

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

## XIII. Products of the reactions taking place in acidified solutions of lanthanum and yttrium vanadates

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The composition of products formed in the  $\text{La}(\text{VO}_3)_3\text{—HNO}_3\text{—H}_2\text{O}$  and  $\text{Y}(\text{VO}_3)_3\text{—HNO}_3\text{—H}_2\text{O}$  systems was studied. The polyvanadates of the composition  $\text{La}(\text{HV}_6\text{O}_{16})_3 \cdot x\text{H}_2\text{O}$  ( $x = 19\text{—}21$ ),  $\text{La}_2(\text{V}_6\text{O}_{16})_3 \cdot x\text{H}_2\text{O}$  ( $x = 24\text{—}25$ ), and  $\text{Y}(\text{HV}_6\text{O}_{16})_3 \cdot x\text{H}_2\text{O}$  ( $x = 23\text{—}25$ ) were separated and the optimum conditions of their preparation were found.

The study of the  $\text{M}^{\text{I}}\text{VO}_3$  ( $\text{M}^{\text{II}}(\text{VO}_3)_2$ )— $\text{HNO}_3$  ( $\text{HClO}_4$ )— $\text{H}_2\text{O}$  systems [1—9] showed that in dependence on acidity degree  $Z$ , temperature, concentration of vanadium in solution and on reaction time, the mentioned uni- and bivalent cations form solid polyvanadates of the composition:

- a)  $\text{M}_2^{\text{I}}\text{V}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$  ( $\text{M}^{\text{I}} = \text{Na}, \text{K}$ ) resp.  $\text{M}^{\text{II}}\text{V}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ),
- b)  $\text{M}^{\text{I}}\text{HV}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$  ( $\text{M}^{\text{I}} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{NH}_4^+$ ) resp.  $\text{M}^{\text{II}}(\text{HV}_6\text{O}_{16})_2 \cdot x\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Cd}, \text{Mn}$ ),
- c)  $\text{M}_2^{\text{I}}\text{V}_6\text{O}_{16}$  ( $\text{M}^{\text{I}} = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}, \text{NH}_4^+$ ).

From this viewpoint it was interesting to find out whether the trivalent lanthanum and yttrium cations form, at similar reaction conditions, the mentioned types of polyvanadates. We report here on the results of our investigations dealing with this problem and with optimization of reaction conditions for preparation of pure compounds as well.

### Experimental

$\text{V}_2\text{O}_5$  was prepared by thermal decomposition of the purified  $\text{NH}_4\text{VO}_3$  [10, 11]. The other commercial chemicals were of anal. grade.

Vanadium(V) and vanadium(IV) were estimated by titration with iron(II) sulfate ( $c(\text{FeSO}_4) = 0.1 \text{ mol dm}^{-3}$ ) and potassium permanganate ( $c(\text{KMnO}_4) = 0.01 \text{ mol dm}^{-3}$ ), respectively. Lanthanum and yttrium were titrated by complexon III ( $c(\text{complexon}) = 0.01 \text{ mol dm}^{-3}$ ) using xylenol orange [12]. The published analytical procedure was modified as the vanadate ions present in solution interfered with the colour change of

indicator. Vanadium was bound by addition of  $\text{H}_2\text{O}_2$  as a peroxo complex which did not disturb the estimation of La and Y. The water content was estimated gravimetrically.

pH was measured on a PHM 22 pH-meter (Radiometer) equipped with a GK 2401 C high-temperature electrode. The infrared spectra in nujol mulls were registered on a Specord M 80 spectrophotometer (Zeiss, Jena). The X-ray diffraction patterns were registered on a Philips diffractometer with PW 1050 goniometer, using  $\text{CuK}\alpha$  radiation.

The reaction solutions of vanadates (La and Y) with the  $n(\text{La (Y)}) : n(\text{V})$  ratio 1 : 3 were prepared by mixing peroxidic solution of  $\text{V}_2\text{O}_5$  and aqueous solution of  $\text{La}(\text{NO}_3)_3$ , resp.  $\text{Y}(\text{NO}_3)_3$ . In these solutions, the acidity degree  $Z = n(\text{HNO}_3) : n(\text{V})$  was adjusted to 0—3 by addition of required amount of nitric acid ( $c(\text{HNO}_3) = 1.0 \text{ mol dm}^{-3}$ ). After filling up the solution to  $500 \text{ cm}^3$  the vanadium concentration was  $0.03 \text{ mol dm}^{-3}$ . The temporarily formed vanadium(V) peroxo species were decomposed to oxo anions by heating. The reactions were carried out at 40, 60, and  $80^\circ\text{C}$ , the reaction time (24 h or 4 d) was found experimentally in dependence upon the amount of the product formed. With respect to the importance of pH at the formation of individual types of polyvanadates [1, 2], pH was measured immediately after preparation of reaction solutions, in course of the reaction each 24 h and before isolation of the products. After isolation the separated solid products were washed with distilled water and dried at room temperature.

From the viewpoint of composition of the products, besides the mentioned reaction systems, also a system in which the solutions of lanthanum and yttrium vanadates were prepared using the corresponding acetate, was studied at  $60^\circ\text{C}$ , in the  $Z$  range 1.80—2.00. The other reaction conditions were not changed.

