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著者	SUZUKI Shin, INOUE Yasushi, KISHIMOTO Mokuyoshi
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	17/18
page range	293-299
year	1965
URL	http://hdl.handle.net/10097/27261

Hot Atom Chemistry of ^{76}As Using Benzenearsonic Acid as a Target*

Shin SUZUKI, Yasushi INOUE and Mokuyoshi KISHIMOTO

The Research Institute for Iron, Steel and Other Metals

(Received September, 1965)

Synopsis

The enrichment of ^{76}As by means of the hot atom effect of neutron capture reaction has been carried out by using benzenearsonic acid as a target. Arsenites were carefully removed in advance from benzenearsonic acid. After irradiating for 2 hours in the pneumatic tube of atomic pile JRR-1 (thermal neutron flux is about $10^{11}\text{n/cm}^2\cdot\text{sec.}$), benzenearsonic acid was dissolved in 12 ml of 11 N hydrochloric acid. Resulting solution was then shaken with 10 ml of benzene and the recoiled arsenic was extracted into benzene layer. This layer was stripped with water, and ^{76}As was obtained in aqueous solution. The present enrichment method is advantageous in that radiochemically and chemically pure ^{76}As is obtained by comparatively simple and rapid procedures in a single oxidation state of trivalency in diluted hydrochloric acid solution. And it was found that the retention value of recoil fragments was about 15~20% and about 80% of it was present in trivalent state.

I. Introduction

The method for the enrichment of ^{76}As by means of hot atom effect of zirconium benzenearsonate has been reported.⁽¹⁾ Insolubility of the target in water and in diluted hydrochloric acid and the low thermal neutron absorption and activation cross sections of zirconium were advantageously used in this method. On this basis, radiochemically and chemically pure ^{76}As was obtained by a comparatively simple procedure with the enrichment factor of approximately 1.2×10^4 . Moreover, the oxidation state of ^{76}As thus obtained was examined with the results that 55~70% was trivalent state. This method, however, has such shortcomings as the inconvenience of solid-liquid extraction and the presence of 0.02~0.12% radiochemical impurities composed of ^{97}Zr originating from zirconium intentionally introduced in the target. Consequently, to obtain radiochemically pure ^{76}As , a further chemical separation should be done after the extraction of it from the target. Therefore, it is considered that benzenearsonic acid itself can advantageously be used instead of its zirconium salt if the method for the separation of recoil fragments can be found. As a result of detailed investigations, trivalent arsenic in concentrated hydrochloric acid solution was found to be selectively extracted into benzene and the enrichment of ^{76}As was under-

* The 1216th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the J. Chem. Soc. Jap., **83** (1962), 1027.

(1) S. Suzuki, M. Saito and Y. Inoue, J. Chem. Soc. Jap., **83** (1962), 1023. Sci. Rep. RITU, **17** (1965), 267.

taken by this method. The oxidation state of recoil fragments and the value of retention were also investigated.

II. Experiments

1. Reagents and apparatus

Benzene-arsenic acid: To remove arsenious oxide which might be contained in benzene-arsenic acid, the purification was carried out by the following procedure. 1 g of benzene-arsenic acid (Merck's guaranteed reagent) was dissolved into 10 ml of concentrated hydrochloric acid, transferred to a separatory funnel and shaken with 10 ml of benzene. After the benzene phase was discarded, a new 10 ml portion of benzene was added to the aqueous phase and the extraction was repeated. This procedure was continued till the trivalent arsenic was completely eliminated. Hydrochloric acid phase was run into a beaker, and dried on a water bath. A few milliliters of water was then added and evaporated to dryness. This procedure was repeated a few times and then hydrochloric acid was completely driven off by heating the residue for 1~2 hr in an air bath at 120°C. The lumps of benzene-arsenic acid thus purified were pulverized prior to use.

All other reagents and apparatus were those the same as in the preceding report.⁽¹⁾

2. Fundamental investigations on the method of separation

Benzene extraction of tri- and quinque-valent arsenic: G.O. Brick and his co-workers⁽²⁾ reported their results on the solvent extraction equilibrium of trivalent arsenic between hydrochloric acid solution and various organic solvents. According to their results, trivalent arsenic can be extracted into benzene from concentrated hydrochloric acid, that is, the distribution coefficients are 17.7 and 18.3 from 10.3 and 11.9 N hydrochloric acid, respectively. The distribution coefficient of quinquevalent arsenic is less than 0.003 and it cannot be extracted into benzene as described by M. Green and J.A. Kofalas.⁽³⁾

To make sure these results, trivalent and quinquevalent arsenic were extracted from 10 ml of 11 N hydrochloric acid solution into 10 ml of benzene. When 750 μg of trivalent arsenic was used, 93.8~95.6% and 99.6~99.8% of it were extracted by single and duplicate extraction, respectively. Trivalent arsenic in benzene phase was quantitatively back extracted into 5 ml of water.

