Reports of the Academy of Sciences of the USSR

Academician I. V. TANANAEV and G. B. SEIFER

1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1962. Volume 144, No. 6

CHEMISTRY

Academician I. V. TANANAEV and G. B. SEIFER

ON NORMAL NIOBIUM ORTHOPHOSPHATE

The phosphoric-acid derivatives of niobium known from the literature data [1–5] are salts of the cations NbO_2^+ or NbO^{3+}. There are no data in the literature on a salt of Nb^{5+}, i.e., normal niobium phosphate. It could be assumed that this is due either to the impossibility of the existence of such a compound, or to the absence of sufficient conditions for its formation.

Derivatives of the cation NbO_2^+ were obtained from sulfuric-acid solutions of Nb_2O_5 by the action on them of acid ammonium or sodium phosphates [3–5]. The concentration of H_2SO_4 in the initial mixtures varied within the range 2–6 N. The precipitate that separated from the mixtures had the composition $(NbO_2)_2HPO_4 \cdot 2.5H_2O$, which upon subsequent thermal treatment was converted into pyrophosphate $(NbO_2)_4P_2O_7$ [5]. Phosphoric-acid derivatives of the cation NbO^{3+} were obtained from analogous mixtures at concentrations of free sulfuric acid of $\sim$ 10–15 N [3,4]. After calcination of the separated precipitate, the final product had the composition $Nb_2O_5 \cdot P_2O_5$, which corresponds to the previously described orthophosphate $NbOPO_4$ [2].

If one proceeds from the assumption that normal niobium phosphate is nevertheless capable of existing, then to obtain it one should create conditions that, as far as possible, exclude hydrolysis of the Nb^{5+} ion. In other words, synthesis must be carried out in the most highly concentrated H_3PO_4 solutions possible. To test this assumption, niobium phosphate was synthesized by the interaction of freshly precipitated and washed $Nb_2O_5 \cdot xH_2O$ with an excess of molten crystalline H_3PO_4. As the transparent solutions formed were evaporated, a finely crystalline white precipitate separated from them. To separate the latter from the mother liquor, the mixture was cooled and diluted with absolute alcohol. The precipitate was separated by filtration. Part of it was washed with alcohol to remove excess H_3PO_4 and dried in air, after which chemical analysis gave the ratio $PO_4^{3-} : Nb^{5+}$ in the resulting substance. Another part of the precipitate was freed from excess phosphoric acid by calcination at 1200° (no melting of the residue was observed under these conditions). The composition of the calcined

product was established by its chemical analysis for the content of Nb^{5+} and phosphorus. The amount of oxygen was calculated by difference.

Analysis of the obtained samples was carried out after dissolving a weighed portion in a mixture of HF and H_2SO_4, or by fusion with K_2CO_3. When the sample was decomposed with a mixture of hydrofluoric and sulfuric acids, niobium was precipitated in the form $Nb_2O_5 \cdot xH_2O$, and phosphorus was determined from the filtrate with magnesia mixture. In the case of decomposition of the sample by fusion with K_2CO_3, niobium was precipitated by the tannin method after dissolving the melt in $H_2C_2O_4$. The mean ratio $PO_4^{3-} : Nb^{5+}$ in the air-dry sample, obtained from three analyses, was found to be 1.62. The theoretical value of this ratio for the compound $Nb_3(PO_4)_5$ is 1.67, which lies within the possible errors of analysis.

The average percentage content of niobium, phosphorus, and oxygen (calculated by difference) in the calcined sample, obtained from six mutually concordant analyses, is 36.6% Nb, 21.3% P, and 42.2% O, which corresponds to the ratio $PO_4^{3-} : Nb^{5+} = 1.75$. The theoretical content

of these constituents in the compound $Nb_3(PO_4)_5$ is, respectively, 36.9%, 20.6%, and 42.5%. Thus, the percentage content of the components found by analysis in the calcined sample agrees satisfactorily with that theoretically calculated from the formula $Nb_3(PO_4)_5$.

The correctness of this formula is further substantiated by the results, given below, of chemical and physicochemical investigation of the substance obtained. First of all, microscopic, phase, and X-ray analyses established the individuality of the compound obtained (whose refractive index is about 1.751).

The absence in the calcined sample of NbO_2^+ and NbO^{3+} ions was established by reaction with NaF, described for the detection of zirconyl ions (7). The essence of this reaction is that F' ions can displace oxygen from compounds capable of forming only slightly dissociated derivatives with fluorine ions. As a result of such displacement, OH' ions appear in solution, the presence of which can be qualitatively established from the coloration of phenolphthalein. The absence of coloration of the latter even after 30 minutes' boiling of a weighed portion of the sample of the substance obtained with NaF solution indicated the absence of niobyl ions in it.

By qualitative reactions with $AgNO_3$, $Zn(C_2H_3O_2)_2$, ammonium molybdate, and $Al(NO_3)_3$, used for the identification of various phosphate anions (8), it was established that the sample under investigation contains phosphorus only in the form of PO_4^{3-}. By comparing the infrared spectrograms of the compound studied with literature data (6), the absence in it of niobyl ions and of $P_2O_7^{4-}$, $P_3O_{10}^{5-}$ ions, and the presence of orthophosphate ions were confirmed.

Calcined normal niobium orthophosphate $Nb_3(PO_4)_5$ is a finely crystalline white powder with a density of 2.83 ± 0.04 g/cm^3 (determined in toluene at 20°), diamagnetic, and having a specific electrical resistivity of $2.4 \cdot 10^7$ $\Omega \cdot$ cm at

20°. It is insoluble in water, HNO_3, HCl, H_2SO_4, and NH_4OH, but dissolves on heating in hydrofluoric acid and in solutions of caustic alkalis.

At present, the possibility of obtaining analogous derivatives of tantalum and vanadium is being studied.

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

Received
4 IV 1962

CITED LITERATURE

1. H. R. Schoeller, W. H. Webb, *Analyst*, **61**, 585 (1936).
2. R. B. Hahn, *J. Am. Chem. Soc.*, **73**, 5091 (1951).
3. D. I. Kurbatov, N. V. Demenev, ZhPKh, **29**, 1747 (1956).
4. A. K. Sharo va, A. P. Shtin, Izv. SO AN SSSR, No. 9, 40 (1959).
5. A. P. Shtin, Izv. SO AN SSSR, No. 3, 68 (1961).
6. S. Z. Haider, *Anal. Chim. Acta*, **24**, 250 (1961).
7. I. V. Tananaev, L. S. Guzeeva, *Chemistry of Rare Elements*, issue 2, 46 (1955).
8. M. C. Sneed, R. C. Brasted, *Comprehensive Inorganic Chemistry*, **5**, 144 (1956).

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