

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

## XI. Products of the reactions taking place in acidified solutions of potassium metavanadate

L. ULICKÁ

*Department of Inorganic Chemistry, Faculty of Natural Sciences,  
Comenius University, CS-842 15 Bratislava*

Received 2 October 1985

The influence of temperature, vanadium concentration, acidity of reaction solution, and reaction time on composition of the products obtained from the  $\text{KVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  system was investigated. It has been established that  $\text{K}_2\text{V}_6\text{O}_{16}$ ,  $\text{K}(\text{HVO}_6)\cdot 3\text{H}_2\text{O}$ , and  $\text{K}_2\text{V}_6\text{O}_{16}\cdot 2\text{H}_2\text{O}$  arise under the examined reaction conditions. The degree of acidity of solution has the most significant influence on composition of the products obtained from solutions within the range from 40°C to 80°C. At the temperature of 22°C, the reaction time also becomes significant. The purity of the prepared  $\text{K}_2\text{V}_6\text{O}_{16}\cdot 2\text{H}_2\text{O}$  was verified by differential thermal analysis.

Изучено влияние температуры, концентрации ванадия, кислотности реакционного раствора и продолжительности реакции на состав продуктов, полученных в системе  $\text{KVO}_3\text{—HNO}_3\text{—H}_2\text{O}$ . Обнаружено, что в изучаемых условиях реакции образуются  $\text{K}_2\text{V}_6\text{O}_{16}$ ,  $\text{K}(\text{HVO}_6)\cdot 3\text{H}_2\text{O}$  и  $\text{K}_2\text{V}_6\text{O}_{16}\cdot 2\text{H}_2\text{O}$ . Сильнее всего на состав продуктов, получаемых из растворов с температурами 40°C—80°C влияет степень кислотности раствора, а при температуре 22°C значительное влияние имеет и продолжительность реакции. С помощью дифференциального термического анализа также проверялась чистота полученного  $\text{K}_2\text{V}_6\text{O}_{16}\cdot 2\text{H}_2\text{O}$ .

The present results obtained by studying the influence of temperature, vanadium concentration, and degree of acidity of solution on composition of the solid polyvanadates of some univalent metals and ammonium point out that the preparation of a certain type of polyvanadate is to a great extent dependent on the given cation [1—3]. The influence of acidity of reaction solution on composition of the potassium vanadates obtained from solutions at laboratory temperature is the topic of papers [4, 5]. The authors of paper [6] pay attention to the influence of temperature and vanadium concentration on composition of the solid substances.

The results obtained by investigating the mutual influence of temperature, vanadium concentration, acidity of reaction solution, and reaction time on composition of the products originating in the  $\text{KVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  system are presented in this paper. A part of this paper is also devoted to the syntheses aimed at preparing the hydrate of potassium hexavanadate and to verification of its purity.

## Experimental

Anhydrous potassium metavanadate was prepared according to literature [7]. Its composition was identified by chemical analysis, infrared spectroscopy, and X-ray phase analysis.

The content of vanadium(V) in the prepared samples was determined volumetrically by titration with iron(II) sulfate [8] ( $c = 0.1 \text{ mol dm}^{-3}$ ) while the content of potassium was determined with a flame photometer Flapho 4 (Zeiss, Jena) by using an interference filter for potassium [9].

The pH values of solutions were measured with a pH-meter 26 (Radiometer, Copenhagen) by using a combined electrode GK 2401 C.

The infrared spectra were taken with a spectrometer "Spectromaster Grubb Parsons" by using the nujol technique.

The diffraction patterns of powdered samples were recorded with a diffractograph Philips equipped with a goniometer PW 1050. For this purpose, the  $\text{CuK}\alpha$  radiation was used.

The differential thermal analysis was performed with a derivatograph Q 1500 D (MOM, Budapest). The weighed amounts of substance used for this analysis were equal to 150 mg and the rate of heating was  $10^\circ\text{C min}^{-1}$ .

The concentration of vanadium in starting solutions of potassium metavanadate was  $0.1 \text{ mol dm}^{-3}$  and  $0.2 \text{ mol dm}^{-3}$ . The degree of acidification of solution ( $Z = n(\text{HNO}_3)/n(\text{V})$ ,  $n$  = substance amount) was adjusted with nitric acid of  $1 \text{ mol dm}^{-3}$  concentration.

