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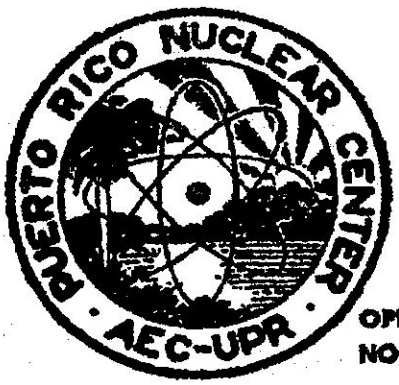
CHEMICAL STATE OF Sb^{125} FORMED IN TIN COMPOUNDS IRRADIATED WITH NEUTRONS



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"Chemical State of Sb^{125} formed in Tin Compounds Irradiated with Neutrons"

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Work performed at Puerto Rico Nuclear Center, Mayaguez, P. R., under U. S. Atomic Energy Commission Contract AT-(40-1)-1833.

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ABSTRACT

The chemical state of Sb^{125} obtained in the β-decay of neutron irradiated Sn compounds was studied. The compounds irradiated were SnO, SnO_2, $K_2Sn(OH)_6$ and $HSnO_4$. The results obtained suggest that the distritubion of Sb^{V} and Sb^{III} depends on the composition and constitution of the irradiated compound.

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Previous work by Baro and Aten[1, 2] demonstrated that the yield of As^{77} in the pentavalent state formed in the neutron irradiations of simple germanium and selenium compounds, is dependent on the oxygen content, and is the same as the value obtained for As^{76} in the similar As compound. The same dependence was observed in neutron irradiated antimony oxides[3]. Andersen and Knutsen[4] investigated the Sn^{125} β^- Sb^{125} system using complex tin compounds synthetized from Sn^{125}, but their results did not compare well with the above.

In this work, the same system is studied using simple tin compounds irradiated with neutrons.

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1. G. Baró and A. H. Aten, Jr. - Chem. Effects of Nucl. Transf., IAEA - STI-PUB 34, Vol. 2, 233 (1961).

2. G. Baró - Thesis - Universidad de Bs. As. and IKO of Amsterdam (1961).

3. J. F. Facetti - J. Inorg. Nucl. Chem. 25, 759 (1963).

4. T. Andersen and A. Knutsen - J. Inorg. Nucl. Chem. 23, 191 (1961).

EXPERIMENTAL

Materials:

The irradiated materials were tin oxides (analytical grades), potassium stannate and "perstannic acid".

The oxides, SnO and SnO_2, were desiccated at 80°C and stored in the desiccator. The $K_2Sn(OH)_6$ was prepared from SnO_2 and fused KOH. After separating from the mixture, the crude salt was washed with ethyl alcohol and recrystallized from water, in vacuo. Small needle-like and probably trigonal crystals were obtained. They were extremely hygroscopic. The $HSnO_4$[5] was prepared according to Tanatar[6, 7], by crushing recently precipitated SnO_2 with H_2O_2. The mixture was heated with an infrared lamp at 70°C, filtered and the procedure repeated several times. A fine white, non-hygroscopic powder was obtained. Such material, however, proved to be microcrystalline and not amorphous as previously stated[6].

The two species were studied by X-ray diffraction, and their crystalline patterns shown to be different from those of the starting materials. In preliminaries experiments, the most intense lines for $K_2Sn(OH)_6$ were obtained at the corresponding d values of 4.17, 3.00, and 2.76A and for the $HSnO_4$ at 3.34, 2.65, and 1.75A.

Both, $K_2Sn(OH)_6$ and $HSnO_4$ are very soluble in dilute HCl acid. The former also dissolves very easily in water.

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5. W. Schumb, C. Satterfield, and L. R. Wentworth (Hydrogen Peroxide - A. C. S. Monograph Series - 665 - Reinhold Pub - (1955) attribute the formula $H_2Sn_2O_7$ to this compound.

6. S. Tanatar - Ber. deutch. chem. Gess. 34, 1184 (1905).

7. P. Pascal - Nouveau Traite de Chimie Minerale - Tome VIII (fasc 3) 285-461, Masson et cie (1963).

Irradiations:

The samples were irradiated in evacuated pyrex ampoules, in the PRNC Pile with a neutron flux of 3.2×10^{16} cm^{-2}. Some samples of $K_2Sn(OH)_6$, were submitted to previous crushing.

After irradiations, the samples were allowed to decay in their sealed ampoules at room temperature during periods from two weeks up to two months.

Chemical procedures:

The samples were dissolved in HCl or in KOH in the presence of Sb^{III} and Sb^{V} carriers. The Sb^{5} species were extracted with isopropyl ether[8]. In addition, the antimony activities were purified from tin contaminations using ethyl acetate as extractant[9].

The yield was treated using carriers labeled with Sb^{124}. In every case the cool, i.e. non irradiated compound was dissolved under the same conditions as the irradiated compound. In the case of $HSnO_4$, all the Sb^{124} yielded in the dissolution of the cool sample was in the pentavalent state as expected. However, when the hot material was processed, no more than 8% of the tracer in the trivalent state changed its oxidation state.

Counting procedures and radiochemical purity:

These were carried out as previously described[3].

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8. N. A. Bonner - J. Am. Chem. Soc. 71, 3909 (1949).

