Influence of temperature, vanadium concentration, and degree of solution acidification on composition of the solid products

VIII. Products of the reactions taking place in acidified solutions of barium and cadmium metavanadate

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The influence of temperature, vanadium concentration in solution, degree of acidification, and contact time of the solid phase with reaction solution on composition of the solid substances which were formed in systems containing $M^{II}(VO_3)_2$, HX, and H_2O ($M^{II} = Ba$, Cd; $X = NO_3^-$, ClO_4^-) was investigated. Thus polyvanadates of the composition $Ba(VO_3)_2 \cdot H_2O$, $Ba_3V_{10}O_{28} \cdot 19H_2O$, $BaV_6O_{16} \cdot 5H_2O$, $Ba(HV_6O_{16})_2 \cdot 9H_2O$, and substances of variable composition $M^{II}_{1-x}H_{2x}V_6O_{16} \cdot nH_2O$ ($x < 0.5$) were obtained.

Изучалось влияние температуры, концентрации ванадия в растворе, степени кислотности и продолжительности контакта твердой фазы с реакционным раствором на состав твердых соединений, образующихся в системах, содержащих $M^{II}(VO_3)_2$, HX и H_2O ($M^{II} = Ba$, Cd; $X = NO_3^-$, ClO_4^-). Были получены поливанадаты состава $Ba(VO_3)_2 \cdot H_2O$, $Ba_3V_{10}O_{28} \cdot 19H_2O$, $BaV_6O_{16} \cdot 5H_2O$, $Ba(HV_6O_{16})_2 \cdot 9H_2O$ и вещества переменного состава $M^{II}_{1-x}H_{2x}V_6O_{16} \cdot nH_2O$($x < 0,5$).

There are known papers which give documentary evidence for the influence of several factors on composition of the solid polyvanadates obtained from acid aqueous solutions [1—11]. The interpretation of the results obtained, in particular, in the region of more acidic solutions is not, for the time being, uniform and moreover, relatively small attention has been paid to the influence of temperature on composition of the solid substances isolated from solutions. Similarly, it is open what properties of the atoms of metallic elements are responsible for their ability to form polyvanadate of a given composition.

This paper deals with the influence of reaction conditions on composition of vanadates containing metals, the atoms of which are in equal oxidation state but exhibit different bonding properties. Common property of both investigated metals, *i.e.* barium and cadmium consists in the fact that they form vanadates poorly soluble in water.

Experimental

Barium and cadmium metavanadates were prepared by the methods described in papers [12, 13] and [14], respectively. Other chemicals used were anal. grade reagents of Czechoslovak production.

Barium was determined gravimetrically and cadmium was determined complexometrically by means of eriochrome black T. Vanadium(V) and vanadium(IV) was estimated volumetrically by using the solution of iron(II) sulfate ($c = 0.1$ mol dm^{-3}) or potassium permanganate ($c = 0.01$ mol dm^{-3}).

The pH value of solutions was measured with a pH-meter PHM 22 Radiometer equipped with an Ag|AgCl electrode. The infrared spectra of the prepared substances were taken on an instrument Perkin—Elmer 1800 by using the technique of nujol suspension. The powder diffraction patterns were obtained with a diffractograph Philips equipped with a goniometer PW 1058 by the use of CuK_α radiation.

Because of poor solubility of barium and cadmium metavanadates in water, these compounds were dissolved in dilute solution of hydrogen peroxide (volume ratio 1 : 10). To the solutions obtained, such quantity of acid was added ($c_{HX} = 1$ mol dm^{-3}) that the degree of acidity was as follows (Table 1).

Table 1

Degree of acidity in reaction systems

Reaction system	$Z = n(HX)/n(V)$					
$Ba(VO_3)_2$—HNO_3—H_2O	0.4	0.6	0.8	1.0	2.0	3.0
$Cd(VO_3)_2$—$HClO_4$—H_2O	0.4	0.6	0.67	0.73	0.8	0.85

Intermediate peroxidic bonds were destroyed by boiling. The reactions took place at temperatures 40 °C, 60 °C, and 80 °C. They were regarded as completed if the pH value of reaction mixture was constant or varied very little. This criterion was fulfilled for barium after 24 h except for the syntheses at Z (40 °C) = 0.8 and 1 the reaction time of which was 9 and 6 days. The solutions were stirred during reactions and a constant volume was held. The concentration of vanadium in starting solutions of barium metavanadate was 0.02 mol dm^{-3} while it varied in the range 0.02—0.2 mol dm^{-3} in solutions of cadmium metavanadate (the step being 0.02 mol dm^{-3}). The different reaction conditions in the systems containing barium and cadmium have been given by the fact that barium vanadates are practically insoluble while cadmium vanadates are more soluble. Besides, the solubility of individual types of cadmium vanadates in the used reaction medium exhibits only small differences, which was an unfavourable factor especially when we wanted to isolate only one type of vanadate from solution.

