Reports of the Academy of Sciences of the USSR

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Volume 164, No. 2

CHEMISTRY

S. M. Sinitsyna, N. M. Sinitsyn

On the Interaction of Uranyl Halides with tri-*n*-Butylphosphine Oxide

(Presented by Academician I. I. Chernyaev, February 22, 1965)

The study of the composition, structure, and properties of complex compounds with extractant molecules that pass into the organic phase during extraction is of interest for understanding the chemistry of extraction and for the quantitative evaluation of extraction equilibria. In recent years, works have appeared in the literature on the study of complex compounds of uranyl with various organophosphorus extractants ([1–3]). However, the composition and properties of such compounds have been studied mainly in solutions. It was shown that, upon interaction of tri-*n*-butylphosphine oxide (TBPO) with uranyl salts, the composition of the complex compounds formed in solutions corresponds to the formula $[UO_2A_2(TBPO)_2]$ ([4]), where $A = NO_3^-$, Br^-, CH_3COO^-. Analogous compounds are also formed with tri-*n*-butyl phosphate (TBP) ([5]). In the individual state, only nitrate compounds of uranyl have been obtained ([1,6]).

In the present work a series of complex uranyl dihalides with TBPO has been synthesized, their composition and some properties have been determined, and the structure of these compounds is discussed.

The synthesis was carried out as follows. A weighed portion of freshly prepared uranium trioxide was dissolved in concentrated hydrohalic acid, taken in a strictly stoichiometric amount. Then a 20% solution of TBPO in *n*-heptane was added to the solution in the molar ratio U : TBPO = 1 : 2. The compounds formed separated as a second organic layer, which was separated from the liquid phases, thoroughly washed with heptane and water, and dried first in air and then in a vacuum desiccator over anhydrous calcium chloride to constant weight. All the compounds obtained are practically insoluble in water and in saturated hydrocarbons, but dissolve well in ammonium carbonate solutions, in benzene, and in all common oxygen-containing organic solvents. In bright light, gradual reduction of uranium to lower valence states is observed.

Greenish-yellow crystals of phosphine oxide uranyl difluoride begin to precipitate after several months.

Found, %: U 40.3, 40.7, 40.0; C 31.7-31.8, 32.17;
H 4.88, 4.69
$[(UO_2)_6F_{12}(TBPO)_8]$. Calculated, %: U 39.8; C 32.1; H 60.1

The temperature at the onset of decomposition is 290°. The molecular weight of all synthesized compounds was determined in benzene by the cryoscopic method. For $[(UO_2)_6F_{12}(TBPO)_8]$, 3320 was found; calculated for the hexamer, 3592.

Yellow crystals of uranyl phosphine oxide dichloride begin to precipitate after two weeks.

$$\text{Found, \%: } U\ 29.7,\ 30.7,\ 30.4,\ 30.2;\ C\ 37.2,\ 37.7,\ 37.9,\ 36.4,\ 37.6;\ H\ 5.7,\ 6.2,\ 7.0,\ 6.9;\ Cl\ 8.8,\ 9.0$$

$$[\mathrm{UO_2Cl_2(TBPO)_2}].\quad \text{Calculated, \%: } U\ 30.6;\ C\ 37.1;\ H\ 6.95;\ Cl\ 9.14$$

The initial decomposition temperature is 380°. The molecular weight for $[UO_2Cl_2(TBPO)_2]$ was found to be 1100 (with a sample of 0.98 g, $\Delta T = 0.2°$) and 1570 (with a sample of 0.47 g, $\Delta T = 0.07°$); calculated for the monomer, 777, and for the dimer, 1554.

Yellow crystals of uranyl phosphine oxide dibromide precipitate on the second day.

$$\text{Found, \%: } U\ 26.6,\ 27.0;\ C\ 31.9,\ 32.6;\ H\ 5.5,\ 6.5;\ Br\ 20.8,\ 19.9$$

$$[\mathrm{UO_2Br_2(TBPO)_2}].\quad \text{Calculated, \%: } U\ 27.5;\ C\ 33.3;\ H\ 6.2;\ Br\ 18.5$$

The initial decomposition temperature is 270°. The molecular weight for $[UO_2Br_2(TBPO)_2]$ was found to be 830; calculated for the monomer, 866.

