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Abstract

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STUDY OF THE MECHANISM OF FORMATION OF AQUEOUS HIGH-MOLECULAR TUNGSTATES BY INFRARED SPECTROSCOPY

Earlier (^{1,2}) we showed that the process of formation, in an acidified solution of Na_2WO_4, of one of the most important aquopolyso compounds of tungsten –sodium paratungstate, $Na_{10}W_{12}O_{41} \cdot 28H_2O$–proceeds by a monomolecular mechanism through rearrangement of an intermediate metastable complex consisting, apparently, of molecules of tungstic acid, WO_4^{2-} ions, HWO_4^-, and H_3O^+, interacting with one another by the formation of hydrogen bonds. The rearrangement consists in the formation of bridging oxygen bonds between tungsten atoms with the liberation of water molecules.

In the present work, certain elementary processes occurring upon acidification of a Na_2WO_4 solution have been studied with the use of IR spectroscopy, in order to make more detailed the general kinetic principles of the formation of sodium paratungstate found earlier (^{2}). In view of the small number of publications on the IR spectroscopy of tungstates (^{3,4}), the IR spectra of a number of solid tungsten compounds were first studied. The spectra were recorded on IKS-12 and IKS-14 spectrophotometers at frequencies of 670–1700* (NaCl prism), corresponding to vibrations of the tungstate anion and deformation vibrations of water molecules. Solid samples were prepared as suspensions in Vaseline oil or as pressed pellets with potassium bromide. Solutions were recorded in cells made of polished AgCl, cooled with running water. The substances studied contained no impurities of nitrates or organic substances.

On considering the IR spectra of solid tungsten compounds in the frequency region 1000–1700 (Fig. 1), attention is drawn to the presence, in white tungstic acid, of bands at 1410, 1200, 1100, and, in sodium paratungstate, bands at 1388 and 1100, which indicates the presence in these compounds of hydroxyl groups of different nature bonded to the W atom. The bands 1200, 1100, 1388 are very weak. Among the indicated bands the most intense is 1410, which may be assigned to a complex vibration arising from interaction between the vibration of the hydroxyl group and the W–O bond, analogous to what occurs in certain carboxylic acids associated by hydrogen bonds.

In work (^{5}) the possibility of the existence in tungstic acids of hydroxyl groups joined through hydrogen bonds was noted. The band 1100 may be assigned to vibrations of hydroxonium ions (^{6,7}), present in approximately the same state as in $(H_3O)Cl$, $(H_3O)Br$, etc. Judging from the very weak intensity of this band,

Fig. 1 and Fig. 2: infrared absorption spectra

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the amount of such ions in white tungstic acid and sodium paratungstate is small. However, it must be borne in mind that the width, height, and position of the bands of the H_3O^+ cation may change upon its entry into complex compounds; there is no literature on this question, and therefore it is impossible to determine the full content of H_3O^+ from this band. In addition to hydroxyls bonded to the W atom, white tungstic acid and sodium paratungstate contain water molecules, as indicated by the bands 1670 and 1640.

Thus, in the compounds considered there are three types of bound water: 1) in the form of hydroxyls bonded to the W atom, 2) water molecules having a crystal-hydrate character and located inside the crystal lattice, or else in an adsorbed state, 3) ions

* All frequencies are given in cm^{-1}.

hydroxonium. In yellow tungstic acid there are no bands corresponding to deformation vibrations of hydroxyl groups and hydroxonium ions (Fig. 1); consequently, it contains only one type of water: water of crystallization, to which the single band in the frequency range 1000–1700, the 1660 band, corresponds.

In the region of vibrations of the tungsten-oxygen motif (650–1000), the IR spectrum of yellow tungstic acid is similar to the IR spectrum of WO_3 (the small differences are possibly connected with the influence of H_2O molecules on vibrations of the WO_3 lattice). Therefore yellow tungstic acid is similar to the crystalline hydrate of tungstic anhydride $WO_3 \cdot H_2O$, which agrees with a recently published work (8). The existence of a definite hydrate is also indicated by the study of its dehydration (9).

Fig. 1. Infrared absorption spectra of tungsten compounds.
1—white tungstic acid, 2—yellow tungstic acid, 3—tungstic anhydride, 4—sodium paratungstate

Fig. 2. Infrared absorption spectra of tungstates.
1—$Na_2WO_4 \cdot 2H_2O$, 2—$Na_2W_2O_7$, 3—$Na_2W_4O_{13}$,
4—$Na_2W_4O_{13} \cdot 10H_2O$ (sodium metatungstate)

Freshly prepared white tungstic acid, in its structure, corresponds more closely to the formula $(WO)_x(OH)_{4x} \cdot yH_2O$; it contains hydroxyl and adsorbed water. When the acid is heated, the hydroxyl groups interact with one another, accompanied by the release of water and the formation of yellow tungstic acid. In summary, the process may be represented as

$$(WO)_x(OH)_{4x} \cdot yH_2O \rightarrow (WO_2)_x(OH)_{2x} \cdot xH_2O + yH_2O \rightarrow (WO_3)_x \cdot xH_2O + (y+x)H_2O.$$

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

The water released as a result of intramolecular condensation of hydroxyl groups partially remains inside the WO_3 lattice. Adsorbed water is removed on heating. It is difficult to distinguish, in the IR spectrum of deformation vibrations, hydrate water from adsorbed water; however, the form of the dehydration curve of white tungstic acid indicates the adsorption nature of the water molecules present in it (9).