The reaction solutions of constant volume of  $100 \text{ cm}^3$  were held at  $22^\circ\text{C}$ ,  $40^\circ\text{C}$ ,  $60^\circ\text{C}$  or  $80^\circ\text{C}$  and stirred with electromagnetic stirrer in the course of reaction.\* The arisen product was separated from the solution after the following time intervals since the formation of the solid phase: 15 min, 60 min, 24 h (temperature  $40\text{—}80^\circ\text{C}$ ) and 1 day—60 days (temperature  $22^\circ\text{C}$ ). The obtained substances were dried in air at laboratory temperature. Their composition was determined on the basis of chemical analysis, infrared spectroscopy, and X-ray phase analysis.

## Results and discussion

The composition of the products isolated from solutions exhibiting temperatures  $40\text{—}80^\circ\text{C}$  is shown in Table 1. It is obvious from this list that the

---

\* We also carried out some experiments in which the reaction solutions were not stirred. The results thus obtained will be discussed separately.

Table 1  
Composition of the products and reaction conditions of their formation

$\theta = 40^\circ\text{C}$				$\theta = 60^\circ\text{C}$				$\theta = 80^\circ\text{C}$			
Z	$\frac{t}{h}$	$c(V)/(\text{mol dm}^{-3})$		Z	$\frac{t}{h}$	$c(V)/(\text{mol dm}^{-3})$		Z	$\frac{t}{h}$	$c(V)/(\text{mol dm}^{-3})$	
		0.1	0.2			0.1	0.2			0.1	0.2
0.4	24	a	H*	0.4	24	H*	H*	0.4	24	H	H
0.6	24	H + HH	H*	0.6	24	H	H	0.6	24	H	H
0.8	1	HH + H	HH + H	0.8	0.25	HH + H	HH + H	0.8	0.25	HH	HH + H
	24	H + HH	HH + H		1	HH + H	HH + H		1	H + HH	H + HH
1.0	1	HH + H	HH	1.0	0.25	HH	HH + H	1.0	0.25	HH	HH
	24	HH + H	HH + H		1	HH + H	HH + H		1	HH	HH
2.0	1	HH	HH + H	2.0	0.25	HH	HH + H	2.0	0.25	HH	HH
	24	H + HH	H + HH		1	HH	HH + H		1	HH	HH
3.0	1	HH	HH	3.0	0.25	HH	HH	3.0	0.25	HH	HH
	24	HH	H + HH		1	HH	HH		1	HH	HH

H —  $\text{K}_2\text{V}_6\text{O}_{16}$ , HH —  $\text{K}(\text{H}(\text{V}_6\text{O}_{16})_3 \cdot 3\text{H}_2\text{O})$ .

\* Traces, probably  $\text{K}_6\text{V}_{10}\text{O}_{28} \cdot 10\text{H}_2\text{O}$ .

a) The solid substance did not appear in the stated time interval.

composition of the vanadates isolated from the investigated system is predominantly affected by the degree of acidification of solution Z. The orange potassium hexavanadate of  $K_2V_6O_{16}$  composition arises at the lowest investigated values of Z as a dominant or single component of the product while the dark-brown hydrogen hexavanadate  $KHV_6O_{16} \cdot 3H_2O$  appears at higher values of Z. The infrared spectra of both compounds are represented in Fig. 1 (a, b).

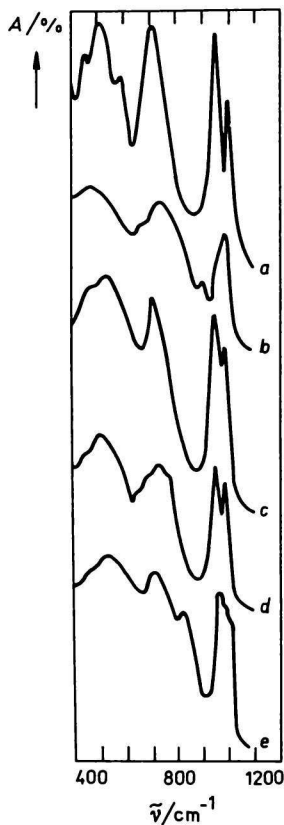


Fig. 1. Infrared spectra.  
 a)  $K_2V_6O_{16}$ ; b)  $KHV_6O_{16} \cdot 3H_2O$ ; c)  $K_2V_6O_{16} \cdot 2H_2O$ ; d) product c, dehydrated at  $\theta = 380^\circ C$ ; e) primary product.