Dark-violet crystals of uranyl phosphine oxide diiodide form after several hours.

$$\text{Found, \%: } U\ 18.2,\ 19.0,\ 18.8;\ C\ 35.9,\ 35.5,\ 35.7;\ H\ 6.9,\ 6.5,\ 7.2;\ J\ 20.2,\ 19.8$$

$$[\mathrm{UO_2J_2(TBPO)_3}].\quad \text{Calculated, \%: } U\ 20.2;\ C\ 36.7;\ H\ 6.9;\ J\ 21.6$$

The initial decomposition temperature is 240°. When $[UO_2J_2(TBPO)_3]$ is treated with an excess of TBPO, large needle-shaped brick-red crystals precipitate.

$$\text{Found, \%: } U\ 16.8,\ 17.3;\ C\ 40.1,\ 40.0;\ H\ 8.1,\ 7.3,\ 7.9;\ J\ 17.8,\ 18.4$$

$[UO_2J_2(TBPO)_4]$. Calculated, %: U 17.1; C 41.3; H 7.7; J 18.2

The initial decomposition temperature is 240°. The molecular weight for $[UO_2J_2(TBPO)_4]$ was found to be 864; calculated for the monomer, 1396. Such a discrepancy between the found and calculated values of the molecular weight is probably due to partial dissociation of the iodo complex. Special studies are required to clarify this question.

The data of elemental analysis for the fluoro-, chloro-, and bromo complexes agree quite well with the proposed formulas; the slight lowering of the analytical results in the uranyl iodides is apparently explained by the presence of water in the composition of the complexes.

Comparison of the composition of the uranium compounds obtained showed that there is a tendency toward an increase in the number of TBPO molecules in the inner sphere of the complexes as the displacing ability of the halides decreases in the series $F > Cl > Br > J$ (7). In the same sequence, the ability of the compounds to crystallize increases.

Determination of the molecular weights of the uranyl phosphine oxide dihalides obtained indicates that the probability of formation of bridging bonds

[[diagram of bridging J bonds between two uranium centers]]

increases with an increase in the strength of the bond of the halide with uranyl.

Indeed, the uranyl fluoro complex in benzene is hexameric, whereas the chloro complex is partially associated into dimeric molecules. The bromo and iodo complexes are monomeric.

On the basis of the data obtained, the structure of the hexameric uranyl fluorocomplex may be represented as follows:

[schematic structure: a chain of six uranium atoms bridged by fluorine atoms, with terminal and pendant $R_3P{=}O$ groups coordinated to uranium]

$R = C_4H_9$.

where the uranyl oxygen atoms are arranged perpendicular to the plane of the drawing. In this compound the uranyl grouping has coordination number 5, as in uranyl pentafluoride (7). For the dimeric molecule $[UO_2Cl_2(TBPO)_2]$, coordination number 5 is realized, whereas in the island structure the coordination number is 4.

Thus, direct experimental evidence has been obtained for the first time for the existence of uranyl compounds with bridging bonds through a halide, and it has been shown that the reaction of complex formation of uranyl halide salts with TBPO cannot be represented by a single general equation for all uranyl dihalides. The nature of the halide in the inner sphere of the complex has a substantial influence on the composition, structure, and properties of uranyl phosphine oxide dihalides.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

Received
26 XII 1964

REFERENCES CITED

1. L. L. Burger, *J. Phys. Chem.*, **5**, 62, 520 (1958).
2. J. Kennedy, *Chem. and Ind.*, **30**, 950 (1958).
3. V. S. Voden, G. P. Nikitina, M. F. Pushlenkov, *Radiokhimiya*, **1**, 2, 121 (1959).
4. E. V. Komarov, M. F. Pushlenkov, *Radiokhimiya*, **3**, 5, 575 (1961).
5. E. V. Komarov, M. F. Pushlenkov, *Radiokhimiya*, **3**, 5, 567 (1961).
6. A. V. Nikolaev, N. M. Sinitsyn, S. M. Shubina, *Collection. Extraction*, vol. 2, Moscow, 1962, p. 63.
7. *Complex Compounds of Uranium*, Nauka, Moscow, 1964.

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