Hot-Atom Chemistry of Arsenates.—Effect of Cation, Water of Crystallization and Irradiation Temperature on the Retention of Radioarsenic in Neutron-irradiated Solid Arsenates

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On the retention of radioarsenic as arsenate after neutron irradiation of arsenic acid or sodium arsenates in a solid state or in an aqueous solution, several investigators have obtained various results[1-5]. Typical results given by these workers are shown in Table I.

In the present investigation, the effect of cation, water of crystallization in molecules, irradiation temperature and storage time have been studied. The nuclide under investigation is 26.8 h ^{76}As, a hard-beta-emitter (E_{max}= 2.965 MeV.) with accompanying gamma rays.

Experimental

Arsenates of lithium, ammonium, sodium, potassium, cobalt(II) and barium were used as target materials for neutron irradiation. Irradiation of

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[1] W. F. Libby, *J. Am. Chem. Soc.*, **62**, 1930 (1940).

[2] P. Süe, *J. Chim. Phys.*, **45**, 177 (1948).

[3] H. Müller and E. Broda, *Monath.*, **82**, 48 (1951).

[4] J. Malý and R. Šimáňová, *Chem. listy*, **49**, 814 (1955).

[5] H. Kawahara and G. Harbottle, *J. Inorg. Nuclear Chem.*, **9**, 240 (1959).

TABLE I. TYPICAL RESULTS OBTAINED BY EARLIER WORKERS ON THE HOT-ATOM CHEMISTRY OF ARSENATES

Investigator	Investigated As(V) compound	Retention %	Note
W. F. Libby	H_3AsO_4 (solid)	93±10	Dissolved in H_2O
	H_3AsO_4 (soln.)	100±3	
	H_3AsO_4 (solid)	75±15	Dissolved in 6 N H_2SO_4
	H_3AsO_4 (solid)	75±15	Dissolved in 6 N NaOH
P. Süe	Na_2HAsO_4 (solid)	55~62	
	Na_2HAsO_4 (soln.)	38~59	
H. Müller and E. Broda	Na_2HAsO_4 (soln.)	14.4~16.3	Independent on concn., pH value and temperature
	Na_2HAsO_4 (solid)	65	Slow neutron irradiation
	Na_2HAsO_4 (solid)	74.5	Fast neutron irradiation
J. Malý and R. Simánová	$Na_2HAsO_4\cdot 7H_2O$ (solid)	67	
G. Harbottle and H. Kawahara	As_2O_5 (solid)	46.8±1.7	Irradiated at room temperature
	As_2O_5 (solid)	40.8±1.6	Irradiated at dry-ice temperature
	Na_2HAsO_4 (solid)	55.9±0.3	Irradiated at dry-ice temperature

these salts was carried out for 2.5 to 3 hr. with neutrons produced by Be-D reaction. Deuterons were accelerated by the cyclotron of the Institute of Physical and Chemical Research, Tokyo. The flux was approximately 10^7n/cm^2. sec. Neutrons were thermalized through a paraffin block or through water. In some cases, they were slowed down through ethanol. The temperatures of the bombardment site were −196°C (liquid nitrogen), −72°C (mixture of dry ice and ethanol), and room temperature.

After irradiation, each of the irradiated samples was dissolved in water containing an arsenic(III) carrier (arsenite solution). To this solution were added magnesia mixture and ammonia water to precipitate ammonium magnesium arsenate, $NH_4\cdot MgAsO_4\cdot 6H_2O$. The precipitate was dissolved in hydrochloric acid, hold-back carrier of arsenic(III) was added, and then precipitation was repeated by adding ammonia and an excess of a magnesia mixture. Hydrogen peroxide was added to the combined filtrate to oxidize arsenic(III). The precipitate formed contained radioarsenic, which was originally in the valence state of III as a result of the recoil process or a subsequent reaction. The precipitate was again dissolved in hydrochloric acid and diluted to 25 ml. The β-activity of each fraction was measured with a dipping counter. Finally, the retention value of radioarsenic as arsenate was calculated on each salt as follows:

$$R=\frac{I(\mathrm{AsV})}{I(\mathrm{AsIII})+I(\mathrm{AsV})}\times 100\ (\%)$$

were I is the intensity of radioactivity.

