Chemistry

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1958

SovietRxiv

Abstract

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THE NATURE OF WATER IN HETEROPOLY COMPOUNDS

TUNGSTEN HETEROPOLY ACIDS

(Presented by Academician I. I. Chernyaev, October 5, 1957)

According to the basic hypotheses on the structure of heteropoly acids, their general formulas may be represented as $H_{12-m}[R(Me_2O_7)_6]_r \cdot H_2O$ (according to Miolati–Rosenheim [1,2]) or as $H_{8-m}[R(Me_3O_{10})_4] \cdot nH_2O$ (according to X-ray structural data [3]), where R is the complex-forming atom (phosphorus, silicon, boron, etc.), Me is a metal (tungsten, molybdenum, etc.), m is the valence of the complex-forming atom, and r and n are the number of molecules of water of crystallization. In accordance with these formulas, the basicity of the heteropoly acids ($12 - m$ and $8 - m$) should be different. Heteropoly acids synthesized by crystallization from aqueous solutions may be obtained, depending on the conditions, with different amounts of water of crystallization. According to Kraus [4], they form six series of crystallochemically distinct hydrates.

On the basis of the study of dehydration processes of certain aquopoly compounds [5], and subsequently also of heteropoly compounds [6], at high temperatures, the proposition was advanced concerning a special role of part of the water molecules in these compounds. However, as a result of studying the strength of the bond of water in certain aquopoly compounds by using stable isotopes of hydrogen and oxygen–deuterium and oxygen O^{18}–Vikt. I. Spitsyn and coworkers [7] were unable to establish differences in the nature of the bond of water or the existence of "special" water molecules in these compounds.

West and Audris [8] found that, on the differential thermograms of preparations of phospho- and silicotungstic and phospho- and silicomolybdic heteropoly acids dried over sulfuric acid, there are two thermal effects which, in the authors' opinion, correspond: the first (endothermic) to the removal of zeolite-type water, and the second (exothermic) to decomposition of the heteropoly compound.

E. A. Nikitina and E. V. Buris [9], as a result of a thermographic study of the same acids, came to the conclusion that their basicity corresponds to that predicted for them by the coordination theory.

We have carried out a study of a series of tungsten and molybdenum heteropoly acids and their salts, using various methods of physicochemical analysis. The

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

results obtained are of definite interest for judging the role and physicochemical nature of water in these compounds. Here we present some data obtained jointly with M. P. Sokolova and N. A. Krotov in the study of phosphotungstic and silicotungstic heteropoly acids. These acids were synthesized by well-known methods [10].

The compounds investigated possess typical differential thermograms and thermogravimetric polytherms of dehydration (curves of water content–temperature), obtained simultaneously with the thermograms. Comparison of the endothermic effects observed on the thermograms of preparations of different degrees of hydration with the corresponding stages of hydration on the respective polytherms makes it possible to draw definite conclusions both about the nature of the processes taking place upon heating and about the physicochemical nature of the products thereby formed.

We studied preparations of phosphotungstic acid of various degrees of hydration. Curve *I* in Fig. 1 corresponds to the thermogram of a preparation of this acid with a total water content x, calculated per molecule

Fig. 1. Thermograms of samples of heteropoly acids of different degrees of hydration: *I*–phosphotungstic acid, $x = 31.4\,H_2O$; *II*–the same, $x = 5.0\,H_2O$; *III*–silicotungstic acid, $x = 18.6\,H_2O$; *IV*–the same, $x = 2.0\,H_2O$.

of the residue $P_2O_5 \cdot 24WO_3$, equal to 31.4 mol ($n = 14.2$). The preparation was obtained by partial dehydration over sulfuric acid of a highly hydrated sample ($cx = 61.0$ mol), crystallized at room temperature.

Curve *I* in Fig. 2 corresponds to the polytherm of the water content x, calculated from the percentage loss of water during heating.

On polytherm *I* (Fig. 2) there are two clearly expressed, almost vertical sections — and — at ordinates $x = 31H_2O$ and $3H_2O$, and an inclined section — in the region from $x = 16H_2O$ to $13H_2O$. The ordinates $x = 31H_2O$ and $13H_2O$ correspond, as recalculation shows, to the previously studied compounds $H_3[P(W_3O_{10})_4] \cdot nH_2O$ with $n = 14$ (triclinic hydrate) and $n = 5$ (cubic hydrate) ([4]). The ordinate $x = 3\,H_2O$ ($n = 0$) corresponds to the compound $3H_2O \cdot P_2O_5 \cdot 24WO_3$, or anhydrous phosphotungstic acid $H_3[P(W_3O_{10})_4]$.

Fig. 2. Dehydration polytherms (composition–temperature curves) of samples: *I*–phosphotungstic acid, $x = 31.4\,H_2O$; *II*–silicotungstic acid, $x = 18.6\,H_2O$.

Three clearly expressed endothermic effects, observed on thermogram *I* in Fig.

