach, K.-D. Kirchner and M. Haselhorst, *Chem. Ber.*, **88**, 487 (1955).

6) In such proportion hot-atom data (Ref. 2) have been obtained.

more exactly located by point-set readings using mannual control.

Radiometric Determination of Solubilities. *Materials.* As a radiotracter, an ^{124}Sb isotope of a known radioactivity (*ca.* 10^5 cpm/mmol-oxyhalide) was precipitated according to the directions presented above. The radiochemical purity was also checked by the manner described above.

Procedure. A known amount of the antimony oxyhalide(^{124}Sb) was suspended in a reaction flask containing 50 m*l* of distilled water. After the suspension had been equilibriated for 20 hr (in a thermostat ± 0.2°C), an aliquot (*ca.* 2 m*l*) of the suspended solution was pipetted out and centrifuged for 5 min. A known amount of the centrifugate was then pipetted into a measuring tube and counted with an NaI(Tl) well cristal and a scaler. The comparison of the activity with that of a standard specific-activity solution indicated the solubility.

Results and Discussion

Hydrolytic Behavior of Antimony Tribromide. If the radioactivities of the residue and the centrifugate are *m* and *n* respectively, the following equation can be proposed:

$$\frac{m+n}{3}\mathrm{SbBr_3}^* + \frac{n}{2}\mathrm{H_2O} \rightarrow$$

$$\mathrm{Sb}_{(m+n)/3}\mathrm{O}_{n/2}\mathrm{Br}_m{}^* + n\mathrm{HBr}^* \qquad (3)$$

where an asterisk represents the ^{82}Br isotope. The *m* and *n* values thus obtained in cpm or in percentage of the total activity, are listed in Table 1.

TABLE 1. RADIOMETRIC DETERMINATION OF THE HYDROLYTIC BEHAVIOR OF ANTIMONY TRIBROMIDE BY USING BROMIDE-82 AS A TRACER

No.	Radioactivities of Residue (antimony oxybromide) *m*		Centrifugate (bromide ion) *n*	
	cpm	%	cpm	%
1	18361	19.7	74714	80.3
2	18963	20.4	74037	79.6
3	16040	17.4	76304	82.6
4	16160	17.7	74981	82.3
5	19430	19.4	79486	80.6
6	13932	15.7	74891	84.3
7	18044	19.6	74007	80.4
Av.		18.4±1.6		81.6±1.6

If the reaction (1) is predominant, the *m* value in percentage should be close to 33.3; if the reaction (2) is predominant, the *m* value in percentage should be close to 16.7. The average value of *m* in percentage in Table 1 is 18.4±1.6, which indicates that the composition of the obtained antimony oxybromide is $Sb_4O_5Br_2$.

Identification by X-Ray Diffraction. The X-ray diffraction patterns of the samples are shown in Fig. 1. The results of the diffraction of the oxychloride and the -bromide showed them to be $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$ respectively, according to the data of the ASTM cards.[7]

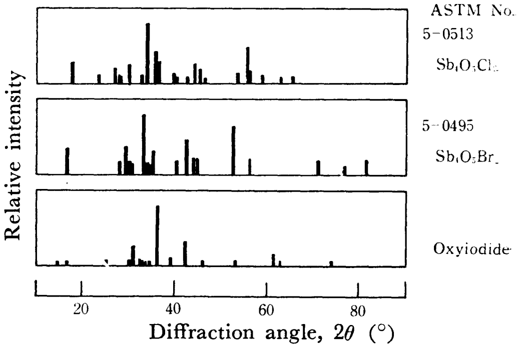

Fig. 1. X-Ray diffraction patterns of antimony oxyhalides.

X-Ray Spectrochemical Analysis. The *Kα*-line intensity of the relevant element was measured before and after the addition of a known amount of the element to the sample. After the determination of the intensity ratio of these two, the percentage of the element in the original sample could be calcurated from the following relationship:[8]

$$x=\frac{R\cdot w}{(1-R)\cdot W+w}\times 100(\%) \qquad (4)$$

where *x*, *R*, *W*, and *w* are the percentage of the element in the original sample, the intensity ratio (intensity of the *Kα* element before addition, I_x)/(intensity of the *Kα* element after addition, I_s), the weight of the sample, and the weight of the standard element respectively.

The analyzed elements were Sb, Br, and I. The results of the X-ray spectrochemical analysis are listed in Table 2. The values of oxygen were calculated by subtracting the percentages of two atoms from 100%.