Other investigated factors influence mainly the purity of the product, especially from the view-point of relative proportion of both above-mentioned compounds. It has been found that the purest substances are to be obtained at the highest investigated temperature and the lowest vanadium concentration in the solution. The rate of formation of the solid substance increases with the degree of acidity of the solution. Provided  $Z > 1$ , the reaction time has practically no influence on composition of the product. Provided  $Z = 0.8-1.0$ , hydrogen hexavanadate is primarily formed. However, it can be according to temperature

and vanadium concentration either fully or partially transformed into anhydrous hexavanadate.

The formation of a hydrate of  $K_2V_6O_{16} \cdot nH_2O$  composition was not observed under experimental conditions stated in Table 1, *i.e.* if the reaction solutions were stirred. This result becomes interesting in comparison with literature according to which the temperature of reaction solution suited for preparation of the hydrate of potassium hexavanadate is 40 °C and 85 °C [6] or even 20 °C [10]. The authors of paper [1] obtained the analogous sodium salt by reaction in the  $NaVO_3-HNO_3-H_2O$  system at 60 °C while the reaction solutions were left in rest. Because of this fact, we performed a series of experiments at the above-mentioned temperatures while the value of  $Z$  varied in the range from 0.55 to 0.75 and the solutions were left in rest until their pH value was constant. The expected dark-red substance was formed under these conditions, but it always appeared together with anhydrous potassium hexavanadate  $K_2V_6O_{16}$ . In the effort to prepare this substance without undesirable contaminations, we gradually reduced the temperature of the reaction solution. It has been found that the purity of the product was affected least at the temperature of 22 °C. At this temperature, the reaction solutions could already be stirred, owing to which the rate of formation of the substance was increased without impairment of its quality. The best analytical parameters were observed for the substance isolated from the solution in which the vanadium concentration, degree of acidity, and reaction time were  $c(V) = 0.2 \text{ mol dm}^{-3}$ ,  $Z = 0.65$ , and 21 days, respectively. The chemical analysis allows to express the composition of the substance by the formula  $K_2V_6O_{16} \cdot 2H_2O$ . The infrared spectrum of this substance (Fig. 1c) suggests a certain structural analogy with  $Na_2V_6O_{16} \cdot 3H_2O$  [1]. The X-ray diffraction pattern of the prepared substance indicates a relatively low degree of arrangement of its structure. From this point of view, the hydrate of potassium hexavanadate resembles  $KHV_6O_{16} \cdot 3H_2O$  (Fig. 2a, 2e) and is rather different from  $K_2V_6O_{16}$  (Fig. 2d) the crystal structure of which is known [11].

Owing to the assumed differences between the crystal structures of the hydrated hexavanadate and anhydrous potassium hexavanadate we also investigated the way of crystal water liberation from the structure of the prepared substance. The results of differential thermal analysis which are presented in Fig. 3 are analogous with the results published in paper [10]. However, the authors of this paper did not examine the changes due to dehydration and subsequent heating of the anhydrous substance. The dehydration of  $K_2V_6O_{16} \cdot 2H_2O$  takes place in the temperature interval from 20 °C to 260 °C as a one-step process. The dehydrated hexavanadate preserves its original dark-red colour and, to a great degree, its structural arrangement, too (Fig. 2b) up to the temperature of 350 °C. At this temperature, the modification of anhydrous salt with poor structural order starts to be transformed into the crystalline modifica-

tion of orange colour. Another process indicated by infrared spectroscopy (Fig. 1*d*) and X-ray diffraction method (Fig. 2*c*) takes place in the temperature interval 350 °C—405 °C, too. Besides the diffractions corresponding to  $K_2V_6O_{16}$  (orange modification), there are another diffractions in the X-ray powder diffraction pattern. According to [12], the orange  $K_2V_6O_{16}$  is stable up to the temperature of 415 °C and moreover, its decomposition products exhibit diffractions at angles  $\theta$  which are different from the angles corresponding to the additional diffractions in Fig. 2*c*. It means that the prepared hydrate of potassium hexavanadate is contaminated by an admixture of other substance which decomposes in the temperature interval 350 °C—405 °C. The decomposition products of the admixture may also influence further thermochemical reactions because the decomposition of anhydrous potassium hexavanadate does not proceed in the way ascertained for the pure substance [12]. Besides  $KVO_3$ ,

