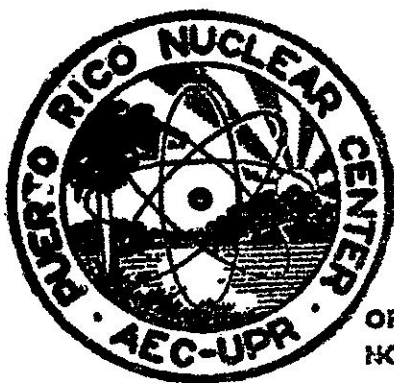


PUERTO RICO NUCLEAR CENTER

DISTRIBUTION OF RADIOACTIVE ANTIMONY
FORMED BY NEUTRON CAPTURE IN
ANTIMONY COMPOUNDS

J. F. FACETTI



OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT
NO. AT (40-1)-1833 FOR U. S. ATOMIC ENERGY COMMISSION



DISTRIBUTION OF RADIOACTIVE ANTIMONY FORMED BY NEUTRON CAPTURE IN ANTIMONY COMPOUNDS

J. F. FACETTI*

Nuclear Science and Technology Division Puerto Rico Nuclear Centre†
Mayaguez, Puerto Rico

(Received 28 October 1962; in revised form 30 December 1962)

Abstract—Antimony compounds were irradiated with neutrons and the distribution of radioactive Sb^{122} and Sb^{124} between the tri and pentavalent oxidation states determined, after dissolving the samples in either fused potassium hydroxide or concentrated hydrochloric acid. The results suggest that the new species reach their final oxidation state in the crystal, either during, or a short time after, irradiation. In addition, the results show a linear relation between the composition of the oxide and the percentage of radioactive Sb(v) similar to that obtained by other workers with arsenic oxides.

THE results of several other workers⁽¹⁻⁴⁾ on the distribution of the radioactive arsenic, formed by the (n, γ) processes on arsenic oxides, indicate the importance of carrying out similar studies with antimony oxides.

Antimony, having similar properties to arsenic, forms three oxides commonly written as Sb_2O_3 , Sb_2O_4 and Sb_2O_5 . The irradiation of antimony gives the radioisotopes ^{122}Sb and ^{124}Sb , of known characteristics.⁽⁵⁾

EXPERIMENTAL

A. Materials

The irradiated antimony compounds were the three oxides and potassium antimoniate.

The oxides used were Sb_2O_3 and Sb_2O_4 of "pro-analysis" grade, and Sb_2O_5 of spectroscopic purity. They were used without further purification; the Sb_2O_4 was supplied by Johnson and Matthey (London, England).

In order to check the crystallographic identity of the oxides their X-ray diffraction patterns were measured by the powder method, using a conventional X-ray machine and identified by the ASTM data.⁽⁶⁾

It was established that the irradiated Sb_2O_3 corresponds to the senarmonite structure.^(4,7) The Sb_2O_4 commonly known as antimony tetroxide is considered to be $SbSbO_4$,⁽⁸⁾ and its X-ray patterns agreed with the reported data.⁽⁹⁾ The two irradiated pentoxides (Fisher Scientific and K and K Laboratories) did not have the same structure, as was indicated by their diffraction diagrams.

* On leave of absence from the University of Asunción, Paraguay.

† Operated by the University of Puerto Rico for the Atomic Energy Commission.

(1) A. G. MADDOCK and M. M. DE MAINE. *Canad. J. Chem.* **34**, 441 (1956).

(2) H. KAWAHARA and G. HARBOTTLE. *J. Inorg. Nucl. Chem.* **9**, 240 (1959).

(3) G. B. BARO and A. H. ATEN. *Proc. Symp. on Chemical Effects of Nuclear Transformation. I. A.* E.A. STI-PUB 34, Vol. 2, 233 (1961).

(4) G. B. BARO, Thesis, Universidad de Buenos Aires (1961).

(5) D. STROMINGER, J. HOLLANDER and G. SEABORG. *Table of Isotopes. Rev. Mod. Phys.* **30**, 585 (1958).

(6) X-Ray Powder Data File and Index to the X-ray Powder Data File.

(7) Y. K. SYRKIN and M. DYATKINA, *The Structure of Molecules and the Chemical Bond*, pp 331-332. Butterworths, London (1950).

(8) L. DIHLSTROM and A. WESTGREN. *Z. Anorg. Chem.* **235**, 153 (1937).

The amounts irradiated were about 150 mg. It is difficult to obtain the oxides perfectly free of moisture. The oxides were accordingly oven dried at 120°C for several hours, and stored at room temperature *in vacuo*, in the presence of silica gel. The samples were sealed *in vacuo* in quartz or Pyrex ampoules and then irradiated.

