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Abstract

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INVESTIGATION OF THE MECHANISM OF FORMATION OF HIGH-MOLECULAR TUNGSTEN COMPOUNDS BY DILATOMETRIC AND SPECTROPHOTOMETRIC METHODS

The mechanism of the reactions forming aqueous high-molecular tungsten compounds, which arise in an acidified solution of normal sodium tungstate, has not yet been sufficiently studied. It was established by one of us ([1,2]) that the reactions occurring here are slow and that a significant role in them is played by the simultaneous presence in the solution of hydroxonium ions, tungstate ions, and molecules of tungstic acid, which interact with one another through the formation of hydrogen bonds. During crystallization of compounds from aqueous solution, some of the hydrogen bonds may be replaced by bonds between WO_4^{2-} tetrahedra through shared oxygen atoms.

We studied, by dilatometric and spectrophotometric methods, the kinetics of the processes (occurring upon acidification of normal sodium tungstate) that lead to the formation of the aquopoly compound of paratungstate and to its crystallization from aqueous solution. The dilatometer was a sphere of volume 108 cm^3 with a long capillary. The temperature of the dilatometer in the thermostat was maintained with an accuracy of ± 0.01–$0.02°$. The volume of the solution in the capillary was read with a microscope eyepiece to an accuracy of $\pm 3 \cdot 10^{-4}$ ml. It was established that the temperature inside the dilatometer throughout the entire experiment was equal to the temperature of the thermostat. Solutions of Na_2WO_4 acidified with nitric acid were drawn through the capillary by means of a vacuum apparatus. Between the beginning of the first measurement and acidification there elapsed 30–40 min—the time required for establishment of thermal equilibrium. Since the process lasts several hours, neglect of this time cannot affect the determination of the order of the reaction of interest to us.

Fig. 1. Dilatometric curves. Concentration of $Na_2WO_4 \cdot 2H_2O$, 1 mol/l; scale division on the ordinate axis, $5.3 \cdot 10^{-3}$ ml.

Fig. 2. Determination of the order of the reactions of formation and the crystallization process of sodium paratungstate by dilatometric and spectrophotometric data. 1—formation of paratungstate (dilatometric method); pH 5.7; $H^+/WO_4^{2-} = 1.16$; $t = 26.7°$; 2—crystallization of paratungstate from an acidified Na_2WO_4 solution; $H^+/WO_4^{2-} = 0.70$; pH 8.2; $t = 26.7°$; 3—formation of hexatungstate ions (spectrophotometric method); $H^+/WO_4^{2-} = 0.73$; pH 6.6; $t = 100°$

Figure 2: Fig. 2. Determination of the order of the reactions of formation and the crystallization process of sodium paratungstate by dilatometric and spectrophotometric data. 1—formation of paratungstate (dilatometric method); pH 5.7; $H^+/WO_4^{2-} = 1.16$; $t = 26.7°$; 2—crystallization of paratungstate from an acidified Na_2WO_4 solution; $H^+/WO_4^{2-} = 0.70$; pH 8.2; $t = 26.7°$; 3—formation of hexatungstate ions (spectrophotometric method); $H^+/WO_4^{2-} = 0.73$; pH 6.6; $t = 100°$

1 —pH 8.2; $H^+/WO_4^{2-} = 0.70$; $t = 26.7°$;
2 —pH 6.3; $H^+/WO_4^{2-} = 1.14$; $t = 26.7°$;
3 —pH 5.7; $H^+/WO_4^{2-} = 1.16$; $t = 26.7°$;
4 —pH 8.2; $H^+/WO_4^{2-} = 0.70$; $t = 47.5°$;
5 —crystallization of pure sodium paratungstate. Concentration of $Na_{10}W_{12}O_{41} \cdot 28H_2O$, 0.0061 mol/l.

The curve of volume changes has a minimum (Fig. 1). The decrease in the volume of the solution is associated with the formation of the compound—sodium paratungstate—and the increase with its crystallization. Both branches of the curve were studied in detail. The order of the process of formation of the aquopoly compound with respect to the concentration of WO_4^{2-} ions, calculated on the basis of the initial ···

of rates proved to be equal to 1 (Fig. 2) at a constant ratio H^+/WO_4^{2-}, where H^+ corresponds to the amount of acid added to the Na_2WO_4 solution.

The process of crystallization of the salt formed was also studied. It was established that the increase in the volume of the solution is strictly proportional to the amount of salt crystallized out. At pH 8.2 and an Na_2WO_4 concentration of 1 mol/liter, the change in the volume of the solution was $0.6 \cdot 10^{-2}$ ml/g. Since at the given ratio H^+/WO_4^{2-} the amount of sodium paratungstate formed is directly proportional to the concentration of Na_2WO_4, then in the equation for the rate of crystallization of the salt $V_k = K_k C_p^n$, where V is the initial rate of crystallization, C_p is the concentration of paratungstate, and K_k is a constant, to determine the order of the crystallization process one may substitute the concentration of Na_2WO_4 for the concentration of paratungstate. The order of the process of crystallization of sodium paratungstate from an acidified solution of normal sodium tungstate at $H^+/WO_4^{2-} = \text{const}$ with respect to the concentration of WO_4^{2-} ions proved to be equal to 3 (Fig. 2).

