Distribution of Valence States of Recoil Antimony Atoms in Inorganic Compounds

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Potassium antimonate was irradiated with thermal neutrons to investigate the distribution of recoil antimony atoms between the tri- and pentavalent states. The retention values were found to be decreased linearly with the decrease of the amounts of crystalline water in the compound. It may be supposed that the OH radical in the crystal may play an important role on the valence states of recoil antimony atoms.

This supposition might be reasonable as compared with the results obtained for the antimony exchange reaction in a heterogeneous system (liq.-solid system).

1. Introduction

As to the study of antimony recoil chemistry, T. Andersen, et al.¹⁾ and J.F. Facetti²⁾ investigated the distribution of valence of recoil antimony atoms formed by the thermal neutron irradiation of potassium antimonate. It has been found by J.F. Facetti²⁾ that the ratio of oxygen atoms to antimony atoms in the compound is the main factor in determining the distribution of the radioactive antimony between the tri- and pentavalent states.

In the present work, the values of the retention were investigated on the neutron irradiated potassium antimonate using both the C.P. reagent (Wako Co., Ltd.) and the synthesized compound, and effects of the crystalline water on the retention of ¹²⁴Sb(V) were investigated.

2. Experimental

2-1 Material and Reagents

Material: Two sorts of potassium antimonate compounds were used; (A) the C.P. "potassium pyro-antimonate" (Wako Co., Ltd. reagent), without further purification, (B) KSb(OH)₆ synthesized according to the method of Brauer³⁾.

These samples were submitted to the following pre-irradiation treatments.

- (1) Samples A₁ and B₁ were used without pre-treatment.
- (2) Samples A₂ and B₂ were heated at 290±

5°C for 12 hrs.

- (3) Samples A₃ and B₃ were heated at 290±5°C for 24 hrs.

Antimony tracer: ¹²⁴Sb obtained from Oak Ridge National Laboratory (U.S.A.) was used for the studies of the exchange reaction. It was a Processed Unit and the chemical form was antimony (III) chloride in a hydrochloric acid solution.

Other reagents: The isopropyl ether used for extraction was of reagent grade extra pure and purified by distillation. It was made free from peroxide by shaking repeatedly with ferrous-ammonium sulfate solution acidified with sulfuric acid. Other chemicals were of reagent grade extra pure and used without further treatment.

2-2 Irradiation

The samples were irradiated for 5 minutes in the JRR-1 or JRR-2 nuclear reactor with thermal neutron flux of 4×10^{11} or 4×10^{13} neutrons·cm⁻²·sec⁻¹, respectively*.

2-3 Chemical procedure and counting

The irradiated samples were dissolved in 6 N hydrochloric acid containing both the Sb(III) and Sb(V) carriers. For separating ¹²⁴Sb(V) and ¹²⁴Sb(III) from each other the isopropyl ether extraction method used by N.A. Bonner⁴⁾

* Some preliminary investigations were made by the use of the reactor of Tsing Hua University of Taiwan.

was applied. The activities both in the acid layer and in the ether layer were measured with the scintillation counter*. From both activities the retention of $^{*}\text{Sb}(\text{V})$ was calculated.

A single channel pulse-height analyser** was used to determine the nuclides formed by the neutron capture process. A peak of about 0.6 MeV was observed (^{122}Sb : 0.57 MeV; ^{124}Sb : 0.60 MeV). Measuring the decay of the ir-

radiated sample by the G-M counter**, the half-life of the major activity was found to be 2.8 days (of ^{122}Sb) and that of the residual activity was found to be 60 days (of ^{124}Sb).

3. Results

3.1 Retention of $\text{Sb}(\text{V})$

The tables 1 and 2 show the results on the distribution of recoil antimony atoms between tri- and pentavalent states.

It can be seen that the distribution of the

Table 1 Retention values of $^{*}\text{Sb}(\text{V})$ in the sample A

Sample No.	Preirradiation treatment	$^{*}\text{Sb}(\text{III})$ (%)	$^{*}\text{Sb}(\text{V})$ (%)	Retention of $^{*}\text{Sb}(\text{V})$ aver. (%)	Irradiation time (min)	Neutron flux ($\text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$)
A ₁	None	12.6	87.4	86.8 ± 0.4	5	4×10^{13}
		13.6	86.4			
A ₂	$290 \pm 5^{\circ}\text{C}$ 12 hrs.	34.7	65.3	66.0 ± 4.3	5	4×10^{11}
		33.1	66.9			
		34.1	65.7			
A ₃	$290 \pm 5^{\circ}\text{C}$ 24 hrs.	30.8	69.2	67.1 ± 4.3	5	4×10^{11}
		31.3	68.7			
		36.6	63.4			

Table 2 Retention values of $^{*}\text{Sb}(\text{V})$ in the sample B

Sample No.	Preirradiation treatment	$^{*}\text{Sb}(\text{III})$ (%)	$^{*}\text{Sb}(\text{V})$ (%)	Retention of $^{*}\text{Sb}(\text{V})$ aver. (%)	Irradiation time (min)	Neutron flux ($\text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$)
B ₁	None	15.0	85.0	85.2 ± 0.6	5	4×10^{13}
		14.6	85.4			
		14.9	85.1			
B ₂	$290 \pm 5^{\circ}\text{C}$ 12 hrs.	53.1	46.9	45.1 ± 9.8	5	4×10^{11}
		56.2	43.8			
		56.8	43.2			
B ₃	$290 \pm 5^{\circ}\text{C}$ 24 hrs.	53.4	46.6	42.5 ± 3.0	5	4×10^{11}
		56.2	43.8			
		57.8	42.2			
		58.4	41.6			

valence of the radioactive antimony depends upon the duration of the pre-irradiation treatment. This tendency shows a good agreement with the results given by J.F. Facetti²⁾. Also it can be seen that the retention of $^{*}\text{Sb}(\text{V})$ for the non-treated samples shows higher values than the previously published data^{1), 2)}.

