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Studies of the Behavior of Trivalent Uranium in an Aqueous Solution. I. Its Reduction and Its Stability in Various Acid Solutions

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Various methods for the reduction of hexavalent uranium to the trivalent state were examined. It was found that the liquid-zinc-amalgam method is simple and rapid, and gives a high yield with a good reproducibility in hydrochloric, sulfuric, and perchloric acid solutions. The percentage of reduction is over 99% in a 0.5 N hydrochloric acid solution. Next, the stability of trivalent uranium in these media was investigated; it was observed that the trivalent uranium ion is fairly stable in any hydrochloric, sulfuric and perchloric acid solutions at a low concentration of the acids in the absence of atmospheric oxygen, but that it becomes unstable as the acid concentration increases. Both the percentage of reduction by the liquid-zinc-amalgam method and the stability of trivalent uranium are highest in a hydrochloric acid solution, next highest in a perchloric acid solution, and lowest in a sulfuric acid solution.

Uranium ions in solution form one of the most intricate and interesting domains in the chemistry of this element. Four oxidation states are known for uranium ions in an aqueous solution: the tri-, tetra-, penta-, and hexapositive states, and the hydrolytic reactions, oxidation-reduction equilibria, and complex ion formation characteristic of the ions in the various oxidation states, except for the trivalent state, have been the subject of much study.

Regarding the presence of the trivalent uranium ion in an aqueous solution, Someya1) first reported that hexavalent uranium in a hydrochloric acid solution can be reduced to the trivalent state by the liquid zinc amalgam. However, only a limited amount of information has been obtained on the properties of the trivalent uranium ion in an aqueous solution. Stewart2) and Jörgensen3) reported on the absorption spectra of trivalent uranium in a hydrochloric acid solution as well as in a perchloric acid solution, and those spectra are cited by Seaborg and others in their textbooks.4-9) There is a brief description given in those books of how the trivalent uranium ion is unstable in an aqueous solution, how it is rapidly oxidized to the tetravalent state with the evolution of hydrogen, and how strongly acidified solutions appear to be more stable. It has been the previously-accepted conclusion that the rapid oxidation of the trivalent uranium ion makes the study of the solution chemistry difficult; therefore, exact data are unavailable.

The author conducted a study on the preparation of trivalent uranium, and found that the reduction of hexavalent uranium to the trivalent state by the liquid zinc amalgam is the simplest method, that it can give fairly high yields, and that the trivalent uranium ion obtained can be stabilized to a considerable extent in an aqueous solution by the proper selection of the kind of acid and of the concentration of acids, as long as all atmospheric oxygen is excluded. Furthermore, it was observed that trivalent uranium is more stable in a diluted acid solution than in a concentrated one. These observations are contrary to the previously-accepted view.

On the basis of the above facts, the author plans to conduct a detailed study of the chemical behavior of the trivalent uranium ion in an aqueous solution; in this paper studies of the reduction of the hexavalent state to the trivalent state by the liquid zinc amalgam in hydrochloric, sulfuric, and perchloric acid solutions, and of the stability of the

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1) K. Someya *Z. Anorg. Allgem. Chem.*, **161**, 46 (1927).

2) D. C. Stewart, ANL-4812 (1952).

3) C. K. Jörgensen, *Acta Chem. Scand.*, **10**, 1503 (1956).

4) R. J. Meyer and E. Pietsch, "Gmelins Handbuch der Anorganischen Chemie," 8th Edition, System No. 55, Verlag Chemie, G. m. b. H., Berlin (1936).

5) J. J. Katz and E. Rabinowitz, "The Chemistry of Uranium," National Nuclear Energy Series, Division VIII, Volume 5, McGraw-Hill Book Co., Inc., New York (1951).

6) G. T. Seaborg, "The Actinide Series" in "Comprehensive Inorganic Chemistry," Vol. 1, ed. by M. C. Sneed, J. L. Maynard and R. C. Brasted, D. van Nostrand Company, Inc., New York (1953), Chap. 3, p. 161.

7) H. R. Hoekstra and J. J. Katz, "The Chemistry of Uranium" in "The Actinide Elements," National Nuclear Energy Series, Division IV, Vol. 14A, ed. by G. T. Seaborg and J. J. Katz, McGraw-Hill Book Co., Inc., New York (1954), Chap. 6, p. 130.

8) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley & Sons, Inc., New York (1957), Chap. 5, p. 94.

9) J. E. Grindler, "The Radiochemistry of Uranium," NAS-NS 3050, U. S. Atomic Energy Commission (1962).

trivalent uranium ion in those media will be described.