Fig. 3. UV absorption spectra

Figure 3: Fig. 3. UV absorption spectra

Fig. 2. Determination of the order of the reactions of formation and the crystallization process of sodium paratungstate by dilatometric and spectrophotometric data.
1—formation of paratungstate (dilatometric method); pH 5.7; $H^+/WO_4^{2-} = 1.16$; $t = 26.7^\circ$;
2—crystallization of paratungstate from an acidified Na_2WO_4 solution; $H^+/WO_4^{2-} = 0.70$; pH 8.2; $t = 26.7^\circ$;
3—formation of hexatungstate ions (spectrophotometric method); $H^+/WO_4^{2-} = 0.73$; pH 6.6; $t = 100^\circ$.

Fig. 3. UV absorption spectra.
1—freshly prepared acidified Na_2WO_4 solution; concentration 0.03 mol/liter; pH 6.6; $H^+/WO_4^{2-} = 0.73$; $t = 100^\circ$;
2—after 15 min.;
3—after 60 min.; during measurement the solutions were diluted 100-fold;
4—freshly prepared solution of $Na_{10}W_{12}O_{41} \cdot 28H_2O$; conc. $2.86 \cdot 10^{-5}$ mol/liter; $t = 100^\circ$;
5—after 2 min.;
6—after 4 h;
7—after 16 h;
8—solution of $Na_{10}W_{12}O_{41} \cdot 28H_2O$; concentration $2.86 \cdot 10^{-3}$ mol/liter; holding time 10 h; $t = 100^\circ$; during measurement the solution was diluted 100-fold;
9—suspension of H_2WO_4 in water ($\sim 5 \cdot 10^{-3}$ g/liter).

The absorption spectra were measured on an SF-4 spectrophotometer in the ultraviolet region using thermostated quartz cuvettes 1 cm thick. The absorption spectra of the acidified Na_2WO_4 solution (Fig. 3), recorded immediately after acidification, are a curve falling steeply downward. However, after some time a plateau appears on the curve with a center at $\lambda = 256$ mμ, characteristic of the spectrum of hexatungstate ions obtained upon decomposition of the paratungstate anion $W_{12}O_{41}^{10-}$ (3). The kinetics of the process of formation of hexatungstate ions was studied in detail by measuring the intensi-

the absorption at $\lambda = 256$ mμ with time (Fig. 4). The order of the reaction with respect to WO_4^{2-}, determined by the method of initial rates at a constant ratio H^+/WO_4^{2-}, proved to be equal to 1 (Fig. 2). From the change in the initial rates V_1, V_2, as a function of the temperatures T_1, T_2, the activation energy was determined from the formula

$$V_1/V_2 = e^{-\frac{E}{RT_1}}/e^{-\frac{E}{RT_2}},$$

and proved to be 10.8 kcal/mole (Fig. 4).

Fig. 4

Figure 4: Fig. 4

The process of decomposition of the paratungstate anion was also studied by the spectrophotometric method. It was established that, at a paratungstate concentration of $\sim 10^{-5}$ mole/liter, decomposition proceeds in two stages (Figs. 3 and 4, curves $7'$ and $7''$):

$$W_{12}O_{41}^{10-} \cdot 28H_2O = 2HW_6O_{21}^{5-} \cdot 13.5H_2O = 5WO_4^{2-} + 7H_2WO_4 + 21H_2O.$$

1st stage 2nd stage

The first stage, which is the reaction of depolymerization of paratungstate ions into hexatungstate ions, proceeds according to first order, with an activation energy of 6 kcal/mole; the second, corresponding to complete cleavage of the hexatungstate ions to WO_4^{2-} and H_2WO_4, is characterized by an activation energy of 11.5 kcal/mole and also proceeds according to first order.

Fig. 4. Change in optical density at $\lambda = 256$ mμ, corresponding to the formation of hexatungstate ions in an acidified solution of normal tungstate and to the decomposition of the paratungstate anion. Formation of hexatungstate ions; pH 6.6; $H^+/WO_4^{2-} = 0.73$. Concentration of Na_2WO_4 and temperature of the experiments: 1—0.05 mole/liter; $t = 100°$; 2—0.03 mole/liter; $t = 100°$; 3—0.03 mole/liter; $t = 79°$; 4—0.03 mole/liter; $t = 60°$; 5—0.015 mole/liter; $t = 100°$. During measurement the solutions were diluted 100-fold. Decomposition of the paratungstate anion. Concentration of $Na_{10}W_{12}O_{41} \cdot 28H_2O$ $2.8 \cdot 10^{-5}$ mole/liter; 6—$t = 43.7°$; 7—$t = 100°$ (the two stages of decomposition are visible, corresponding to curves $7'$ and $7''$).