When 720 μg of quinquevalent arsenic was extracted with benzene, 0.7~2.7% and 1.3~5.3% were extracted into benzene by single extraction and duplicate extraction, respectively. For reducing quinquevalent arsenic, four drops of concentrated hydrobromic acid solution and a small amount of hydroxylamine hydrochloride were added to 10 ml of 11 N hydrochloric acid solution of quinquevalent arsenic. The solution thus prepared was mixed thoroughly and stood till the yellow color of bromine disappeared. In this case, 94.2~94.3% of arsenic

(2) G.O. Brick, P. Kafalas, R.A. Sharp, E.L. Weiss and J.W. Irvine, *J. Amer. Chem. Soc.*, **79** (1957), 1303.

(3) M. Green and J.A. Kofalas, *J. Phys. Chem.*, **22** (1954), 760.

was extracted into benzene. When the extraction was repeated twice, 99.7% of arsenic was extracted. Considering the oxidation reduction potentials of As (III)–As (V) and Br_2 – Br^- , quinquivalent arsenic cannot quantitatively be reduced to trivalent state by this method and the extractability as high as trivalent arsenic seems to be strange. This high extractability may be explained by the transference of this redox equilibrium to the direction of trivalent state due to the removal of trivalent arsenic from aqueous phase. The arsenic was determined by molybdenum blue method⁽⁴⁾ after the destruction of organic matter by nitric acid throughout this experiment.

The stability of benzenearsonic acid against hydrochloric acid and hydrobromic acid: It is necessary for the separation of recoil fragments by the above method to treat the irradiated target by hydrochloric acid and hydrobromic acid. The absorption spectra of benzenearsonic acid and the amount of arsenic freed from the target by decomposition were measured to know if the reagent was decomposed by this procedure. When 4 mg of benzenearsonic acid was dissolved in 12 ml of concentrated hydrochloric acid and stood overnight or heated to dryness on a water bath, its absorption spectrum shown in Fig. 1 did not change

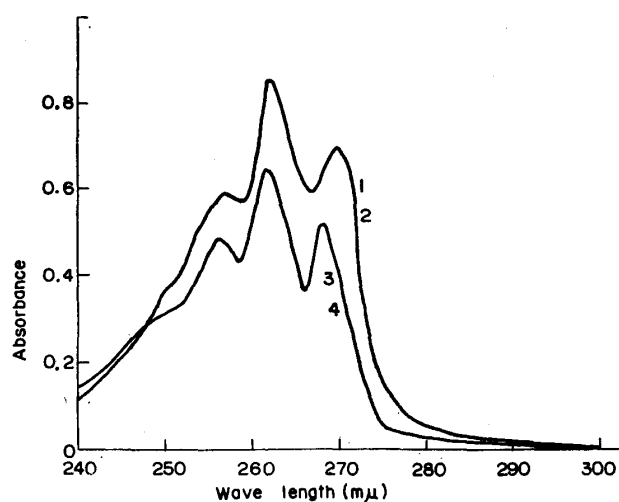


Fig. 1. Absorption spectra of benzenearsonic acid ($1.6 \times 10^{-2}\%$)

1. Not irradiated
2. $8.8 \times 10^5\text{r}$ in 4.8 N HCl
3. Not irradiated in H_2O
4. $8.8 \times 10^5\text{r}$

at all. When four drops of concentrated hydrobromic acid was added to it, benzenearsonic acid was completely decomposed by the evaporation to dryness. But only a part of it was decomposed when its solution containing a small amount of hydrobromic acid was stood at room temperature.

Benzene extraction of benzenearsonic acid: 4 mg of benzenearsonic acid in 12 ml of 11 N hydrochloric acid solution was not extracted at all into 10 ml of benzene, and 100% of this compound remained in the aqueous phase. But, if four

drops of concentrated hydrobromic acid and a small amount of hydroxylamine hydrochloride were added to the hydrochloric acid solution of benzenearsonic acid and stood till the yellow color disappeared, about 1% of arsenic in benzenearsonic acid was extracted. This is not attributable to the extraction of benzenearsonic acid itself but to the decomposition of it by the action of hydrobromic acid.

