CHEMISTRY

N. I. BLINOVA, V. M. SOLNTSEV, and Yu. M. TOLMACHEV

1961

SovietRxiv

Abstract

Full Text

CHEMISTRY

N. I. BLINOVA, V. M. SOLNTSEV, and Yu. M. TOLMACHEV

ON CERTAIN FEATURES OF THE INTERACTION OF URANIUM PROTOXIDE-OXIDE WITH ACIDS

(Presented by Academician A. A. Grinberg, May 24, 1961)

In studying the kinetics of dissolution of uranium protoxide-oxide in acids ([1]) and investigating the equivalence of uranium atoms in this oxide, we discovered the following interesting phenomenon.

It is known that, upon complete dissolution of uranium protoxide-oxide in acids in the absence of oxidizing agents, UO_2^{2+} and U^{4+} ions are formed in a ratio of 2 : 1. It turned out that at the initial stage of dissolution, predominantly hexavalent uranium passes into solution. The ratio of the amounts of uranium VI and uranium IV in the resulting solution exceeds the ratio 2 : 1 many times over. It should be noted, however, that during the course of these investigations articles appeared by Spitsyn, Nesmeyanova, and Kanevskii ([2]), as well as by Nesmeyanova and Alkhazashvili ([3]), in which the observation of a similar phenomenon during the dissolution of U_3O_8 in H_2SO_4 is reported and brief numerical data are given.

We carried out a detailed investigation of this phenomenon. The dissolution of two different samples of highly pure uranium protoxide-oxide was studied in sulfuric, hydrochloric, and acetic acids. The experiments were performed as follows. A weighed portion of U_3O_8 powder was introduced into the acid solution. Dissolution was carried out in a CO_2 atmosphere at a constant temperature maintained to an accuracy of 1°C. After a definite time, the resulting solution and part of the remaining powder were analyzed for the content of UIV and UVI. If necessary, the undissolved powder was treated with a fresh portion of acid and dissolution was continued. The content of UIV in each resulting solution was determined by titration with a $KMnO_4$ solution. The total content of uranium IV and VI was determined by precipitating ammonium diuranate and subsequently igniting it to U_3O_8.

The portion of powder taken for analysis was completely dissolved in sulfuric acid in a CO_2 atmosphere, after which the contents of uranium IV and VI were determined by the same method.

Table 1 gives the conditions of a series of experiments and the values of the

ratios of the amounts of uranium VI and IV that passed into solution at the initial stage of dissolution.

Thus, at the beginning of the process of dissolution of U_3O_8 in sulfuric and hydrochloric acids, the ratios of the amounts of UVI and UIV passing into solution exceed the ratio 2 : 1 by 30–40 times, and in acetic acid by as much as 150 times.

Table 1

Acid concentration	Amount of acid taken for the experiment, ml	Dissolution temperature, °C	Weighed portion of U_3O_8, mg	Time from the start of dissolution to sampling of the solution for analysis, min	Amount of dissolved oxide in % of the initial weighed portion	Ratio UVI : UIV in solution
$2M$ H_2SO_4	20	25	500	100	3	76 : 1
$11.7M$ $HClO_4$	10	90	390	10	20	60 : 1
$1.7M$ CH_3COOH	10	90	200	40	13	> 300 : 1

Table 2 gives the ratios of the amounts of UVI and UIV passing into solution at various time intervals. In the experiment, 390 mg of U_3O_8 was taken. Dissolution was carried out in $HClO_4$ at 90°. The error of the values of the ratios UVI : UIV given in the tables is estimated by us as $\pm 5\%$. As can be seen from the data of Table 2, in this experiment, 2 hours after the beginning of dissolution, the ratio of the amounts of UVI and UIV in solution reached the value 1 : 1. Subsequently, until the end of dissolution, it no longer changed.

Table 2

Time from the beginning of dissolution, min	Ratio of amounts UVI : UIV in solution
10	59 : 1
20	8.7 : 1
35	2.3 : 1
55	1.2 : 1
120	1.0 : 1

We did not carry out systematic determinations of the ratios of the amounts of UVI and UIV in the remaining undissolved U_3O_8 powder. In a number of

separate experiments, on dissolving U_3O_8 samples in acids, the following ratios UVI : UIV were obtained for the undissolved residue (they are given here in decreasing order): 1.85; 1.82; 1.60; 1.55; 1.44; 1.32; 1.10 and, finally, 1.00.

Special attention was devoted to studying the ratios UVI : UIV in the solution and in the precipitate obtained in the final stage of dissolution. Table 3 gives the ratios obtained after a 1 : 1 ratio had been established in the solution and in the precipitate.