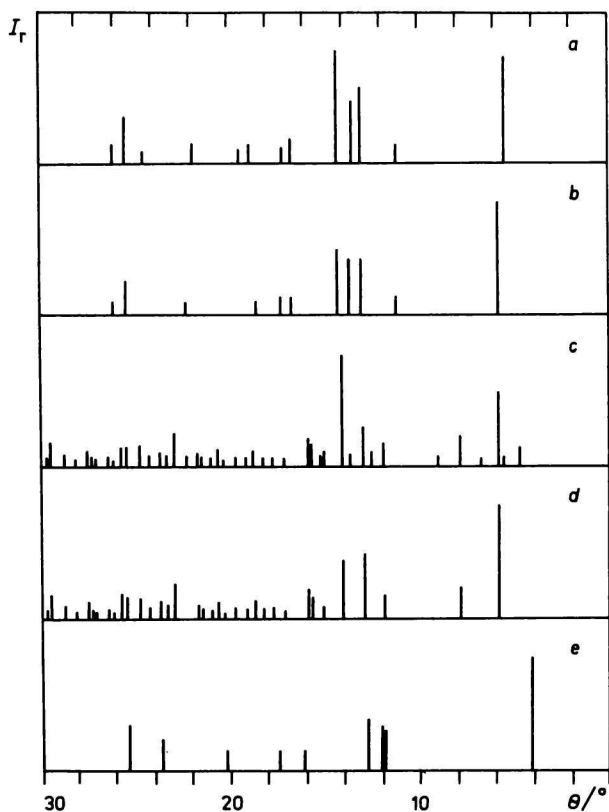


Fig. 2. X-Ray diffraction pattern.

a)  $K_2V_6O_{16} \cdot 2H_2O$ ; b) product a, dehydrated at  $\theta = 260$  °C; c) product a, dehydrated at  $\theta = 380$  °C; d)  $K_2V_6O_{16}$ ; e)  $KHV_6O_{16} \cdot 3H_2O$ .

$K_3V_5O_{14}$ , and  $K_2V_8O_{20.8}$ , an unknown thermally unstable substance was indicated by the X-ray phase analysis as intermediate.

In order to obtain more information about the character of the substance which represents the admixture in the dihydrate of potassium hexavanadate we carried out reactions in which the product was isolated from the solution in certain time intervals. It was found that the ratio of substance amounts of potassium and vanadium was 1 : 4.72 and changed with time to 1 : 3.06. Simultaneously with that changed also the colour of the product to dark-red. The ratio of substance amounts of both elements in the final product corresponds to potassium hexavanadate and the analytically determined contents of potassium and vanadium are in the range of allowed experimental errors consistent with a compound of the composition  $K_2V_6O_{16} \cdot 2H_2O$  ( $w_i(\text{found})$ : 10.95 % K, 44.94 % V, 4.90 %  $H_2O$ ;  $w_i(\text{calc.})$ : 11.57 % K, 45.22 % V, 5.33 %  $H_2O$ ). Simultaneously, the change in product composition was accompanied by a change in infrared spectrum. The intensity of the absorption band at  $\bar{\nu} = 835 \text{ cm}^{-1}$  as well as its shoulder behind  $\bar{\nu} = 1000 \text{ cm}^{-1}$  (Fig. 1e) present in the case of primary product showed a tendency to decrease with time. Owing to this information, it is likely that a small amount of the brown substance arising at the very beginning of reaction is not submitted to further heterogeneous reactions and is present in the final product. The stated values of absorption bands as well as the ratio of the substance amounts of potassium and vanadium in the primary product suggest that it might be the compound for which the authors of paper [10] found the ratio  $n(K) : n(V) = 1 : 5$ .