Results

First, the effect of irradiation temperature and storage time on retention was investigated. The irradiated sample was principally sodium

TABLE II. EFFECT OF IRRADIATION TEMPERATURE, STORAGE TEMPERATURE AND STORAGE TIME ON RETENTION OF NEUTRON-IRRADIATED $Na_2HAsO_4\cdot 7H_2O$

Run No.	Irrad. temp. °C	Storage temp. °C	Storage time hr.	Retention %
1	−196	−196	1	48.3
2	−196	−196	1	47.8
3	−196	−196	16.5	50.0
4	−72	−72	1	50.0
5	−72	−72	1	48.7
6	−72	−72	17	51.4
7	−72	−72	18	51.1
8	−72	−72	18	52.7
9	Room	Room	0.5	64.6
10	Room	Room	1	65.1
11	Room	Room	18	67.8
12	Room	Room	18.5	69.0
13	Room	Room	119	72.6
14	−196	Room	3.5	59.8
15	−196	Room	18.5	60.9
16	−72	Room	1	55.5
17	−72	Room	18.5	64.3
18	150~100	Room	1	68.2
19	150~100	Room	18	69.0
20	Room	Room	0.5	60.9
21	Room	Room	0.5	60.6
22	Room	Room	3.5	63.4
23	Room	Room	22	66.1
24	Room	Room	25	67.2

1—19 Irradiated for 2.5~3.0 hr.
20—24 Irradiated for 1.0 hr.

arsenate, $Na_2HAsO_4\cdot7H_2O$, of an especially pure grade obtained from the Merck Co. The crystal size was not uniform but was roughly within the range of 1~3 mm. in diameter. The results are given in Table II. In the case of irradiation at 150~100°C, the state of the target crystals differed from that at room temperature. Having a large amount of water of crystallization, the crystal melted at these high temperatures, and then the water was evaporated. The target had probably been partly changed into $Na_4As_2O_7$.

The results of the irradiation of Li_3AsO_4 and $H_4As_2O_7$ at low or room temperatures are shown in Table III. Further, the dependence of retention upon storage time was investigated for several kinds of arsenates, the results being given in Table IV.

TABLE III. EFFECT OF IRRADIATION TEMPERATURE, STORAGE TEMPERATURE AND STORAGE TIME ON RETENTION OF IRRADIATED Li_3AsO_4 AND $H_4As_2O_7$

Compound	Irrad. temp. °C	Storage temp. °C	Storage time hr.	Retention %
Li_3AsO_4	−196	−196	1	36.2
Li_3AsO_4	−196	−196	4	36.2
Li_3AsO_4	Room	Room	1	40.6
$H_4As_2O_7$	−72	−72	1	45.4
$H_4As_2O_7$	Room	Room	1	55.2

TABLE IV. DEPENDENCE OF RETENTION UPON STORAGE TIME

Compound	Storage time hr.	Retention %
Li_3AsO_4	1.0	40.6
Li_3AsO_4	4.0	44.0
Li_3AsO_4	21.0	44.0
Li_3AsO_4	24.5	46.4
$Na_3AsO_4\cdot12H_2O$	1.0	39.5
$Na_3AsO_4\cdot12H_2O$	42.5	40.9
$Na_2HAsO_4\cdot7H_2O$	0.5	64.6
$Na_2HAsO_4\cdot7H_2O$	1.0	65.1
$Na_2HAsO_4\cdot7H_2O$	18.0	67.8
$Na_2HAsO_4\cdot7H_2O$	119	72.6
$NaH_2AsO_4\cdot2H_2O$	1.0	46.9
$NaH_2AsO_4\cdot2H_2O$	42.5	54.0
$KH_2AsO_4\cdot H_2O$	1	54.9
$KH_2AsO_4\cdot H_2O$	23.0	59.5
$BaHAsO_4$	1.0	49.4
$BaHAsO_4$	24.5	51.5
$Co_3(AsO_4)_2\cdot8H_2O$	1.0	21.1
$Co_3(AsO_4)_2\cdot8H_2O$	24.5	50.5

Irradiated salts were stored at room temperature.

In general, the results show a gradual increase in retention values, i. e., an increase in the arsenic(V) fraction, when the irradiated salts are stored at room temperature.

TABLE V. RETENTIONS IN IRRADIATED CRYSTALLINE ARSENATES

Arsenate	Retention %
Li_3AsO_4	40.6±1.1
$(NH_4)_3AsO_4\cdot3H_2O$	41.0±0.5
$Na_3AsO_4\cdot12H_2O$	39.5±0.1
$(NH_4)_2HAsO_4$	46.8±0.4
$Na_2HAsO_4\cdot7H_2O$	65.1±0.5
$Co_3(AsO_4)_2\cdot8H_2O$	21.1±0.6
NaH_2AsO_4	52.7±1.0
$NaH_2AsO_4\cdot2H_2O$	46.9±0.3
$KH_2AsO_4\cdot H_2O$	54.9±0.1
$BaHAsO_4$	51.8±2.4
$BaHAsO_4\cdot H_2O$	49.6±0.2

Fluctuation of obtained retention value was shown after mean value in the form such as 41.0±0.5.

In Table V, the results of the irradiation of various kinds of crystalline arsenates are shown; here the effects of cation atom and of water of crystallization can be observed. The given values have been obtained for the irradiation at room temperature and for the storage for one hour. It was found that each salt had its characteristic retention value and that the value for $Na_2HAsO_4\cdot7H_2O$, 65%, agreed with the results of Müller and Broda, and also agreed roughly with those by Malý and Šimáňová, who had obtained the value of 67%.