Another compound irradiated was the commercial analytical grade "potassium pyro-antimoniate". The formula $\text{KSb}(\text{OH})_6$ has been assigned to this compound.^(9,10) The samples were first submitted to the following treatments.

- (A) One pair was heated at 285° for 20 hr, washed with ether and then heated to 285° for 48 hr. These samples were again heated to 500° for 20 min *in vacuo* in the ampoules before sealing off.
- (B) Another pair were heated at 285° for 24 hr and then sealed in their ampoules;
- (C) a third pair were heated at 130° for 24 hr before irradiation.

B. Irradiations

The samples were irradiated for 4 min at 36° in the PRNC nuclear reactor, with a neutron flux of $10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$.

C. Chemical procedures

Immediately or 24 hr after irradiation, the samples were dissolved in fused KOH in the presence of an appropriate inactive carrier, the solution was made 6F in HCl, and the Sb(V) extracted by shaking with isopropyl ether, in the presence of MgCl_2 .⁽¹¹⁾ The samples were in contact with fused KOH for $\frac{1}{2}$ -1 min and then immediately cooled in ice.

Since Sb_2O_3 contains both forms of Sb(III) and Sb(V), no carriers were added for the separation. The Sb_2O_3 and $\text{KSb}(\text{OH})_6$ were also dissolved in concentrated HCl at 60°C.

D. Measurements and radiochemical purity

The samples in acid magnesium chloride solution and in the ether solution were placed in calibrated polyethylene or Pyrex tubes and measured in a NaI (TI) well crystal coupled to a multichannel analyser.

After the short lived isomers had decayed, the long lived isomers $T_{\frac{1}{2}} 2.8$ days and $T_{\frac{1}{2}} 60$ days of ^{122}Sb and ^{124}Sb were measured. In the analyses the gamma peaks of 0.57 and 0.69 MeV for ^{122}Sb , and of 0.60 and 1.69 MeV for ^{124}Sb were measured. The radiochemical purity was confirmed by following the decay. Since there is overlapping of the photopeaks at 0.57 and 0.60 MeV, these were resolved by following their decay rates, and then subtracting the extrapolated 60 day activity of the longer isomer.

RESULTS AND DISCUSSION

Table I shows the distribution of the radioactive ^{122}Sb and ^{124}Sb as Sb(III) and Sb(V).

The yield of Sb(V) in both samples of irradiated antimony pentoxide was the same and showed no apparent effect of their different structures. The distribution of ^{122}Sb and ^{124}Sb in the pentavalent state is essentially the same for all the compounds studied, within the experimental error. No isotopic effect is found in the chemical state of the two radioactive species, in agreement with the published data.^(1,12)

No difference exists between samples processed immediately or 24 hr after irradiation. Therefore, the isomeric transition ^{124m}Sb $T_{\frac{1}{2}} 21$ min presumably does not bring about an increase in the yield of the higher oxidation state.

The results for Sb_2O_3 showed nearly 99 per cent retention, in agreement with previously published data.^(1,12) Retention in Sb_2O_5 was low and the yield of the pentavalent state in Sb_2O_4 was that expected for an equimolar mixture of Sb_2O_3 and Sb_2O_5 .

⁽⁹⁾ L. PAULING. *J. Amer. Chem. Soc.* **55**, 1895 (1933).

⁽¹⁰⁾ N. V. SIDGWICK. *The Chemical Elements and their Compounds*, Vol. 1. P. 788. Oxford (1950).

⁽¹¹⁾ N. BONNER. *J. Amer. Chem. Soc.* **71**, 3909 (1949).

⁽¹²⁾ T. ANDERSEN and A. KNUTSEN. *J. Inorg. Nucl. Chem.* **23**, 191 (1961).

TABLE I

Compound	Solvent	Yield Sb(III)%		Yield Sb(V)%		Number of experiments
		Sb ¹²³	Sb ¹²¹	Sb ¹²³	Sb ¹²¹	
Sb ₂ O ₃	KOH (molten)	98.4 ± 0.4	98.3 ± 0.5	1.6	1.7	2
	HCl (at 60°C)	98.2 ± 0.3	98.3 ± 0.4	1.8	1.7	2
Sb ₂ O ₄	KOH (molten)	87.9 ± 1.1	87.5 ± 1	12.1	12.5	4
Sb ₂ O ₅ Sample I (K and K. Lab.)	KOH (molten)	75.9 ± 0.8	75.9 ± 0.7	24.1	24.1	4
	KOH (molten)	76.5	76.8	23.5	23.2	1
KSb(OH) ₆ treatment (a)	KOH	66.3	66.1	33.7	33.9	1
	HCl (at 60°C)	67.2	67	32.8	33	1
treatment (b)	HCl (at 60°C)	48.1 ± 2.6	48.1 ± 2.6	51.9	51.9	2
treatment (c)	HCl (at 60°C)	29.1	29.5	70.9	70.5	1