These results establish that the composition of the hydrolyzed product of antimony trihalides is $Sb_4O_5X_2$.

TABLE 2. RESULTS OF X-RAY SPECTROCHEMICAL ANALYSIS

Element	Antimony oxibromide		Antimony oxyiodide	
	%	atoms[a)]	%	atoms[a)]
Sb	65.7	4	57.5	4
O	10.3	4.8	8.5	4.5
X	24.0	2.2	34.0	2.2

a) Normalized to Sb: 4.

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7) ASTM Cards No. 5-0495 and 5-0513; M. Estrand, *Acta Chem. Scand.*, **1**, 178 (1947).

8) W. J. Campbell and H. F. Carl, *Anal. Chem.*, **26**, 800 (1954).

TABLE 3. HEAT OF SOLUTION

	Q, kcal/mol
$Sb_4O_5Cl_2$	21.0 ± 0.1
$Sb_4O_5Br_2$	23.3 ± 0.2
$Sb_4O_5I_2$	32.7 ± 0.3

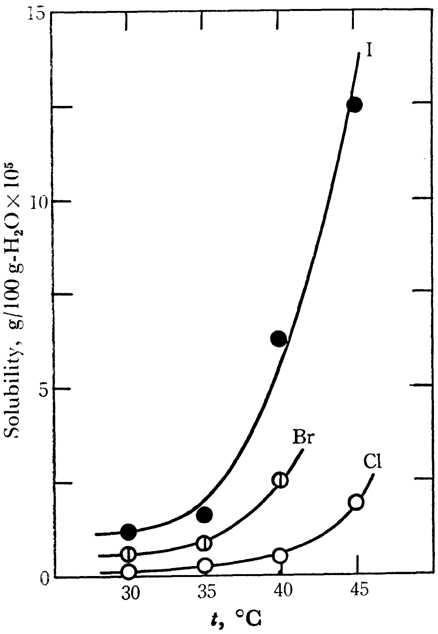

Fig. 2. Solubility curves of $Sb_4O_5X_2$(X: Cl, Br, I). Thermostat±0.2°C

Radiometric Measurement of Solubilities. The data summarized in Table 3 and Fig. 2 indicate that the solubility increases in the following order: Cl<Br<I.

When the solubility, S, is expressed as mol/kg-solvent, the plots of $\log S$ against $1/T$ gives a straight line, as is shown in Fig. 3. When a solid dissolves in a liquid, and when the state of equilibrium is reached, the van't Hoff equation holds between the equilibrium constant, K, and the absolute temperature, T:

$$\partial \ln K/\partial T = Q/\boldsymbol{R}T^2 \tag{5}$$

where Q is the heat of solution. If the heat of solution is taken as constant over the given range of temperature, the general integration of the van't Hoff equation gives, when the equilibrium constant, K, is replaced by the solubility, S:

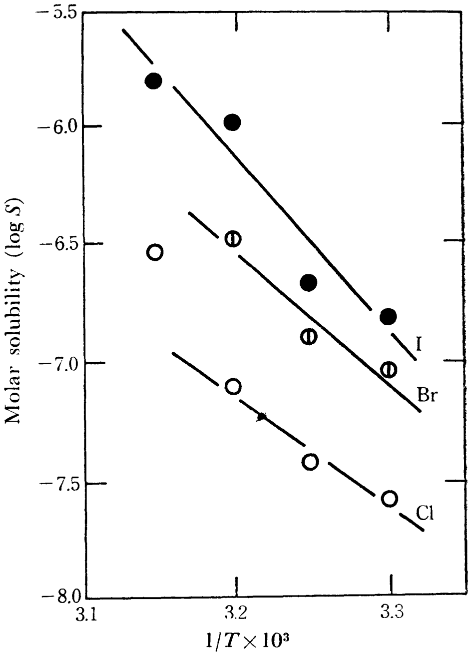

Fig. 3. Dissociation of $Sb_4O_5X_2$ (X: Cl, Br, I).

$$\log S = -\frac{Q}{2.303\boldsymbol{R}}\cdot\frac{1}{T} + \text{constant} \tag{6}$$

Equation (6) is shown in Fig. 3. From the slope, which is equal to $-Q/2.303\boldsymbol{R}$, the heat of solution, which represents the heat of absorption when 1 mol of solution is dissolved afresh in a saturated solution, can be found in Table 3 over the given range of temperature.

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