Results and discussion

The solid products which were formed in the system with barium are summarized in Table 2. It results from this table that metavanadate comes into existence at all used temperatures and lower degrees of acidity *Z*. Its purity decreases with increasing temperature of reaction solutions, reaction time, and values of *Z*. Barium decavanadate was isolated from the investigated system only at 40 °C. This fact may be due to the circumstance that the solubility of this compound in the medium used increases with temperature or hydrolysis-polymerization equilibria in solution are shifted towards lower condensed polyanions.

Table 2

Conditions of formation of barium polyvanadates

Z	θ/°C								
	40			60			80		
	pH_1	pH_2	Product	pH_1	pH_2	Product	pH_1	pH_2	Product
0.4	5.05	4.20	M	4.90	3.30	M	5.35	3.40	$M+X^b$
0.6	3.95	3.75	D	3.81	3.10	$M+X^b$	4.50	3.10	$M+X^b$
0.8	3.00	3.00	$H+M^a$	3.18	3.15	$H+M^b$	3.05	3.65	H
1.0	2.70	2.85	P	2.80	3.05	P	2.70	2.95	P
2.0	2.10	2.10	P	2.20	2.20	HH	2.15	2.05	HH
3.0	1.85	1.80	P	2.00	1.90	HH	2.00	1.80	HH

pH_1 — after preparation of solution; pH_2 — before separation of the solid phase; M — $Ba(VO_3)_2 \cdot H_2O$; D — $Ba_3V_{10}O_{28} \cdot 19H_2O$; H — $BaV_6O_{16} \cdot 5H_2O$; HH — $Ba(HV_6O_{16})_2 \cdot 9H_2O$; *a*) not unambiguously confirmed; *b*) small admixture; X — nonidentified brown substance; P — product discussed in the text.

Products different from the above-mentioned ones were formed in solutions with $Z \geqq 0.8$. These products were brown or red-brown substances the structure of which exhibited small degree of arrangement as evident from character of the

X-ray powder patterns. The product obtained at 80 °C and $Z = 0.8$ may be regarded as $BaV_6O_{16} \cdot 5H_2O$ (theoretical composition: 38.74 % V and 17.40 % Ba; found experimentally: 38.56 % V and 17.30 % Ba) while the product obtained at 60 °C and $Z = 2.0$ or 3.0 may be $Ba(HV_6O_{16})_2 \cdot 9H_2O$ (theoretical composition: 42.90 % V and 9.64 % Ba; found experimentally: 42.91 % V and 9.80 % Ba). These formulae are based not only on chemical analyses but also on infrared spectra of both substances. The absorption bands characteristic of hexavanadates [7, 15] occur at $\tilde{\nu} = 970\ \mathrm{cm^{-1}}$ and $1010\ \mathrm{cm^{-1}}$ in the infrared spectrum of the first compound (Fig. 1). The infrared spectrum of the second compound is different in the region $\tilde{\nu} = 900$—$1010\ \mathrm{cm^{-1}}$ but its character is analogous to the spectra of compounds with the composition $M^IHV_6O_{16}$ $n H_2O$ [9, 11] or $M^{II}(HV_6O_{16})_2 \cdot nH_2O$ [8, 10] ($M^I = NH_4^+$, Na; M^{II} = Ca, Sr). It follows from the results of paper [10] that the absorption band which occurs at $\tilde{\nu} = 920\ \mathrm{cm^{-1}}$ in the spectrum of these compounds may be assigned to bending vibrations δ(VOH). Owing to this fact, we regard the compounds with the ratio $n(M^{II}) : n(V) = 1:6$ as hydrogen hexavanadates and not dodecavanadates in contrast to the view put forward by the authors of paper [7] in relation with calcium, strontium, barium, and magnesium polyvanadates. Besides these hexavanadates,

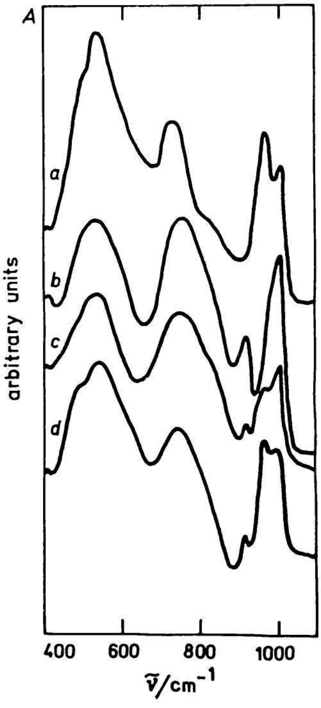

Fig. 1. Infrared spectra of the compounds: *a*) $BaV_6O_{16} \cdot 5H_2O$; *b*) $Ba(HV_6O_{16})_2 \cdot 9H_2O$; *c*) product "P"; *d*) $Cd_{0.9}H_{0.2}V_6O_{16} \cdot nH_2O$.