Experimental

Reagents. Various acid solutions of hexavalent uranium were prepared as follows. A suitable amount of uranyl nitrate, of the highest purity, was heated almost to dryness several times with hydrochloric, sulfuric, or perchloric acid in order to convert the salt into each form completely; the residue was then dissolved in an appropriate quantity of a hydrochloric, sulfuric, or perchloric acid solution in order to prepare acid solution of varying concentrations. The concentration of the uranium was determined by first reducing the hexavalent uranium to the tetravalent state in the air with the liquid zinc amalgam, then titrating the tetravalent uranium with a standard solution of 0.01 N potassium dichromate, using sodium diphenylamine sulfonate as an indicator.[10] The concentrations of these uranyl solutions were found to range from 3—5×10^{-3} M.

The liquid zinc amalgam was prepared as follows.[11] About 3 to 4 g of pure granular zinc were washed well with dilute sulfuric acid and heated on a water bath for about an hour with about 100 g of mercury and a small quantity of dilute sulfuric acid (1+10). After cooling, the amalgam was stored in some dilute sulfuric acid; before use, it was washed thoroughly with water and separated from any solid substance by the use of a separating funnel.

All the other chemicals used were of the highest purity.

Apparatus. For the reduction procedure with the liquid zinc amalgam, the reduction apparatus[11] shown in Fig. 1 was used. All the parts were made of Pyrex glass except for the rubber tubing, G.

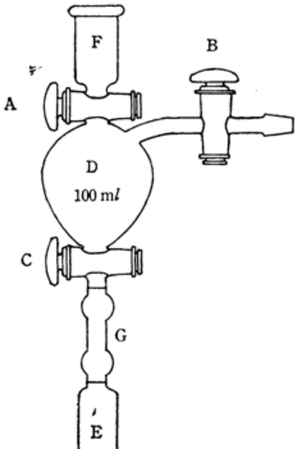

Fig. 1. Reduction apparatus for liquid zinc amalgam method.

Procedures. The experimental procedure for the reduction of the hexavalent uranium to the trivalent state with the liquid zinc amalgam was as follows. An acid solution of the same concentration as that of the hexavalent uranium sample solution was deoxygenated completely by bubbling argon, nitrogen, or carbon dioxide through, and then placed completely in both the amalgam receiver, E, and the rubber tubing, G. By connecting the rubber tubing, G, with the reduction apparatus, with the C stopcock open as is shown in Fig. 1, the part below the C stopcock was filled with the deoxygenated acid solution and the air was completely driven out of the part below the C stopcock. The C stopcock was then closed and 10 m*l* of the uranyl solution was added into the vessel, D, through the F part, and to this mixture there was added about 40 m*l* of an acid solution with the same concentration as the sample solution, while the F part was being washed. After about 10 m*l* of the liquid zinc amalgam had next been added to the vessel, D, from the F part, an inert gas was admitted from the B stopcock for 2 to 3 min to drive the air out of the vessel, D, completely. All the stopcocks were then closed and the apparatus was shaken vigorously by hand for 1 to 5 min in order to complete the reduction. When the C stopcock was opened carefully and the rubber tubing was pressed at G with the fingers, the amalgam came down into the receiver, E, and the acid solution in it took its place, washing the amalgam on its way up. In this way all the amalgam could be separated completely from the solution without any loss of the solution.

The percentage of the reduction of hexavalent uranium to the trivalent state in various acid solutions was determined by titrating the concentration of the trivalent uranium obtained with the above-mentioned procedure. A suitable quantity of a standard solution of 0.01 N potassium dichromate was added to the F part and then the A stopcock was opened a little. By this the standard solution could be gradually introduced into the vessel, D, through the A stopcock without giving air any chance to enter the vessel, D, until the state of oxidation insensitive to atmospheric oxygen had been reached. About 5 m*l* of a mixed solution of sulfuric acid, phosphoric acid, and water (3+3+14) and 2 to 3 drops of a 0.2% sodium diphenylamine sulfonate solution were added. After the end point of the titration had been carefully determined using the standard dichromate solution, the percentage of the reduction of hexavalent uranium to the trivalent state was calculated.

The stability of trivalent uranium in an aqueous solution was determined by keeping the reduced solution prepared in the above-mentioned manner in an inert gas atmosphere for a given period of time, and by titrating trivalent uranium by the method described above.

All the experiments were carried out at room temperature.

Results and Discussion

Method for Reducing Hexavalent Uranium to Trivalent Uranium. There are dry methods as well as wet methods for obtaining trivalent uranium. The author examined the reduction of uranium tetrachloride by hydrogen as the dry method.[12] However, this method requires a

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[10] T. Nakazono, *Nippon Kagaku Kwaishi (J. Chem. Soc. Japan)*, **42**, 761 (1921).

