BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1711—1712 (1971)

The Chemical Behavior of the ^{72}As Formed by the EC Decay of ^{72}Se in an Organic Solvent

Takeshi SOTOBAYASHI, Toshio SUZUKI, and Tomohiko NODA
Department of Chemistry, Faculty of Science, University of Niigata, Niigata

(Received December 24, 1970)

Many papers have been published on the chemistry of a hot atom formed as a result of isomeric transition with internal conversion or negative beta decay.[1-6] Since, however, little information is available on the chemical behavior of an EC-decay product, we attempted to study the chemical behavior of 26-h ^{72}As, an EC-decay product of 8.4-d ^{72}Se, in an organic solvent. In the present work, some organic-solvent solutions of two selenium compounds of different chemical natures (selenocyanate complex and selenium tetrabromide) were prepared by a liquid-liquid extraction method, and the separation of ^{72}As from the solvent solution and the oxidation state of the separated ^{72}As were studied.

TABLE 1. THE NUCLEAR PROPERTIES OF ^{72}As AND PROTON-INDUCED SELENIUM ISOTOPES

Type of production	Nuclide	Half-life	Mode of decay	Major γ-radiations (keV)
—	^{72}As	26 h	EC, β^+	510, 835
p,4n	^{72}Se	8.4d	EC	46
p,3n	^{73}Se	42m, 7.1m	EC	359, 685
p,2n	^{74}Se	stable	—	—
p, n	^{75}Se	120 d	EC	120, 136, 265, 280, 401

An arsenic trioxide target was irradiated with 30-MeV protons in the frequency-modulated cyclotron of the Institute for Nuclear Study of the University of Tokyo. Table 1 shows the nuclear properties of ^{72}As and proton-induced selenium isotopes. The ^{72}Se and ^{75}Se were γ-spectrometrically identified in the target two weeks after the irradiation. The target was dissolved in 6M hydrochloric acid, together with a selenium carrier (SeO_2). Elemental selenium was precipitated by passing sulfur dioxide through the target solution. The precipitate was separately dissolved in 0.1M potassium cyanide and 4M hydrobromic acid, and then converted into potassium selenocyanate and selenium tetrabromide respectively. From these two radioselenium solutions (0.1 mg Se/m*l*), two kinds of organic solutions of purified radioselenium were prepared by the following two procedures. All the radioactivities were γ-spectrometrically measured by using a 3 in × 3 in NaI(Tl) scintillation detector coupled with an 800-channel pulse-height analyzer.

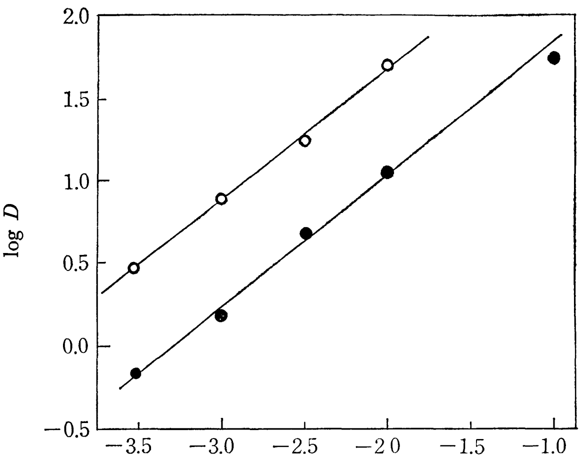

Fig. 1. log *D* *vs*. log (L$^+$X$^-$) plot.
L$^+$X$^-$: TPA or TAMA,
—●—: Extraction of Se^{72,75} with TPA in chloroform,
—○—: Extraction of Se^{72,75} with TAMA in chloroform.

First, radioselenium was extracted from the 0.1M potassim cyanide solution into a chloroform solution of 0.01—0.001M tetraphenylarsonium chloride (TPA) or 0.1—0.01M trialkylmethylammonium chloride (TAMA),[7] which had been pre-equilibrated with a 0.1M potassium cyanide solution. Figure 1 shows the extraction behavior of radioselenium with TPA or TAMA in chloroform; the logarithm of the distribution ratio, (D), is plotted against that of the concentration of the extracting reagent (TPA or TAMA). These log-log plots, with an equal slope of about 0.82, suggest that the extracted species with TPA and TAMA were, as expected, $Ph_4As^+SeCN^-$ and $R_3MeN^+SeCN^-$ [7] respectively. Secondly, radioselenium was quantitatively extracted into benzene containing 1 *w*/*v* % phenol from a 4M hydrobromic acid solution. The chemical form of the extracted selenium species is believed to be $SeBr_4$.[8] These two sample solutions (chloroform and benzene) were allowed to stand in a glass vessel for more than one day to obtain a sufficient amount of ^{72}As growing from ^{72}Se. Thereafter, each organic solution was transferred to a second vessel. The inner walls of the emptied vessel were carefully washed with a small portion of the respective solvent