3. Enrichment of ^{76}As

It is clear from the above investigations that the benzene extraction from the concentrated hydrochloric acid solution of irradiated target is suitable for the separation of trivalent arsenic. For the extraction of quinquevalent arsenic, however, the reduction by a suitable reducing agent is necessary. For this purpose, ferrous ions, sulfur dioxide, hydrobromic acid and hydroiodic acid were examined. Of these, ferrous ions and sulfur dioxide gave a low extractability and hydroiodic acid decomposed benzenearsonic acid considerably even at room temperature. They were, thus, not suitable for the enrichment of ^{76}As . Hydrobromic acid is most adequate for this purpose, but the addition of hydrobromic acid renders the enrichment factor to ^{76}As a decrease because of the unfavourable partial decomposition of benzenearsonic acid as stated earlier. However, the enrichment of ^{76}As is possible even by the omission of reduction procedure if a little lowering of yield is tolerated, because a greater part of recoil fragments is trivalent as stated later. From the above consideration, the following procedure was adopted:

Purified benzenearsonic acid, sealed in polyethylene bag, was irradiated in the pneumatic tube of JRR-1 (thermal neutron flux is about $10^{11}\text{n/cm}^2\cdot\text{sec.}$) at the Japan Atomic Energy Research Institute for 2 hr. This was dissolved in 10 ml of 11 N hydrochloric acid and shaken with 10 ml benzene in a separatory funnel. After the two phases were separated from each other, the benzene phase was transferred to another separatory funnel and washed with 5 ml of concentrated hydrochloric acid. ^{76}As in benzene phase was then stripped with 5 ml of water. An aliquot of this solution was taken for the measurement of β -radioactivity. At the same time the determination of arsenic was made and the specific activity was estimated. With the comparison of the above specific activity and that of the target the enrichment factor was calculated.

4. Estimation of the oxidation state and the value of retention.

On the basis of the results of section 2 and the method described in the foregoing report⁽¹⁾, the oxidation state and the value of retention were determined by the method illustrated in Fig. 2. In this method, the reduction with hydrobromic acid was applied to the determination of radioactivity originating from $\text{As(III)} + \text{As(V)}$. The decomposition of benzenearsonic acid by this procedure was 1% at the most, so that this procedure might give a reasonable value within the experimental error. The retention value was estimated from the difference of radioactivities between I and III in Fig. 2. The oxidation state was calculated from the values obtained in II and III in the same figure.

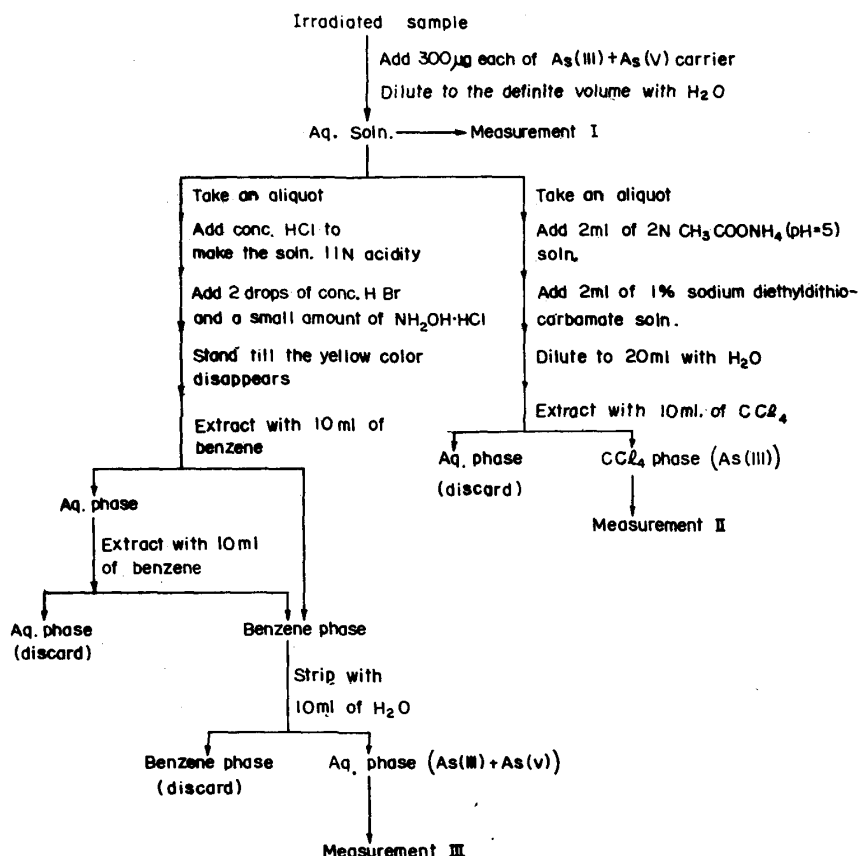


Fig. 2. Separation scheme of benzenearsonic acid, As(III) and As(V)