[11] T. Nakazono, *ibid.*, **42**, 526 (1921).

[12] T. Moeller, "Inorganic Syntheses," Vol. 5, p. 145 (1957).

complicated apparatus and is tedious in operation; in addition, it is time-consuming and has the disadvantage of yielding only chloride. As the wet method, the author first attempted the electrolytic reduction of the uranyl chloride solution using a platinum or a mercury cathode, but found that the reduction was possible only to the tetravalent state. On the other hand, the reduction with the liquid zinc amalgam is simple in operation and gives a high yield within a short period of time and with a good reproducibility. It thus offers the most convenient method for studying the chemical behavior of trivalent uranium in an aqueous solution, and so was used in all the later experiments.

Percentage of the Reduction of Hexavalent Uranium to the Trivalent State by Liquid Zinc Amalgam in Various Solutions. The percentage of the reduction of the hexavalent state to the trivalent state are shown in Table 1 at various concentrations of hydrochloric, sulfuric, and perchloric acids. As is apparent from the table, hexavalent uranium can be reduced to the trivalent state by the liquid-zinc-amalgam method in an inert gas atmosphere in hydrochloric acid, sulfuric acid, or perchloric acid. The reduction was more complete in a hydrochloric acid solution than in other media, and the percentage of reduction was 99.1% in a 0.5 N hydrochloric acid solution, a nearly complete reduction. A perchloric acid solution gave the next best result; similarly to hydrochloric acid, 0.5 N of the concentration gave the best value, about a 80% reduction. A sulfuric acid solution gave the poorest reduction among the three acids examined; the best value for this medium was about 60%. However, in a sulfuric acid solution the percentage of reduction did not change so much with the acid concentration as in the other two acids.

TABLE 1. PERCENTAGE OF THE REDUCTION OF THE URANYL ION TO THE TRIVALENT STATE BY THE LIQUID ZINC AMALGAM IN VARIOUS ACID SOLUTIONS

Kind of acid	Concn. of acid N	Percentage of reduction, %
HCl	0.01	65.4
	0.05	80.6
	0.1	89.9
	0.5	99.1
	2.0	95.2
	6.0	91.9
	12.0	91.9
$HClO_4$	0.01	52.9
	0.05	60.3
	0.1	62.1
	0.5	80.3
	2.0	75.9
	6.0	62.1
H_2SO_4	0.01	51.0
	0.05	56.9
	0.1	59.9
	0.5	60.0
	2.0	60.9
	6.0	47.7
	10.0	41.6

Each of the percentage of the reduction is the mean value of five experiments.

Stability of Trivalent Uranium in Various Acid Solutions. As is apparent from the experimental results shown in Figs. 2, 3, and 4, trivalent uranium is fairly stable in hydrochloric acid, sulfuric acid, or perchloric acid at low concentrations of the acids, but becomes unstable as the acid concentration increases. The stability is highest in a hydrochloric acid solution, next highest in a perchloric acid solution, and lowest in a sulfuric acid solution. This is the same order as for the percentage of reduction by the liquid-zinc-amalgam method. However, when the acid concentration increases beyond a certain point,

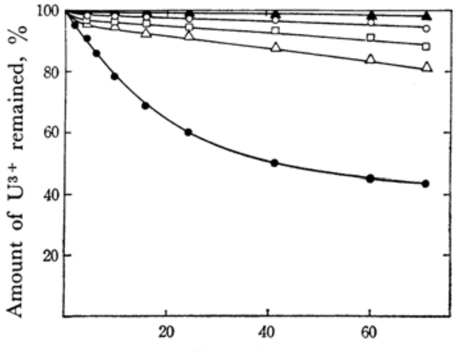

Fig. 2. Stability of trivalent uranium in hydrochloric acid solution.

▲: 0.05 N ○: 0.5 N □: 2 N
△: 6 N ●: 12 N

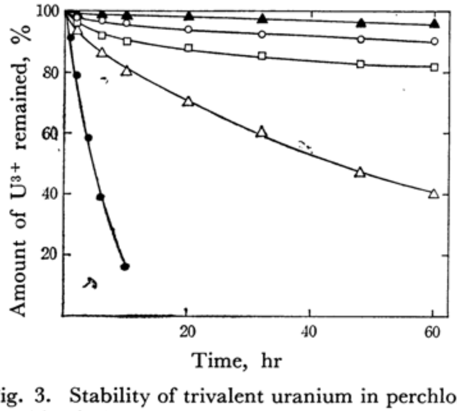

Fig. 3. Stability of trivalent uranium in perchloric acid solution.