we also obtained from solutions with higher degree of acidity other products the nature of which was not unambiguously clear. It is characteristic of these products that the content of barium and vanadium varies according to the degree of acidity of solution Z. The content of barium decreases and the content of vanadium increases with the value of Z. Simultaneously with the change in composition of the products, their infrared spectrum also continuously changes. That especially concerns the shoulder in proximity of $\tilde{\nu} = 970\ \text{cm}^{-1}$ the intensity of which increases with the content of barium in the product. There is no unambiguous explanation of this fact. It may be a mixture of $Ba(HV_6O_{16})_2 \cdot 9H_2O$ and $BaV_6O_{16} \cdot 5H_2O$ or product of variable composition expressed by the formula $Ba_{1-x}H_{2x}V_6O_{16} \cdot nH_2O$. We did not obtain a product with $x > 0.5$ in our syntheses.

By investigating the products formed from the cadmium system, we obtained the results different from those obtained with other hitherto investigated systems of vanadates of other bivalent metals [7, 8, 10]. We did not identify at all cadmium decavanadate in the products in conformity with paper [16]. In agreement with this paper, we did not observe any formation of the tetrahydrate of cadmium metavanadate but only the α-modification of $Cd(VO_3)_2$. This compound was present in all products obtained from the solution in the whole investigated temperature range at the degree of acidity $Z = 0.40$—0.73. At lower values of Z, anhydrous cadmium metavanadate was the prevailing component of the products while it was an admixture in the substances discussed later provided higher values of Z were used. The formation of cadmium metavanadate is unfavourably affected by increasing temperature and decreasing concentration of vanadium in the solution. It may be that this compound is the least soluble cadmium vanadate under most conditions investigated by us.

If the degree of acidity of the solutions was $Z = 0.8$, we obtained brown-red products in which the content of cadmium and vanadium varied according to reaction conditions. With respect to the character of infrared spectra, we classify these products as hexavanadates. Their specification is, to a great degree, affected by the transformation to which the substance primarily formed in solution has been subjected before the product is isolated from the solution. First of all, a dark-brown precipitate appeared. During its formation, the pH value of the solution increased but it decreased in the course of subsequent contact of the precipitate with the solution. The quality of original precipitate changed with pH of the solution. The primary product turned into a very voluminous brown-red substance of fibrous character. For this reason, we investigated the transformations of the products in connection with their contact time with reaction solution or with the pH value of solution in the moment of separation of the final product. We found that the ratio of cadmium and vanadium content in the substance initially increased in favour of cadmium up to the value $n_{Cd} : n_V = 0.9 : 6.0$ and afterwards, it decreased slowly. The products with smaller content of cadmium gave infrared spectra analogous to spectra *b* and *c* in Fig. 1. For amount ratio 0.8 : 6.0 or 0.9 : 6.0, the spectrum did not practically change (Fig. 1*d*). This change in substance quality appreciated in relation with the change in infrared spectrum and pH of the solution may mean that the hydrogen form of cadmium hexavanadate arises primarily in the solution and successively exchanges protons for the cadmium ions. However, it seems that the degree of this exchange is limited by the pH value of solution. This assumption is based on the fact that the solutions of cadmium vanadates have lower pH values than analogous solutions of magnesium, calcium, strontium, and barium vanadates. This fact is related with acidic properties of the cadmium cation and obviously caused that we did not obtain from the cadmium system the hexavanadate of the composition $CdV_6O_{16}\cdot nH_2O$ but $Cd_{0.9}H_{0.2}V_6O_{16}\cdot nH_2O$ ($n = 5$—6, $Z = 0.8$, $\theta = 80\ ^\circ C$, $c_v = 0.02\ \text{mol dm}^{-3}$; theoretical composition: 13.11—13.43 % Cd and 39.64—40.58 % V; found experimentally: 13.24 % Cd and 40.08 % V). With regard to this it is more probable that the red-brown products "P" isolated from the system with barium are substances of the composition $Ba_{(1-x)}H_{2x}V_6O_{16}\cdot nH_2O$ and not mixtures of hexavanadate and its hydrogen form.

The results of investigation of the composition of barium and cadmium vanadates in connection with reaction conditions indirectly, to a certain extent, confirm the opinion of the authors of papers [17, 18] on the decomposition of the decavanadate ion in solution giving meta- and hexavanadate or hydrogen hexavanadate anion. That is especially valid for the results obtained at $Z = 0.6$—0.8 when mixtures of the corresponding solid substances were isolated. Better conditions for the formation of hexavanadates arise at increasing temperatures, owing to which these substances are the only product of reactions at 80 °C and $Z = 0.8$.

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