

PRNC-53 PUERTO RICO NUCLEAR CENTER CHEMICAL STATE OF Sb" FORMED IN TIN COMPOUNDS IRRADIATED WITH NEUTRONS: Foreword by UNIVERSITY OF PUERTO RICO UNDER CONTRACT ECVE No. AT(40-1)-1855 for U.S. ATOMIC ENERGY COMMISSION ---Page Break--- "Chemical State of Sb" formed in Tin Compounds Irradiated with Neutrons" J. P. Facetti Nuclear Science and Technology Division Work performed at Puerto Rico Nuclear Center, Mayaguez, P.R., under U.S. Atomic Energy Commission Contract AT-(40-1)-1855 October, 1964 ---Page Break--- 'The chemical state of Sb obtained in the decay of neutron irradiated Sb compounds was studied. The compounds irradiated were SbO, SnO₂, K₂Sb(O₂)₅ and H₃SbO. The results obtained suggest that the distribution of Sb and SbH depends on the composition and constitution of the irradiated compound ---Page Break--- Chemical state of Sb formed in Tin Compounds Irradiated with Neutrons J.P. Facetti Nuclear Science and Technology Division 'Puerto Rico Nuclear Center Previous work by Baro and Aten demonstrated that the yield of As 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 in the similar As compound. The same dependence was observed in neutron irradiated antimony oxides. Andersen and Knutsen investigated the SbSb system using complex tin compounds synthesized from Sb, 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. Work performed under Contract No. AT(40-1)-1833 of the University of Puerto Rico for the U.S. Atomic Energy Commission. 1. G. Rer6 and A. H. Aten, Jr. - Chem. Effects of Nucl. Transf., IAEA = STI-PUB 34, Vol 2, 233 (1961). 2. G. Baro - Thesis - Universidad de Bs. As. (1962). HD of Amsterdam 3. J.P. Facetti - J. Inorg. Nucl. Chem. 25, 759 (1963). 4. Andersen and A. Knutsen - J. Inorg. Nucl. Chem. 23, 191 (1961). ---Page Break--- EXPERIMENTAL

Material the irradiated materials were tin oxides (analytical grades), potassium stannate and "perstannic acid." The oxides, SnO and SnO₂, were desiccated at 80°C and stored in the desiccator. The K₂Sn(OH)₆ was prepared from SnO₂ 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. SnO₂ was prepared according to Tanatar (6), by crushing recently precipitated SnO₂ with KOH. 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. The two species were studied by X-ray diffraction, and their crystal line patterns were shown to be different from those of the starting materials. In preliminary experiments, the most intense lines for K₂Sn(OH)₆ were obtained at the corresponding d values of 4.17, 3.00, and 2.764 and for the HSnO₃ at 3.34, 2.65, and 1.758. Both K₂Sn(OH)₆ and HSnO₃ are very soluble in dilute HCl acid. The former also dissolves very easily in water. W. Schuub, C. Satterfield, and L. R. Wentworth (Hydrogen Peroxide - ALG. S. Monograph Series - 665 - Reinhold Pub - (1955) attribute the formula H₂SnO₃ to this compound. 6. S. Tanatar - Ber. deutsch, chem. Ges. 34, 1186 (2905). 7. = Nouveau Traite de Chimie Minerale - Tome VIII (fase 3) 285-461, Masson et cie (1963). ---Page Break--- Irradiations: The samples were irradiated in evacuated pyrex ampoules, in the PRNC Pile with a neutron flux of 3.2×10^{15} n/cm². Some samples of K₂Sn(OH)₆ were subjected 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 KOH in the presence of other carriers. The Sb species

were extracted with Leopropyl ether, in addition, the antimony activities were purified from tin (©),