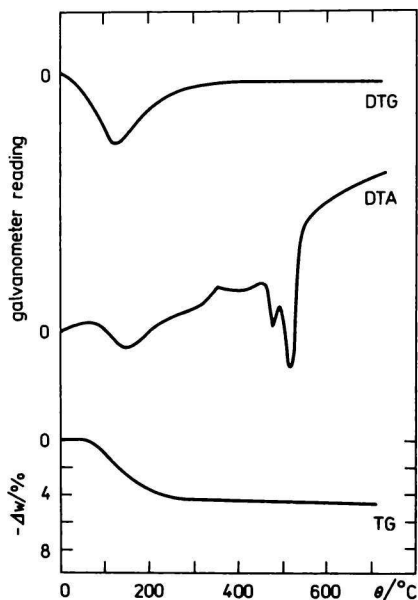


Fig. 3. Thermoanalytical curves of  $K_2V_6O_{16} \cdot 2H_2O$ .

On the basis of the obtained results, we may state that not only temperature, acidity of solution, vanadium concentration, and reaction time but also stirring of the solution may have under certain conditions influence on composition of the products obtained from the  $\text{KVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  system. While  $\text{K}_2\text{V}_6\text{O}_{16}$  and  $\text{K}(\text{H}_2\text{VO}_4)_3 \cdot 3\text{H}_2\text{O}$  are practically formed at all investigated temperatures, the preparation of pure  $\text{K}_2\text{V}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$  requires specific conditions. It is known at present that only potassium can form both anhydrous and hydrated hexavanadate. As the structure of  $\text{K}_2\text{V}_6\text{O}_{16}$  is known [11], the physical investigation of  $\text{K}_2\text{V}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$  may be of major importance for elucidation of structural relations between anhydrous and hydrated vanadates of a given type. The compound hitherto considered to be a pure substance according to literature [6, 10] is not convenient for such investigation and we have to look for new methods of its preparation.

The prepared potassium hexavanadates belong among thermally instable compounds which decompose to give vanadium-oxygen bronzes and other types of vanadates. The final product of the decomposition of hydrogen hexavanadate is of different composition [13] when compared with the product of potassium hexavanadate [12]. It is obvious that the composition of final products of thermal decomposition of both potassium vanadates in question is connected not only with thermal stability of the arising vanadate or bronze but also with stoichiometry of the starting compound.

## References

1. Suchá, V. and Žůrková, L., *Chem. Zvesti* 34, 452 (1980).
2. Žůrková, L. and Ulická, L., *Chem. Zvesti* 36, 809 (1982).
3. Žůrková L., Suchá, V., and Schraml, V., *Chem. Papers* 39, 629 (1985).
4. Zolotavin, V. L., Tolstov, L. K., Fotyev, A. A., and Bukreev, Yu. F., *Dokl. Akad. Nauk SSSR* 175, 395 (1967).
5. Fotyev, A. A. and Tolstov, L. K., *Zh. Neorg. Khim.* 15, 1011 (1970).
6. Ivakin, A. A., Yatsenko, A. P., Goryakova, O. V., and Kruchinina, M. V., *Zh. Neorg. Khim.* 24, 2646 (1979).
7. Jahr, F. and Preuss, F., *Chem. Ber.* 99, 1602 (1966).
8. Tomiček, O., *Kvantitativní analýza*. (Quantitative Analysis.) Státní zdravotnické nakladatelství. (State Publishing House of Public Health.) Prague, 1958.
9. Herrman, R., *Plameňová fotometria*. (Flame Photometry.) Státní zdravotnické nakladatelství. (State Publishing House of Public Health.) Prague, 1968.
10. Ivakin, A. A., Yatsenko, A. P., and Kruchinina, M. V., *Zh. Neorg. Khim.* 26, 2677 (1981).
11. Evans, H. T. and Block, S., *Inorg. Chem.* 5, 1808 (1966).
12. Žůrková, L. and Ulická, L., *Thermochimica Acta* 85, 111 (1985).
13. Ulická, L. and Žůrková, L. *Thermochimica Acta* 92, 481 (1985).

Translated by R. Domanský