Table 3

11.7M $HClO_4$	11.7M $HClO_4$	11.7M $HClO_4$	9.5M H_2SO_4	9.5M H_2SO_4	9.5M H_2SO_4
Time, counted from the moment of establishment of the ratio 1 : 1, min	UVI : UIV in solution	UVI : UIV in precipitate	Time, counted from the moment of establishment of the ratio 1 : 1, min	UVI : UIV in solution	UVI : UIV in precipitate
20	Not det.	1.00	5	Not det.	1.01
40	0.98	1.03	10	0.96	0.98
70	0.96	0.98	15	0.95	1.00
130	1.02	1.01			

From the data presented it is evident that, as U_3O_8 dissolves in acids, a product is formed in the residue with a changing ratio UVI : UIV from 2 : 1 to 1 : 1. After the ratio 1 : 1 is reached, further dissolution does not change the composition of this product. The substance obtained is a black powder with a violet tint. On drying in air, the color of the powder changes to gray-green, and the ratio UVI : UIV becomes close to 2 : 1. In water saturated with CO_2, the substance retains the ratio 1 : 1 for 48 hours. It should be noted that, when U_3O_8 is dissolved in nitric acid, the ratio UVI : UIV in the remaining powder remains equal to 2 : 1 throughout the entire dissolution process.

Discussion of the results. The results obtained above all prove that the uranium atoms in U_3O_8 are not equivalent. It is difficult to find another explanation for the change in the ratio UVI : UIV in the solution and precipitate during the reaction of U_3O_8 with acids. It was noted above that, upon complete dissolution of U_3O_8, for example in H_2SO_4, the ratio UVI : UIV in the resulting solution is always equal to 2 : 1. This fact gave grounds for assigning to uranium protoxide-oxide one of the formulas: $UO_2 \cdot 2UO_3$ or $UO_3 \cdot U_2O_5$. Magnetic and neutron-diffraction measurements ([4,5]) spoke in favor of the formula $U_3O \cdot U_2O_5$. X-ray structural measurements ([6]) testified rather to the equivalence of the U atoms, which is not consistent with any of these formulas.

Our data give grounds to suppose that the product of the dissolution of U_3O_8 in acids at the end of the dissolution process is U_2O_5, which is possibly a compound of pentavalent uranium. On its dissolution in acids, UV should disproportionate into uranium VI and IV in the ratio 1 : 1, which is in complete agreement with the results of our observations.

Nevertheless, this product, i.e., U_2O_5, may be not a compound of pentavalent uranium, but, for example, a compound of the type $UO_3 \cdot UO_2$. The molecules of this compound, dissolving in acid, will likewise give a UVI : UIV ratio equal to 1 : 1. Then U_3O_8 may be, for example, a compound of the type $UO_3 \cdot UO_3 \cdot UO_2$.

On the basis of the available data, preference should perhaps be given to the formula $UO_3 \cdot U_2O_5$. However, it is obvious that a final solution to the question of the structure of U_3O_8 will be obtained only after the chemical properties and structure of U_2O_5 have been studied. It is important to note that, irrespective of the structure of the initial U_3O_8 molecule and of the resulting U_2O_8, the latter reacts with acids considerably more slowly than the initial U_3O_8 molecule. Therefore, the study of the chemical reactions of U_3O_8 must be carried out with this circumstance taken into account.

In conclusion, one may put forward the supposition that the peculiar course of the reaction observed in the interaction of U_3O_8 with acids is characteristic of many chemical compounds. It seems almost obvious that oxides, sulfides, and other compounds of various metals, in which the metal atoms can exhibit different valences, should in some cases react analogously. It is possible that similar behavior will be observed, for example, in basic and double salts, as well as in other classes of compounds.

Radium Institute
named after V. G. Khlopin
Academy of Sciences of the USSR

Received
18 V 1961

CITED LITERATURE

1. V. M. Solntsev, Yu. M. Tolmachev, *Radiokhimiya*, **2**, No. 2, 187 (1961).

2. V. I. Spitsyn, G. M. Nesmeyanova, E. A. Kanevskii, *ZhNKh*, **5**, 1938 (1960).

3. G. M. Nesmeyanova, G. M. Alkhazashvili, *Atomic Energy*, **8**, 330 (1960).

4. H. Haraldsen, R. Bakken, *Naturwiss.*, **28**, 127 (1940).

5. Arne F. Andresen, *Acta Crystallogr.*, **11**, 612 (1958).

6. J. Katz, E. Rabinowitch, *The Chemistry of Uranium*, Foreign Literature Publishing House, 1954, p. 203.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.