3.2 Crystalline water in $\text{KSbO}_3 \cdot x\text{H}_2\text{O}$

Potassium antimonate can be expressed by the compositional formula $\text{KSbO}_3 \cdot x\text{H}_2\text{O}$ ***. The tables 3 and 4 show the amounts of the crystalline water***.

3.3 Relation between retention and crystalline water

By plotting the retention of $^{*}\text{Sb}(\text{V})$ versus the amounts of the crystalline water, a linear

relation was obtained as shown in the Fig. 1.

3.4 Isotopic exchange reaction in heterogeneous system (liq.-solid system)

The effects of HCl concentration on the exchange rate between $\text{Sb}(\text{III})$ in the HCl solution and $\text{Sb}(\text{V})$ in $\text{KSb}(\text{OH})_6$ precipitates

* JRC Co., Ltd. made, using NaI crystal as a scintillator

** Detectolab. Products made

*** JRC Co., Ltd. made

J.F. Facetti²⁾ expressed the formula of potassium antimonate pre-treated at a high temperature as the hypothetical formula KSbO_3 .

*** The amounts of the crystalline water were calculated from the gravimetric antimony determination by the modified sulfide method³⁾.

Table 3 Results of antimony analysis and of crystalline water calculation in the sample A

Sample No.	KSb(OH) ₆ (mg)	ppt. of Sb ₂ S ₃ (mg)	Sb found (mg)	Sb(%) in KSbO ₃ ·xH ₂ O	crystalline	water
					(x)	aver.
A ₁	72.8	43.6	31.3	42.9	4.16	4.24
	72.5	43.0	30.8	42.5	4.31	
A ₂	41.8	25.1	18.0	43.1	4.08	3.01
	49.7	34.6	24.8	49.9	1.95	
A ₃	56.0	40.9	29.3	52.4	1.33	1.40
	50.3	36.3	26.0	51.7	1.48	

Table 4 Results of antimony analysis and of crystalline water calculation in the sample B

Sample No.	KSb(OH) ₆ (mg)	ppt. of Sb ₂ S ₃ (mg)	Sb found (mg)	Sb(%) in KSbO ₃ ·xH ₂ O	Crystalline	water
					(x)	aver.
B ₁	—	—	—	—	—	—
B ₂	50.5	35.4	25.4	50.3	1.84	1.60
	50.2	36.5	26.2	52.2	1.35	
B ₃	50.8	37.4	26.8	52.8	1.20	1.09
	50.4	37.9	27.1	53.8	0.97

- : (a) is retention value for KSbO₃ (32.9% from J.F. Facetti)
- (b) is retention value for KSbO₃·3H₂O (=KSb(OH)₆, about 70% from T. Andersen, et al. and J.F. Facetti)
- : Retention values of C.P. compounds
- ⊕: Retention values of synthesized compounds

Fig. 1 Variation of retention with the changes of amounts of crystalline water.

were investigated for the help of understanding the results obtained above*. The results are given in the Fig. 2. It can be seen that the amounts exchanged become smaller in proportion as the acidities increase. At 6N HCl the added *Sb(III) activity was found to be almost unexchanged.

4. Discussion

Summarizing the authors' retention values and T. Andersen and others' values^{1,2)}, a linear

Fig. 2 Isotopic exchange between *Sb(III) and Sb(V) in solid-liquid systems.

relation was observed between the retention and the amounts of crystalline water. This linearity indicates that the crystalline water in the compound affects strongly the distributions of valence of the recoil atoms. The exchange ratios in the heterogeneous system as mentioned above were found to be increased with the decrease of HCl concentrations, i. e. the increase of OH⁻ concentrations. From the results obtained for antimony exchange in Sb(III)-KSb(OH)₆ system, it can be seen that OH⁻ ion might have a promoting action for Sb(III)-Sb(V) exchange. Analogously for the authors' results obtained with solid KSb(OH)₆·xH₂O,

* Mixing KSb(OH)₆ with the HCl solution containing ¹²⁴Sb(III) at the room temperature, the changes of the activities of the supernatant were measured with the lapse of time by a scintillation counter.

OH^- may play an important role for the change of the retention values, which was found that the retention values are increased linearly with the increase of the amounts of crystalline water.

The more extended studies on the relations between the retention values and the chemical structure are thought to be necessary in future.

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要 旨

無機化合物における反跳アンチモン原子の原子価分布

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アンチモン酸カリウムを熱中性子で照射したさいに生ずる反跳アンチモン原子の原子価分布をしらべた。市販および合成したアンチモン酸カリウムの反跳アンチモン原子のリテンション値は、化合物の中性子照射前の熱処理を増すにつれ、すなわち、化合物中の結合水が減少するにつれて直線的に低くなることがわかった。これは結晶中で結合水の OH が促進的に作用してリテンション値を高めるためと推定された。この事実は、異相系（液—固）の交換反応の結果からも十分類推することができる。