Fig. 3. Plot of intensities I of diffraction lines on X-ray patterns of powders of phosphotungstic acid preparations heated at different temperatures. Explanation in the text (I—initial preparation)

Figure 3: Fig. 3. Plot of intensities I of diffraction lines on X-ray patterns of powders of phosphotungstic acid preparations heated at different temperatures. Explanation in the text (I—initial preparation)

1 after the small effect at 50° of the removal of water in excess of the composition $31.0\,H_2O$, correspond to: the first, at 82—120°, corresponding to section — of polytherm I in Fig. 2,—the decomposition of the hydrate $x =$

$= 31.0\ H_2O$ with formation of a phase of variable composition of the limiting composition corresponding to point c ($x = 15.6H_2O$); the second at 154-218°, corresponding to section c—d of the polytherm, to decomposition of this phase with formation of the hydrate $x = 13.0H_2O$; the third at 239-275°, corresponding to section d—e—f of the polytherm, to decomposition of the latter hydrate with formation first of a phase of variable composition corresponding to point e ($x \simeq 7$), subsequently decomposing with formation of the indicated compound $3H_2O \cdot P_2O_5 \cdot 24WO_3$. This compound is stable on heating up to 400° (vertical section f—g). On further heating it decomposes with liberation of 3 mol of water, giving a fourth, diffuse endothermic effect at 500-570°, situated immediately before the following, exothermic effect at 570-575°.

The endothermic effect of decomposition of the indicated compound at 510-595° is clearly seen on thermogram II of Fig. 1 for the preparation $5.0 \cdot H_2O \cdot P_2O_5 \cdot 24WO_3$ (a phase of variable composition), obtained by prolonged heating of the initial sample at 150°. The endothermic effect at 170-270° on the latter thermogram corresponds to decomposition of the indicated phase with formation of the compound $3H_2O \cdot P_2O_5 \cdot 24WO_3$. The amorphous tungsten trioxide WO_3 liberated during decomposition of this compound, as shown by the X-ray study, then crystallizes, giving an exothermic effect at 595-628°, analogous to that on thermogram I.

Fig. 3. Plot of intensities I of diffraction lines on X-ray patterns of powders of phosphotungstic acid preparations heated at different temperatures. Explanation in the text (I—initial preparation)

Figure 3 gives the plot (II) of the intensities of the diffraction lines on the X-ray pattern of the indicated compound, obtained by heating the initial sample at 250° (taken with iron radiation). Heating at 450° (plot III, Fig. 3), i.e., at a temperature lying in the region of decomposition of this compound, led to its almost complete decomposition and amorphization of the preparation (only six lines remained). Further, higher heating leads to the appearance of distinct lines of tungsten trioxide WO_3 (plot IV for the preparation heated at 630°), as is shown by comparison with plot V for pure tungsten trioxide heated at the same temperature, 630°. The two exothermic effects at 895 and 710° present on

cooling curve II in Fig. 1 correspond to polymorphic transformations of WO_3.

We also studied preparations of silicotungstic acid of different degrees of hydration.

Analogously to the preceding case, comparison of the endothermic effects of thermogram III in Fig. 1 for a preparation of this acid (containing 8.6 mol of wat—

···with steps on the corresponding polytherm **II** in Fig. 2 indicates the formation of hydrates with $x = 16$ H_2O and 8 H_2O and of the compound $2H_2O \cdot SiO_2 \cdot 12WO_3$, which in composition corresponds to the anhydrous silicotungstic acid $H_4[Si(W_3O_{10})_4]$ (vertical segment *e*— of the polytherm);

Here, too, the amorphous tungsten trioxide WO_3, formed as one of the decomposition products, crystallizes, giving exothermic effects on thermograms **III** and **IV** (at 494—513° and 502—575°). The formation, during heating, of the acids of the hydrates of constant and variable composition cited above is confirmed by the study of composition–temperature diagrams obtained under equilibrium conditions. Recalculation of the compositions of the hydrates of constant composition found to the X-ray structural formulas $H_3[P(W_3O_{10})_4] \cdot nH_2O$ and $H_4[Si(W_3O_{10})_4] \cdot nH_2O$ gives the following values for the coefficient n: 14 and 5 for phosphotungstic acid, and 14 and 6 for silicotungstic acid. For the first acid, the formation of phases of variable composition is also observed within values of n from 6.3 to 5 and from 2.1 to 0.

In its physicochemical nature, the water in these hydrates is water of crystallization. It is completely removed upon heating to 250°. This process is reversible and does not lead to destruction of the heteropolyacid.

Of particular interest is the formation, established by us during thermal decomposition, of the compounds $3H_2O \cdot P_2O_5 \cdot 24WO_3$ and $2H_2O \cdot SiO_2 \cdot 12WO_3$, which in composition correspond to the anhydrous acids $H_3[P(W_3O_{10})_4]$ and $H_4[Si(W_3O_{10})_4]$. In its physicochemical nature, the water liberated upon their heating differs from water of crystallization and must be assigned to the type of constitutional, more strongly bound water. It is formed, apparently, from hydrogen ions or oxonium ions ([4,11]) as a result of the irreversible process of decomposition of the substance. The amount of this water corresponds to the fact that three (in the case of phosphotungstic acid) and four (in the case of silicotungstic acid) hydrogen atoms, calculated per one atom of the complex-former, are in the structure in a special position. The number of such atoms coincides with the basicity of these acids as determined by the X-ray structural theory of structure. The process of decomposition of the indicated compounds is, as thermographic study shows, an endothermic process, and not an exothermic one, as West and Audrieth believe ([8]).

The formation, during thermal decomposition of heteropolyacids, of compounds corresponding in composition to the Miolati–Rosenheim formula, as assumed by E. A. Nikitina and E. V. Buris ([9]), does not occur: on the dehydration

polytherms there are no steps corresponding to such compounds, and on the thermograms there are no effects that could correspond to their formation or decomposition.

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

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