▲: 0.01 N ○: 0.05 N □: 0.5 N
△: 2 N ●: 6 N

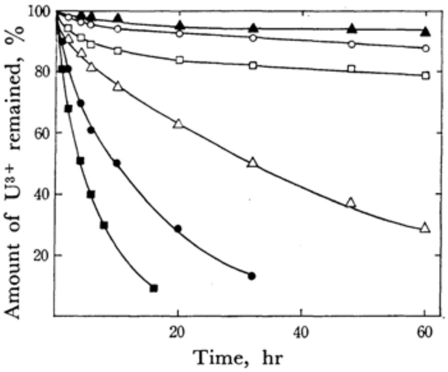

Fig. 4. Stability of trivalent uranium in sulfuric acid solution.
▲: 0.01 N ○: 0.05 N □: 0.5 N
△: 2 N ●: 6 N ■: 10 N

the order of perchloric acid and sulfuric acid is reversed.

In a 0.5 N hydrochloric acid solution, which is a very stable medium and which also gives an almost complete reduction, 98% of the initial amount of the trivalent uranium ion remains after 24 hr, 94% after 72 hr, and 86% after one week. In a 6 N hydrochloric acid solution, about 91% of the initial amount of trivalent uranium remains after 24 hr and 82% after 72 hr. Even in a 12 N hydrochloric acid solution, about 44% of the initial amount of trivalent uranium remains after 72 hr.

In a perchloric acid solution, which is a less stable medium than a hydrochloric acid solution, 91.5% of the initial amount of the trivalent uranium ion remains after 10 hr, 88.5% after 20 hr, and 83% after 48 hr, at the concentration of 0.5 N.

In a sulfuric acid solution, which is the least stable medium, 87% of the initial amount of the trivalent uranium ion remains after 10 hr, 84.5% after 20 hr, and 81% after 48 hr, at the concentration of 0.5 N. In this medium, as in a perchloric acid solution, trivalent uranium is not as stable at concentrations of the acid over 0.5 N.

As has been mentioned above, it has been found that, contrary to a view previously accepted, the rate of the $(2U^{3+}+2H^{+}\leftrightarrows 2U^{4+}+H_2)$ reaction proceeds quite slowly under the conditions described above, and trivalent uranium is reasonably stable in an inert atmosphere, especially at low acid concentrations. However, the re-oxidation occurs gradually, even in the absence of atmospheric oxygen.

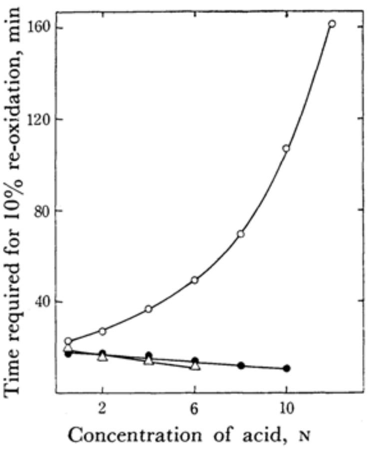

Fig. 5. Stability of trivalent uranium in air.
○: HCl ●: H_2SO_4 △: $HClO_4$

Thus, it is possible that the instability of trivalent uranium hitherto accepted may be due to the presence of oxygen. To check this possibility, a trivalent uranium solution was left in the air without stirring, and then its stability was examined by the method described above. The concentration of the acid was plotted as a function of the time required until 10% of the initial amount of trivalent uranium was re-oxidized. The results, given in Fig. 5, indicate that trivalent uranium is unstable to a considerable extent. As is also evident from this experiment, the stability in a sulfuric or a perchloric acid solution is low and does not change appreciably with the acid concentration. However, in a hydrochloric acid solution the stability increases with the increase in the acid concentration; this observation agrees with the results reported by other investigators.[4-9] It is conceivable that, in the case of a hydrochloric acid solution, a hydrogen chloride gas escapes from the solution as the concentration of hydrochloric acid increases, and that this gas shuts off the air to some extent. At any rate, trivalent uranium is stable enough for us to do experiments without any effects of re-oxidation if the experiments are carried out in the atmosphere of an inert gas and are finished within a short period of time.

Conclusion

It has been found that the reduction of hexavalent uranium to the trivalent state by the liquid-zinc-amalgam method is simple and rapid, and that the trivalent uranium ion in an aqueous solution is stable enough for us to carry out experiments without any effects of re-oxidation as long as all atmospheric oxygen is excluded.

Therefore, studies of other aspects of chemical behavior, such as the absorption spectra, ion exchange, solvent extraction, and co-precipitation, will be continued. These results will be reported in the near future.

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