9. Ch. White and H. Rose - Anal Chem. 25, 351 (1953).

Results and discussion:

The samples were analyzed one week and two months after irradiation. In the first case, the Sb^{125} atoms were largely formed by disintegration of Sn^{125}, $T_{1/2}$ 9 min. and in the second case also by the disintegration of the longer half-life isomer. No difference was found in the distribution of the valence states, as expected[10] from the similarity of the disintegration schemes of the parent nuclides[11]. The results appear in Table I.

The tri- and penta- valent states of Sb^{125} could be formed as follows:

$$SnO \xrightarrow{\beta^-} SbO^+$$

$$SnO_2 \xrightarrow{\beta^-} SbO_2^+$$

On irradiation of SnO, almost all the Sb^{125} species were found in the trivalent state. It is apparent that the dissolution media affect the yield of Sb^V in the irradiated compound. Under acidic conditions, and in the presence of divalent tin, all the radio-antimony atoms were in the trivalent state. When SnO is dissolved in molten KOH, the formation of stannites with strong reducing properties can be expected, but it is known that an internal redox mechanism takes place[8]; in this case, the yield of Sb^{125} in the pentavalent state was measurable. With irradiated SnO_2, the yield of Sb^V was 19.9%.

Both results are higher than those obtained for Sb_2O_3 and Sb_2O_4. Because of the absence of an isotopic effect between the Sb^{122} and Sb^{124}[12], it is apparent that these differences cannot be attributed to such an effect.

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10. V. Nefedov, A. Riukhin, M. A. Toropova, B. Melnikov, Chem. Effects Nucl. Transf. - IAEA STI-PUB 34, Vol. 2, 149 (1961).

11. Nuclear Data Sheets NRC, 6, 91 (1960).

12. A. G. Maddock and M. M. de Maine, Can. J. Chem. 34, 441 (1956).

In the previous work with simple antimony compounds[3], a linear relation was found between the yield of Sb^{122} - Sb^{124} in the pentavalent state and the ratio of oxygen/Sb atoms.

This result is similar to that noted by Baro and Aten in the formation of As from simple germanium and selenium compounds.

The present results do not follow this relation. The differences suggest that the chemical bond and constitution of the irradiated compound play their role in the process, and it must be remembered that the Sb^{125} atoms exist in the lattices as very diluted impurities. SnO and SnO_2 are simple ionic oxides, but Sb_2O_3 (senarmontite structure) is a semi-molecular crystal, and Sb_2O_4 is considered as $SbSbO_4$[13].

It is worth noting that with Sn^{125} Szilard-Chalmers processes can occur. This should affect the valence state of the Sb^{125}, which species are emerging from the spikes where the parent nuclei were trapped, and undergo their own hot or thermal or annealing-like reactions.

In the case of the irradiated $K_2Sn(OH)_6$, the yield of Sb^V was lower than that reported for $KSb(OH)_6$. In recent studies on post-recoil thermal annealing in neutron irradiated $KSb(OH)_6$[14], a possible reducing action has been observed on the Sb atoms due to the F centers and OH groups. During its slowing down, the recoil Sb^{125} can undergo similar reactions with such groups, in the new spikes or in their neighborhood.

As in $KSb(OH)_6$, prior crushing of the $K_2Sn(OH)_6$, yields a lower value for pentavalent Sb. As indicated by Maddock's model[15,16] previous

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13. A. F. Wells - Structural Inorganic Chemistry, 456, Claredon Press - Oxford (1962).
14. J. F. Facetti - Forthcoming publication.
15. A. G. Maddock and J. Vargas - Chem. Effects of Nucl. Transf. IAEA STI-Pub., 1,375 (1961).
16. A. G. Maddock, F. E. Treolar and J. I. Vargas - Trans. Faraday Soc. 59, 924 (1963).

previous treatments increase the density of vacancies and this increases the probability of trapping the fragments during neutron irradiation. Such a mechanism can also apply for β -decay processes.

During the irradiation of $HSnO_4$, the material decomposes. If the ampoules were opened immediately after the irradiation, the presence of O_3 could be detected with neutral KI paper.

When the ampoules were opened after 24 hours, no iodine was liberated. If the non-irradiated material is heated above 100°C it decomposes, but no O_3 was observed.

In addition, the irradiated samples could not be dissolved even in 12M HCl, and the formation of a colloidal material was observed, probably β-stannic acid.

It appears that the material decomposes under irradiation, at least partially, according to:

$$2HSnO_4 \longrightarrow 2SnO_2 + H_2O + O_3$$

although ozone can also be formed through the radiolysis of oxygen[17].

The $HSnO_4$ irradiated samples were accordingly dissolved in molten KOH. The results are in good agreement with those obtained by Andersen and Knutsen with the chlorostanates, where the high yield of Sb^V is due to the halogen, as suggested by them. Likewise the yield found here compared with those obtained in other cases, is sufficiently high to be attributed to the oxidizing nature of the compound.

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17. F. Lampe, E. Weiner and W. Johnston - J. Applied Rad. Isotop. 15, 363 (1964).

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TABLE I

Compound	Solvent	Yield Sb^{125} Sb^{V}	Sb^{III}	Number of Experiments
SnO	HCl	0	100	2
	KOH (molten)	2 ± 0.2	98	3
SnO_2	KOH (molten)	19.9 ± 1	80.1	3
$K_2Sn(OH)_6$	HCl	31.2 ± 2	68.8	2
$K_2Sn(OH)_6$ (crushed)	HCl	26.5 ± 1	73.5	2
$HSnO_4$	KOH (molten)	85.6 ± 3	14.4	3