To study the composition of the ions formed upon acidification of Na_2WO_4 solutions, we compared their IR spectra with the spectra of various—

of solid tungstates (Figs. 2, 3). Acidification was carried out with concentrated HCl under very vigorous stirring. As is seen from Figs. 2 and 3, in acidified Na_2WO_4 solutions over the entire pH range studied, the bands belonging to $Na_2W_2O_7$ are completely absent, and in their general appearance these spectra are entirely different. Thus it is unambiguously demonstrated that in acidified Na_2WO_4 solutions there are no $W_2O_7^{2-}$ anions, which in a number of works (10,11) are assumed to be constituent parts of aquo- and heteropoly compounds. Likewise, under the stated experimental conditions no compounds are formed that are close in structure to sodium meta- and tetratungstate, which is also consistent with other studies (1).

At the initial moment of time the IR spectra of an acidified Na_2WO_4 solution have many bands at 1400, 935, 890, 870, and 760, coinciding in frequency with the bands of white tungstic acid (Figs. 1 and 3). At pH 8.2 the indicated bands are only slightly visible against the background of the intense 825 band belonging to free WO_4^{2-} ions. At pH 6.6 weak bands at 818 and 800 are observed, which apparently belong to the HWO_4^- anion or to a compound of tungstic acid with WO_4^{2-}. It is not yet possible to give a more precise answer concerning the assignment of these bands, especially since their intensity is very low. Free hydronium ions H_3O^+ are apparently absent from the acidified Na_2WO_4 solution, at least in an appreciable amount. At pH 5.8-6, the most distinct similarity is observed between the IR spectrum of the acidified Na_2WO_4 solution, taken at the initial moment of time, and the IR spectrum of white tungstic acid.

Fig. 3. Infrared absorption spectra of freshly prepared Na_2WO_4 solutions at different pH. Concentration 1.75 mol/l. pH values: 1 –8.2; 2 –6.6; 3 –6.3; 4 –5.8-6

Fig. 4. Change in the infrared absorption spectrum of an acidified Na_2WO_4 solution with time. Concentration 1.75 mol/l; pH 5.8-6. Time in min.: 1 –0; 2 –20-30; 3 –50-70; 4 –100-120; 5 –380-400

Observations showed that the IR spectra of the acidified Na_2WO_4 solution gradually change with time. The results of one of the experiments are shown in Fig.

4. The growth of the peaks at 935, 890, and 870 is most clearly noticeable. Beginning at pH 6.3, and especially distinctly at pH 5.8-6, a weakly expressed band at 1400 becomes noticeable; its intensity gradually decreases with time. The latter indicates the occurrence in the solution of polycondensation processes proceeding through the interaction of hydroxyl groups with elimination of water and formation of bridging oxygen bonds. A detailed study of the kinetics of this process by the IR spectra method proved impossible because of the poor reproducibility of the experiments, probably explained by the gradual separation, in the cuvette, with time, of sodium paratungstate crystals, which affect the passage of IR rays.

The results presented allow one to conclude that, upon acidification of an Na_2WO_4 solution, a complex unstable polycompound first arises in it, which most probably includes groupings of the following types:

In the first grouping the WO_4^{2-} anions are linked with the H_3O^+ cations by hydrogen bonds; in the second there are molecules of tungstic acid and WO_4^{2-} ions; in the third, HWO_4^-; in the fourth, only molecules of tungstic acid. Probably the ratio between the amounts of the individual groupings and the type of bond between them in the initially forming unstable polycompound vary depending on the experimental conditions. At higher pH, units of types (1) and (2) have a relatively greater significance; as the pH is lowered, the number of units of types (3) and (4) increases, and the molecular weight of the complex may thereby attain large values as a result of additional bonding of tungstic acid molecules (12).

The metastable compound in solution is gradually regrouped with the formation, apparently at first, of a linearly condensed chain, in which units of types (5) and (6) play an essential role. By analogy with organic polymers, such linear chains, while in solution, are similar in their configuration to a coiled helix; in it further interaction of hydroxyl groups occurs, with elimination of water molecules and transition from a linear to a spatial structure with octahedral coordination of oxygen around W, characteristic of sodium paratungstate. In this way sodium paratungstate is formed in solution, whose anion, according to Lindqvist (13), has the formula $W_{12}O_{46}^{20-}$.

The views set forth are in agreement with concepts concerning the mechanism of formation of high-molecular compounds of the polysilicate and polyphosphate type, according to which (14) the first stage in their preparation is the appearance of the corresponding free acids, which then condense with elimination of water.

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