III. Results

1. Effect of γ -ray irradiation on benzenearsonic acid

The decomposition of benzenearsonic acid caused by the ionized radiation in a nuclear reactor may be one of the factors affecting the enrichment factor. To make clear this point, the effect of γ -ray irradiation was examined. Benzenearsonic acid, sealed in a glass tube, was irradiated at a dose rate of $3.9 \times 10^5 \text{r/hr}^{**}$ at room temperature for 2 hr (total dose was $8.8 \times 10^6 \text{r}$) using the ^{60}Co - γ -ray irradiation facility of the Japan Atomic Energy Research Institute. As shown in Fig. 1, the absorption spectrum of benzenearsonic acid does not change at all by the irradiation. To make sure of this, the amount of arsenic extracted from the irradiated target was determined with the results that about $2 \mu\text{g}$ of arsenic was extracted from 27 mg of the target.

2. Enrichment of ^{76}As

As an example, ^{76}As produced by the thermal neutron irradiation of 130.2 mg of benzenearsonic acid was separated. The yield was 61.7% and the enrichment factor was 2.6×10^3 .

Furthermore, ^{76}As remaining the aqueous phase as a quinquevalent state was extracted after the reduction by hydrobromic acid with the results that the

** This value is considered to be about the same dose rate as in JRR-1.

yield and the enrichment factor were 21.2% and 1.6×10^2 , respectively. In this case the yield signifies the fraction of the extracted radioactivity to the total radioactivity produced in the target.

3. Oxidation state and value of retention.

The results are shown in Table 1. It is apparent from the table that the value of retention is about 15~20% and 80% of the recoiled ^{76}As in the trivalent state.

Table 1. The retention value and the oxidation state.

Standing time after the irradiation (hrs)	Retention value (%)	Per cent of As (III)
18	15.2-21.8	86.4-93.6
42	14.4-15.4	77.1-78.4
67	19.0-20.8	78.4-80.7
90	19.2-20.0	85.3-85.5
139	18.4-20.0	81.7-86.6
186	21.3-25.7	89.6-96.8

IV. Consideration

The enrichment factor obtained by zirconium benzenearsonate was 1.2×10^4 as described in the preceding report⁽¹⁾ and that obtained by the present method was 2.6×10^3 . Consequently, the present method is inferior to the former method in the enrichment factor by one order. But this method is superior to the former one in that the enriched ^{76}As has a uniform oxidation state of trivalency and is completely radiochemically pure. The simplicity and rapidity of the procedure and the freedom from the fear of accidental introduction of chemical impurities are considered to be the common merits in these methods.

It is impossible to presume the accurate value of the enrichment factor only from the results of radiation decomposition of the target, because the temperature in the nuclear reactor during the irradiation is not known and there are many factors affecting the enrichment factor, such as neutron, γ -ray in nuclear reactor and the prompt γ -ray generated from the neutron capture reaction. The amount of arsenious oxide produced by the radiation decomposition of the target, however, may be one of the clues determining the maximum value of the enrichment factor. From this consideration, the maximum enrichment factor of ^{76}As is expected to be 5×10^3 if the yield is supposed to be 100%. The enrichment factor in the present experiment is about the half of the expected value and if one takes the yield of 60% in consideration, this value approximately coincides with the expected one.

With the aim to improve the yield, ^{76}As in a quinquevalent state was extracted after the addition of hydrobromic acid but the enrichment factor was considerably low; accordingly, it will be hard to improve the yield by this method if a high enrichment factor is needed.

The value of retention gradually increased with the increase of standing time, and, in contrast with the case of zirconium complex, the percentage of trivalent arsenic tended to increase little by little. Furthermore, about 80% of

recoiled arsenic was in a trivalent state compared to the value of about 55~70% obtained with zirconium benzenearsonate. To clarify these differences, further investigations should be carried out.

Acknowledgement

In conclusion, the authors wish to thank Prof. H. Gotô for his guidance, discussion and continuous encouragement. And also they indebted to Dr. N. Shibata and the members of laboratory for isotope production in the Japan Atomic Energy Research Institute for their helps in carrying out the present study. A part of the expenses has been defrayed by the Grant-in-Aid by the Ministry of Education.