---

[1] S. Wexler and G. R. Anderson, *J. Chem. Phys.*, **33**, 850 (1960).
[2] S. Wexler, *ibid.*, **36**, 1992 (1962).
[3] J. F. Duncan and F. G. Thomas, *J. Inorg. Nucl. Chem.*, **29**, 869 (1969).
[4] T. Shiokawa, H. Kudo, and T. Omori, This Bulletin, **38**, 1340(1965).
[5] T. Shiokawa and T. Omori, *ibid.*, **42**, 696(1969).
[6] M. Haissinsky, "Nuclear Chemistry and Its Application," (English ed.), Addison-Wesley Pub. Co. Inc., London (1964).
[7] An alkyl group, R, refers to $C_nH_{2n+1}(n=8-10)$.
[8] T. McGee, U. Lynch, and G. G. Boswell, *Talanta*, **15**, 1435 (1968).

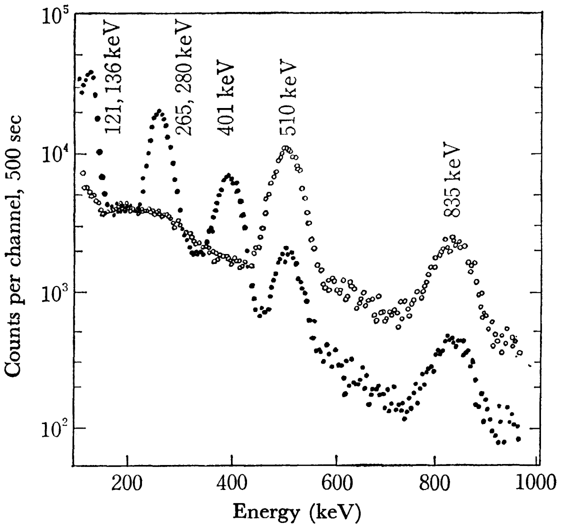

Fig. 2. A set of γ-spectra for an organic phase (TPA, —●—) and its corresponding hydrochloric acid solution containing the deposited fraction of ^{72}As (—○—).

TABLE 2. DEPOSITED FRACTION OF ^{72}As ON VESSEL WALLS AND OXIDATION STATE OF DEPOSITED ^{72} As

Extracting reagent	Aqueous phase	Fraction on vessel walls of ^{72}As (%)	Relative abundance As^{3+} (%)	As^{5+} (%)
TPA, 10^{-3}M	0.1M KCN	81—90	73	27
TPA, 10^{-2}M	0.1M KCN	41—56	75	25
TAMA, $2\cdot10^{-2}$M	0.1M KCN	53	73	27
Benzene[a]	4M HBr	64—77	78	22

[a] The benzene phase contained 1 *w/v* % phenol.

solution, and subsequently with a few milliliters of concentrated hydrochloric acid.

Figure 2 shows the set of γ-spectra for organic and aqueous solutions in the 110- to 1000-keV range. As is shown in Fig. 2, most of the radioselenium proved to remain in the organic solution. Most ^{72}As freshly growing from its parent during equilibration was found in the hydrochloric acid — on the vessel walls. The respective activity fractions of ^{72}As on the walls and in the organic solution were determined by measuring the photopeak areas at 835 keV. The results are summarized in the third column of Table 2.

It should be noted that ^{72}As showed a similar depositing behavior on the vessel walls for the two extracted selenium compounds of different chemical natures. The deposited fraction of ^{72}As seems to decrease with the increase in the concentration of the complexing reagent (TPA). Further, it was found that the fraction of ^{72}As on the walls varied with the ratio of the area in contact with the organic solution to the total volume of the organic solution; the ^{72}As fraction on the walls increased by a factor of 1.5 when the ratio changed from 3.8 to 7.4 cm^2/m*l*. A further examination was carried out in order to determine the percentage abundances in the oxidation state of the deposited ^{72}As obtained in the same way as in the above experiments. As^{3+} and As^{5+} were separated by a conventional hydrochloric acid-benzene extraction method.[9] The results are presented in the last column of Table 2. It may clearly be seen from Table 2 that about 75% of the ^{72}As recovered on the walls existed in the 3+ oxidation state, regardless of the difference in chemical nature of the extracted selenium compound.

From the present observations, it can be said that the effects of an EC decay process, followed by the bond rupture of the ^{72}Se-tagged compounds, probably play a major role in determining the deposition behavior of ^{72}As.

The authors wish to express their appreciation to Prof. Kazumasa Miyano of the Nuclear Physics Laboratory for his helpful discussions.

---

[9] G. O. Brink, P. Kafas, R. A. Sharp, E. L. Lewis, and J. W. Irvine, Jr., *J. Amer. Chem. Soc.*, **79**, 1303 (1957).