Discussion

It is clear from the data of the retention values of irradiated $Na_2HAsO_4\cdot7H_2O$ after one hour's storage that the values at the two lower temperatures are nearly the same, about 50%, and that they show a fairly large difference from the value, 65%, obtained for the irradiation at room temperature. When the irradiated crystals were stored for 17~18 hr. at liquid nitrogen or dry ice-ethanol temperature, the retention values increased very little, while the storage of radioactive crystals at room temperature resulted in a gradual increase in the radioactivity of the 'arsenate' fraction, and the retention values increased. It is considered that, in these cases, the recoil process and subsequent reactions in solids play an important role in the observed retention. The lower values obtained at lower irradiation- and storage temperatures suggest that, after the recoil process, very slow or no subsequent reaction occurred to produce radioarsenic atoms in an oxidation state higher than III.

In the preliminary experiment, solutions containing arsenate or arsenic acid at various pH's were irradiated and the retention values, 15∼21%, were obtained, independent of the pH of the solution*.

Considering the above results, it is quite probable that the chances for recombination or other reactions of the recoil species with collision fragments or with parent molecules may be larger in the solid phase than in the liquid phase because of the large cage energy and the longer lifetime of the 'hot zone'[6]. For example, the following speculation may be true: a recoil fragment containing ^{76}As, which otherwise can oxidize the water upon solution of the irradiated target, may be able to react with oxygen ions or parent species in the neighborhood in the crystal to form a new fragment which is liable to hydrate to arsenate ion when dissolved. This reaction would result in the high initial retention and the gradual increase in its value during storage of irradiated arsenate crystals**.

Low temperatures at the bombardment site would affect the reaction period or the lifetime of the 'hot zone', thus resulting in lower retention than in the case of bombardments at room or higher temperatures. A few experimental data in Table I support the above statement; that is, when target salts which had been irradiated at -196 or -72°C were stored at room temperature, the retention increased rather rapidly with lengthening storage time. It can be thought that the thermal- or radiation annealing effect and storage effect are so remarkable even at room temperature that the slight difference in experimental conditions affects the reproducibility of the experimental results. In fact, when the crystals were irradiated at room temperature for 1 hr. instead of 3 hr., the resulting retention was 60.9% after the storage of the irradiated salts for 0.5 hr. This value is lower than that for 3 hr's irradiation, 64.6%.

The dependence of retention upon irradiation temperature is also observed for arsenates other then sodium arsenate (Table III). It seems that these phenomena are caused by the reaction mechanism described above, although the absolute values of retention are very specific for each salt.

Similar results were obtained from the experiment to investigate the dependence of retention upon storage time of radioactive crystals (Table IV). An increase in retention with storage at room temperature is considered a general tendency for all irradiated arsenated salts, since the activation energy barrier opposing the recombination reaction of recoil arsenic ions with oxygen is assumed to be rather small.

In Table V are shown the retentions in various crystalline arsenates. No regularity can be found in the obtained values with regard to the mass of cation which has collided with a recoil atom, and a model which is based upon elastic-collision between them cannot account for the experimental data, which are common to the studies of the Szilard-Chalmers process in oxyanion salts. Harbottle and Sutin[8] suggested that ammonium ion and water of crystallization would act as reducing agents in the 'hot zone' and would result in low retentions in case of the irradiation of the salts containing them. Our results, although not so remarkable, do not contradict their suggestion. For example, low retentions for $Na_3AsO_4 \cdot 12H_2O$ and $Co_3(AsO_4)_2 \cdot 8H_2O$ are assumed to be due to their high content of water of crystallization; ammonium salts such as $(NH_4)_3AsO_4 \cdot 3H_2O$ and $(NH_4)_2HAsO_4$ also have rather low retentions as compared with those of salts of alkali metals except lithium salts. Further, the retentions of hydrate and anhydrous form of one compound such as $NaH_2AsO_4 \cdot 2H_2O$ and NaH_2AsO_4 can be compared in some cases, and lower values are obtained for hydrate crystals.

The presence of elementary radioarsenic, which has been suggested by Harbottle and Kawahara, could not be confirmed because only the precipitation method was adopted in the present experiment. Perhaps, parallel experiments using several kinds of separation methods would be valuable in studying the behavior of radioarsenic in the state of oxidation number of zero, or in intermediate valency states in the solid phase.

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* Very concentrated arsenic acid solution (2 g. $H_4As_2O_7$/ml.) gives the retention, 37%.

6) G. Harbottle and N. Sutin, *J. Phys. Chem.*, **62**, 1344 (1958).

** A similar argument has been made, with respect to the recombination of the fragments produced by neutron capture in potassium chromate, by Maddock et al.[7]

7) M. M. de Maine, A. G. Maddock and K. Taūgbŏl, *Discuss. Faraday Soc.*, **1957**, 211.

8) G. Harbottle and N. Sutin, "Advances in Inorganic Chemistry and Radiochemistry", Vol. 1, Academic Press, New York (1960). p. 267.