contaminations using ethyl acetate as extractant and with sol%4. In every case, the yield was created using carriers to ease the cool, the non-irradiated compound was dissolved under the same conditions as the irradiated compound. In the case of H₂O, all the 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 0% of the tracer in the trivalent state changed its oxidation state. Counting procedures and radiochemical purity: These were carried out as previously described, M.A. Bonner - J. Am. Chem. Soc. 71, 3909 (1949). Gh. Witte and H. Rove - Anal Chem, 25, 391 (1953). ---Page Break--- 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, 1, 1, 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 from the similarity of the disintegration schemes of the parent nuclides. The results appear in Table T. The tri- and pentavalent states of Sb-125 could be formed after SnO. 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 in the irradiated compound. Under certain conditions, and in the presence of divalent tin, all the radio-antimony atoms were in the tetravalent state. When Sb₂O₃ is dissolved in oleene IDM, the formation of stannites with strong reducing properties can be expected, but it is known that an internal redox mechanism takes place; in this case, the yield of Sb-125 in the pentavalent state was measurable. With irradiated Sb₂O₃, the yield of Sb was 19.9%. Both results are higher than those obtained for Sb₂O₃ and Sb₂O₄. Because of the absence of an isotopic effect between

the Sb!22 and 412) Spl240", It is apparent that these differences cannot be attributed to such an effect. 10. V. Nefedov, A. Riukhin, M.A. Toropov, Mel. Tra B. Melnikov, Chen, Effects f.~ IAEA SII-FUB 34, Vol. 2, 149 (1961). 11. Nuclear Data Sheets MEG, 6, 91 (1960). 12. As G. Maddock and M. M. de Maine, Can. J. Chem. 34, 461 (1956). ---Page Break--- In the previous work with simple antimony compounds, a linear relation was found between the yield of Sb!22 - Sb124 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 antimony 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 Sb125 atoms exist in the lattices as very diluted impurities. SbO and SbO, are stable lone oxides, but Sb₂O₅ (senarontiee structure) is a phenomolecular crystal, and SbO₄ is considered as sosto(!). It is worth noting that with Sb!25 similar-chain processes can occur. This should affect the valence state of the Sb!25, which spectra 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 K₅n(OH)g, the yield of Sb" was recorded lower than that reported for K₅(OH). In recent studies on post-thermal annealing in neutron irradiated R₅b(OH)₅(O₄), 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!25 can undergo similar reactions with such groups, in the new spikes or in their neighborhood. As in K₅b(OB), prior crushing of the K₅n(OI) yields a lower value for pentavalent Sb. As indicated by Maddock's model 5:16) previous 1B. ALF, Wells - Structural Inorganic Chemistry, 456, Clarendon Press - Oxford (1962). Ls. J. F. Facetti - Forthcoming publication. 15. A. G. Maddock and J. Vargas

- Chen. Effects of Nucl. Transf. IAEA Str-Rub., 1,375 (1961). 16. A. G. Maddock, F. B. Treolar and J. I. Vargas - Trans. 59, 926 (1963). Raday Soc. ---Page Break--- -6- 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

HSeO₃, the material decomposes. If the ampoules were opened immediately after the irradiation, the presence of I₂ 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 O₂ 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 tannic acid. It appears that the material decomposes under irradiation, at least partially, according to 21500, 25n0, + #0 + O₂ although ozone can also be formed through the radiolysis of oxygen. The HSeO₃ 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 Sb³⁺ 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. 17, F. Lampe, E. Weiner and W. Johnston = J. Applied Rad. Isotop., 15, 353-1954),

Acknowledgment: The author wishes to thank Dr. H. Bielen for the X-ray measurements, and E. Trabal and S. Torres for their cooperation and counting. ---Page Break--- a TABLE * vera spi?> of Compound Solvent by solid Experiments Compound _Solvent_spv____sbltf_ experiments S00 cl ° 100 2 on (molten) 2402 98 3 Satron "2 (molten) Wott B01 3 RY(08)s wet M2+2 68.8 2 Kn (08), ct B5t1 73.5 2 (crushed) S00, oH (molten) B.643 14 3 ---Page Break---