The fusion with KOH (at 360°C) apparently did not change the distribution between the two valence states as may be seen from the results of dissolving Sb₂O₃ in concentrated HCl. It follows that the majority of the radioactive Sb atoms reach their final oxidation state in the crystal lattice immediately after the nuclear process or possibly a short time after the particle has lost its kinetic energy.⁽¹⁰⁾ In terms of annealing, the fact that there is no change in the retention may be due to the short time at the high temperature in the melt. In addition, reaction between the sample and solvent must also be considered, since this can impede the recombination of recoil atoms with the "crystal vacancies". The neutralization is a rapid reaction. In addition the high concentration of OH in the fused KOH, will accelerate lattice degradation, via the intermediate formation of polyanionic complexes.⁽¹³⁾ It must also be remembered that the vacancies occur as dilute impurities in the irradiated compounds.

The results for pretreated samples of KSb(OH)₆ suggest that the presence of the OH group in the irradiated molecule leads to a greater yield of the higher oxidation state. The low yield in case (A) can be attributed to the loss of water from the compound. The results in case (C) are in agreement with those recently published.⁽¹²⁾

It has been suggested that a linear relation exists between the yield of pentavalent radioactive arsenic and the ratio of oxygen atoms to arsenic atoms in the compound irradiated with neutrons.^(3,4) A similar relation seems to hold for the radioactive pentavalent antimony formed in the irradiation of simple antimony compounds. (See Fig. 1). This linearity, as in the similar case of radioactive arsenic, indicates that

⁽¹³⁾ J. L. AUDRIETH and T. MOELLER, *J. Chem. Educ.* 20, 219 (1943).

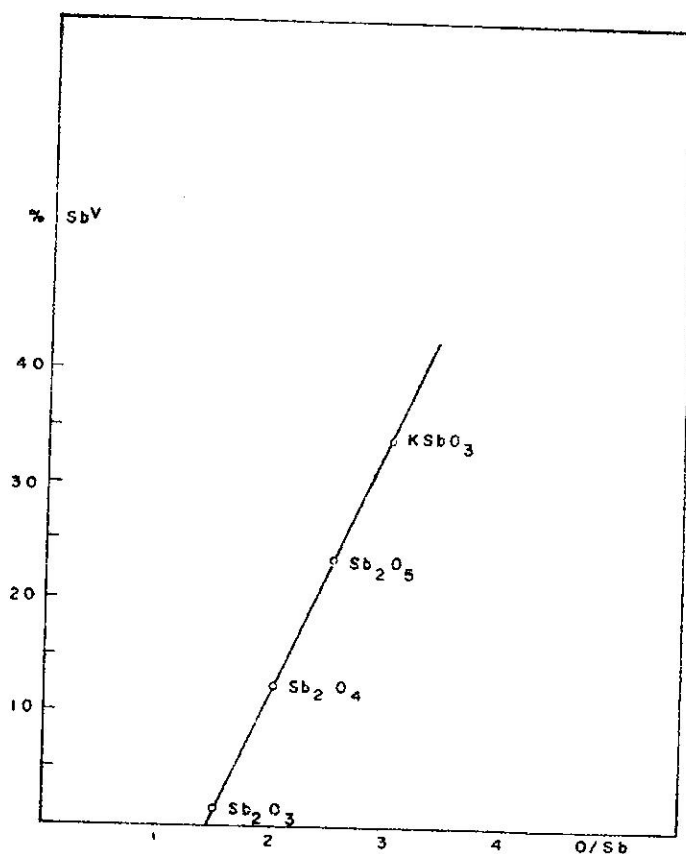


FIG. 1.—Yield of Sb(V)(%) vs oxygen to Sb ratio.

the oxygen content of the compound is the main factor in determining the distribution of the radioactive antimony between the tri and pentavalent states. A significant fact was that the results for $KSb(OH)_6$ submitted to pretreatment (A) fall on the linear relation at a point corresponding to the hypothetical $KSbO_3$.

Acknowledgement—It is a pleasure to thank Dr. G. BARO of the Atomic Energy Commission of Argentina for helpful suggestions and E. TRABAL and S. TORRES of the PRNC for their collaboration in the chemical separations and measurements. The author is also indebted to Dr. F. VÁZQUEZ MARTÍNEZ who kindly performed the X-ray measurements and Dr. O. H. WHEELER of the PRNC for several discussions.