PRNC053

PRNC-53

PUERTO RICO NUCLEAR CENTER

CHEMICAL STATE OF Sb? FORMED

IN TIN COMPOUNDS IRRADIATED

WITH NEUTRONS

: foreanTeD 8Y UVERSTY OF PUERTO ICO NORE CONTRACT

ECVE Wo. at wo-t-iem FOR U5 ATOMIC ReakoY CoMunSOn

---Page Break---

"Chentcal State of So**5 formed in Tin Compounds Irradiated with Neutrons?

3. F. Facettt

Muclear Science and Technology Division

Work performed at Puerto Rico Nuclear Center,

Mayaguez, P..R., under U. S. Atomic Bnergy

Comission Contract AT-(40-1)-1855

october, 1964

---Page Break---

?The chenical state of sb!??

obtained in the Bedecay of neutron

trradiated Sa compounds vas studied. The compounds irradiated vere

S80, $n0z, KzSa(Oit)s ane HSNO. The resulee obtained sugcest chat

the distritubton of sb¥ and SoHE depends on the composition and con

stitution of the (rradieted coupound

---Page Break---

Ghentcal state of $b!25 Formed in Tin

Gonpounds Irradiated vith Neutrons

J.P. Faceret

Muclear Science and Technology Division

?Puerto Rico Nuclear Center

Previous work by Baro and Aten?! 2) denonstrated that the yield

of As?? im the pentavalent state forned in the neutron irradiations of simple germaniun and selenium cospounds, is dependent on the oxygen content, and {s the sane as che value obtained for As?® in the sintlar ?As coupound. The same dependence vas observed in neutron irradiated

antimony oxides). Andersen and Knutsen(4) investigated the snl25

sb!25 ayscen using complex tin conpounde aynthetized fron

sot?5, but their results did not compare well with the above.

In this work, the sane system ts studied using simple tin conpounds

irradiated with neutrons.

?Work performed under Contract No. AT(40-1)-1833 of the University of Puerto Rico for the U. S. Atoaic Energy Comission.

1, G. Rer6 and A. H. Aten, Jr. - chen. Effects of Nucl. Tranaf.,

IAEA = STI-PUB 34, Vol 2, 233 (1961).

2. G. Bar6 = Thesis - Universidad de Bs. As.

(962).

HD of Ansterdan

3. J.P. Facetti - J. Inorg. Nucl. chen. 25, 759 (1963).

4. Andersen and A, Knutsen ~ J. Inorg. Muck. chen, 23, 191 (1961).

---Page Break---

EXPERIMENTAL

Material

the irradiated materials were tin oxides (analytical grades),

potassiua stannate and ?perstannic act

The oxides, Sn0 and $n0,, vere desiccated at 80°C and stored in the desiccator. The K,Sa(OH), vas prepared from Sn0, and fused KOH. After

separating fron che mixture, the crude salt was washed with ethyl alcohol and recrystallized from water, in vacuo. Snail needle-like and

probably trigonal crystals vere obtain

?They vere extronely hysroscopte.

ste ws00, °) vas prepared according to Tanatar ?©? 7), by crushing recently precipitated Sn0, with 10). The mixture was heated with an infrared Lamp at 70°C, filtered and the procedure repeated several tines. A fine white, non-hygroscopte powder was obtained, Such saterial, however, proved to be microcrystalline and not amorphous as previously stated(®).

?The two species were studied by Xeray diffraction, and thetr erystal= Line patterns shown to be different from those of the starting materiale.

In preliminaries experinents, che most intense lines for K,Sn(0i), were obtained at the corresponding ¢ values of 4.17, 3.00, and 2.764 and for the HSn0, a? 3.34, 2.65, and 1.758.

Both, KySn(Oii)g and HSn0, 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 H,$n,0, to this compound.

6. S, Tanatar - Ber. deutch, chem. Ge

34, 1186 (2905).

fal = Nouveau Traite de Chimie Minerale - Tone VIII (fase 3) 285-461, Masson et cle (1963).

---Page Break---

Exradiations:

?The samples were irradiated in evacuated pyrex ampoules, in the

PRNC Pile with a neutron flux of 3.2 x 1015 en?,

Sone samples of

KySn(Ol)g, were subsitced to previous crushing.

After ixradiations, the sonples wore allowed to decay in their

sealed anpoules at room tenperature during periods fron two weeks up to

?evo months.

Shenlcal procedures:

The sanples vere dissolved in HCl oF tn KOH tn tha presence of

oT and sb? carriers. The Sb* species were extracted with Leopropyl

eter, tn addition, the antizony activities vere purified from tin

©),

contaninations using ethyl acetate as extractant

ed vith so!%4, In every

?The yield vas created using carriers 1a!

ease the cool, tc. non irradiated compound was dissolved under the sane

conditions as the irradiated compound. In the eas

ol?

of Hon0,, all the

yielded {n the dissolution of the cool sanple was in the pentax

lent state as expected. However, vhen the hot material was processed,

no more than O% of the tracer in the trivalent atate changed its oxide

cion stare.

Counting procedures and radiochentcal purity:

These vere carried out as previously ¢ercribed?),

M.A. Bonner - J. An. Chen. Soc. 71, 3909 (1949).

9, Gh. Witte and H, Rove - Anal Chen, 25, 391 (1953).