The large difference in the activation energies of the two stages of decomposition of the paratungstate anion may indicate the presence in it of different types of chemical bonds. At higher concentrations of paratungstate ($\sim 10^3$ mole/liter) the process proceeds somewhat differently: the first stage remains the same, while the second corresponds not to cleavage of the hexatungstate ion, but to its conversion into an anion related to metatungstate; associated with this is the appearance of a maximum on the spectrophotometric curve (Fig. 3), similar to the maximum from the metatungstate ion (3). We did not investigate the kinetics of this process in detail.

In general form, the process of formation of aqueous high-molecular tungsten compounds may be represented as follows: when a solution of Na_2WO_4 is acidified, a complex is formed in it that includes H_2WO_4 molecules, WO_4^{2-} or HWO_4^{1-} ions, and HO_3^+, bound to one another by hydrogen bonds. The molecular weight of such an aggregate may differ depending on pH. In more acidic solutions it reaches higher values owing to the addition of further H_2WO_4 molecules (3). Such complexes in solution are unstable and gradually rearrange with the transition of hydrogen bonding into bonding through oxygen bridges, with elimination of water. Partial decomposition of the complex may also occur. In such a case the reaction rate is

$$V = KC_{\text{compl}}^{n}, \tag{1}$$

where C_{compl} is the concentration of the complexes, and K is the reaction-rate constant. At $H^+/WO_4^{2-} = \text{const}$, the quantity C_{compl} is directly proportional to the concentration of Na_2WO_4:

$$C_{\text{compl}} = \alpha C_{WO_4^{2-}}. \tag{2}$$

(α is the proportionality coefficient). Substituting (2) into (1), we obtain $V = K(\alpha C_{WO_4^{2-}})^n$, and further $\lg V = \lg K + n \lg \alpha + n \lg C_{WO_4^{2-}}$. For the rearrangement process, n should be equal to 1, which agrees with the experimental data obtained by us.

From this point of view, for example, the process of formation of sodium paratungstate $Na_{10}W_{12}O_{41} \cdot 28H_2O$ may be represented as follows:

$$7H^+ + 6WO_4^{2-} \longrightarrow H_7W_6O_{24}^{5-}$$

Fast

$$H_7W_6O_{24}^{5-} \xrightarrow[-H_2O]{} H_5W_6O_{23}^{5-} \xrightarrow[-H_2O]{} H_3W_6O_{22}^{5-} \xrightarrow[-H_2O]{} HW_6O_{21}^{5-}$$

Slow

$$2HW_6O_{21}^{5-} \longrightarrow W_{12}O_{41}^{10-} + H_2O \qquad \text{(dimerization)}$$

Slow

The rate of the process is limited by the kinetics of rearrangement of the intermediate metastable complex $H_7W_6O_{24}^{5-}$, constructed entirely on the basis of hydrogen bonds and, in addition, containing bound water. The structural formula of this complex may be depicted as $[H_3O(WO_4)_3(HWO_4)_3(H_3O)_3(H_2O)_n]^{5-}$ or $[3H_2WO_4(WO_4)_2(HWO_4)nH_2O]^{5-}$. In the resulting intermediate polyanions there is a different combination of hydrogen bonds and bonds through oxygen bridges. At higher concentrations of Na_2WO_4, each of the indicated polyanions is capable of dimerizing, giving anions whose composition lies within the range $H_{10}W_{12}O_{46}^{10-}$ ... $W_{12}O_{41}^{10-}$.

In our view, the overall formulas of paratungstate may be represented as:

1) $Na_{10}H_{10}W_{12}O_{46} \cdot 23H_2O$;
2) $Na_{10}H_8W_{12}O_{45} \cdot 24H_2O$;
3) $Na_{10}H_6W_{12}O_{44} \cdot 25H_2O$;
4) $Na_{10}H_4W_{12}O_{43} \cdot 26H_2O$;
5) $Na_{10}H_2W_{12}O_{42} \cdot 27H_2O$;
6) $Na_{10}W_{12}O_{41} \cdot 28H_2O$.

In the first formula there are ten hydrogen bonds, while in the last all bonds are effected through oxygen bridges. It should be noted that the hydrogen atoms forming hydrogen bonds are not capable of substitution, since the latter would lead to decomposition of the given anion. The correspondence of paratungstate to one or another of the indicated formulas depends on the conditions of formation and existence of the compound. In this way the apparent contradiction may be explained, namely that according to X-ray structural data[4] paratungstate corresponds to the anion $W_{12}O_{46}^{10-}$, and not $W_{12}O_{41}^{10-}$, as follows from chemical studies.

An analogous case has recently been described for potassium pentaborate[5], the state of the hydrogen atoms in which, established with the aid of nuclear proton resonance, corresponds to the formula $KH_4B_5O_{10} \cdot 2H_2O$. The previously proposed formula $K(H_3O)_2(H_2B_5O_{10})$[6] is less probable.

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