---Page Break---

The samples vere analyzed one veek and two months after irradiation.
In the fret case, the sb!25 atons vere Largely formed by disintegration
of snl25, 1, /, 9 min. and in the second case also by the disintegration

of the longer half-life isomer. No difference was found in the divtrt-

bution of the valence states, as expected(!©) from the similarity of

the disintegration schenes of the parent nuclides(!!). the resuits

appear in Table T.

The tri- and penta valent states of Sb!25 could be formed a

fottove

Sn0_¢- _ sbo*

seo, ~_ seof

On irradiation of Sn0, almost all the Sb!25 species were found in

fhe trivalent state, TE te apparent that che dtasolucton media affect

the yleld of $0 in the trradlated compound. Under sctdte conditions,

and (a che presence of divalent tin, all the radLo-antigoay atone were

in the teivateat state, When $00 {8 dissolved { eoleen IDM, the forma-

tion of atannites vith

rong reducing properties can be expected, but

it 18 known that an internal redox mechanism takes place (5); in this

case, the yield of sb!25 in che pentavalent atate was measurable. With

frradtated S002, the yield of Sb? vas 19.9%.

Both results are higher than those obtained for $6203 and $5204.

Because of the absence of an isotopic effect between the sb!22 and

412)

spl240"', Le te apparent that these differences cannot be attributed

to such an effect.

10. V. Nefedov, A. Riukhin, M.A. Toropov

Mel. Tra

B. Melnikov, Chen, Hffects

f.~ IAEA SII-FUB 34, Vol. 2, 149 (1961).

11, Muclear Data sheets MEG, 6, 91 (1960).

12. As G. Maddock and M. M. de Maine, Can. J. chen. 34, 461 (1956).

---Page Break---

In the previous work with simple antinony compounds), a linear

relation was found between the yield of sb!22 - gb124 in che pentavalent

state and the ratio of oxygen/Sb atone.

This result is similer to chat noted by Baro and Aten in the forma

tion of Ae from simple germanium at

enium compounds.

The present results do not follow his relation, The differences

fuggest that the cheaical bond end constitution of the irradiated com

pound play thetr role in the process, and it mst be renenbered that

the 80125 atone exist in the lattices as very diluted impurities. S00

tnd 800, are staple Lonle oxides, but £5505 (eenarontiee structure) Le

f eanicnolecolar crystal, and $0504 {8 considered as sosto,(!),

Te de worth noting that with Sn!25 ssi laré-chalners processes can

occur. This should affect the valence state of the sb!25, which spectes

?are energing fron the epikes vhere the parent nuclei were trapped, and

?undergo their omm hot or thermal or annealing-like reactions.

In the case of the irradiated K5n(OH)g, the yield of Sb? was

-recotl

lover then that reported for KS(OH),. In recent studl

on post

theroal annealing in neutron treadiated R5b(0H)5(04, « possible reducing

action has been observed on the Sb atone due to the F centers and OH groups. During ite slowing down, the recoil sb!25 can undergo similar reactions with such groups, in the new spikes or in their neighborhood.

?As in KSb(OB),, prior crushing of the K,Sn(Ol),, yields « lower value

for pentavalent Sb. As indicated by Maddock's oodei 5:16) previous

1B. ALF, Wells - structural Inorganic Chentatry, 456, Claredon Press - ?oxford (1962).

Ls. J. F. Facetti - Forthcoaing 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 - Trane.

59, 926 (1963).

raday Soc.

---Page Break---

Previous treatments increase the density of vacancies and this increases

the probability of crapping the fragments during neutron irradiation.

Sach a mechanisn can also apply for F -decay proce

During the irradiation of Hse0,, the caterial decomposes. If the

acpoules were opened inediately after the irradiation, the presence of

5 could be detected with neutral KI paper.

Wien the anpoules were opened after 24 hours, oo loéine was liberated.

Tf the non-inradiated natertal is heated above 100°C it decorposes, but no

05 was observed.

Im addition, the (rradiated samples could not be dissolved even in

12M Hel, and the formation of 4 colloidal material was observed, probably

featannic acid.

Te appears that the material deconposes under {rragiation, at least

partially, according to

21500, 25n0, + #0 + 05

although ozone can also be forned through the rediolyste of oxygen?),

The HSnO, irradiated samples were accordingly dissolved in molten

KOH. The results are in good azreesent with those obtained by Andersen

and Knutsen with the chlorostanates, vhere the high yield of SbY is due

to the halogen, as susgested dy then. Likeuise the yield found here

compared vith those obtained in other cases, ts suffietently high to

be ateributed to the oxidizing nature of the co=pound,

17, F. Lampe, E. Weiner and W. Johnston = J. applied Rad, Lsotep, 15,

353-1954),

Acknovledgnent :

The author wishes co thank Dr. H. Bielen for the X-ray measurements,

and E. Trabal and $. Torres for their co!)

cedures end counting.

---Page Break---

a

TABLE

* vera spi?> of

Compound Solvent bY soli Experiments

Sepound _Solvent_spv___sbltf_ periments

S00 cl ° 100 2

on

(eolten) 2402 98 3

Sat ron

?2 (nolten) Wott B01 3

RyS0(08)s wet M2+2 68.8 2

Kn (08), ct B5t1 73.5 2

(crushed)

S00, oH

(rolten) B.643 14 3

---Page Break---