## Results and discussion

Our study of composition of the solid products isolated from the  $\text{La}(\text{VO}_3)_3$ — $\text{HNO}_3$ — $\text{H}_2\text{O}$  and  $\text{Y}(\text{VO}_3)_3$ — $\text{HNO}_3$ — $\text{H}_2\text{O}$  systems showed that in each system only one type of compound with a defined  $n(\text{La (Y)}) : n(\text{V})$  ratio is formed (Tables 1 and 2).

Based on IR spectra (Fig. 1) which are analogical, by their character, to the spectra of  $\text{M}^{\text{I}}\text{HV}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$  and  $\text{M}^{\text{II}}(\text{HV}_6\text{O}_{16})_2 \cdot x\text{H}_2\text{O}$  [1—9], respectively, and on the results of chemical analyses we formulated the obtained products as  $\text{M}^{\text{III}}(\text{HV}_6\text{O}_{16})_3 \cdot x\text{H}_2\text{O}$  ( $x = 19$ — $21$  for  $\text{M}^{\text{III}} = \text{La}$ ,  $x = 23$ — $25$  for  $\text{M}^{\text{III}} = \text{Y}$ ). For  $\text{La}(\text{HV}_6\text{O}_{16})_3 \cdot 19$ — $21\text{H}_2\text{O}$   $w_i(\text{calc.})$ : 6.30—6.40 % La, 41.58—42.27 % V, 15.78—17.16 %  $\text{H}_2\text{O}$ ;  $w_i(\text{found})$ : 6.35—6.46 % La, 41.53—42.24 % V, 15.85—17.10 %  $\text{H}_2\text{O}$ . For  $\text{Y}(\text{HV}_6\text{O}_{16})_3 \cdot 23$ — $25\text{H}_2\text{O}$   $w_i(\text{calc.})$ : 3.99—4.06 % Y, 41.17—41.85 % V, 18.91—20.22 %  $\text{H}_2\text{O}$ ;  $w_i(\text{found})$ : 4.00—4.10 % Y, 41.10—41.90 % V, 19.10—20.28 %  $\text{H}_2\text{O}$ . The water content varied with reaction conditions.

The above compounds are dark brown. The X-ray diffraction patterns exhibit only some diffuse diffractions indicating a low ordering of the structure. The calculated interplanar distances are given in Table 3.

Table 1

Formation conditions and the composition of the lanthanum polyvanadates isolated after 24 h and 4 d

$c(\text{V}) = 0.03 \text{ mol dm}^{-3}$	Time	Z	$\theta = 40^\circ\text{C}$			$\theta = 60^\circ\text{C}$			$\theta = 80^\circ\text{C}$		
			pH <sup>a</sup>	$n(\text{La}) : n(\text{V})$	Product	pH <sup>a</sup>	$n(\text{La}) : n(\text{V})$	Product	pH <sup>a</sup>	$n(\text{La}) : n(\text{V})$	Product
24 h	0	0	2.50		—	2.70	0.0735	P	2.80	0.0725	P
		0.2	2.30		—	2.40	0.0719	P	2.50	0.0667	P
		0.4	2.25	0.0694	P	2.30	0.0667	P	2.40	0.0610	P
		0.6	2.15	0.0654	P	2.25	0.0654	P	2.30	0.0606	P
		0.8	2.15	0.0645	P	2.15	0.0637	P	2.20	0.0599	P
		1	2.10	0.0621	P	2.05	0.0633	P	2.10	0.0592	P
		2	1.90	0.0610	P	1.90	0.0592	P	1.85	0.0562	HH
		3	1.75		+	1.80	0.0562	HH	1.80	0.0556	HH
	4 d	0	0	2.65	0.0714	P	2.80	0.0752	P	2.80	0.0746
		0.2	2.45	0.0704	P	2.70	0.0730	P	2.60	0.0714	P
		0.4	2.30	0.0690	P	2.50	0.0690	P	2.30	0.0676	P
		0.6	2.20	0.0671	P	2.30	0.0667	P	2.30	0.0602	P
		0.8	2.15	0.0662	P	2.20	0.0662	P	2.20	0.0599	P
		1	2.10	0.0645	P	2.10	0.0592	P	2.10	0.0595	P
		2	1.80	0.0610	P	1.85	0.0562	HH	1.90	0.0575	P
		3	1.75	0.0610	P	1.80	0.0562	HH	1.80	0.0568	P

P — product discussed in the text; + little amount of product; — product is not formed; HH —  $\text{La}(\text{HV}_6\text{O}_{16})_x \cdot x\text{H}_2\text{O}$ ,  $x = 19\text{--}21$ ,  $n(\text{La}) : n(\text{V}) = 0.0556$ ; *a*) pH of solution before the product was separated.

Table 2

Formation conditions and the composition of the yttrium polyvanadates isolated after 24 h and 4 d

$c(V) = 0.01 \text{ mol dm}^{-3}$	Time	Z	$\theta = 40^\circ\text{C}$			$\theta = 60^\circ\text{C}$			$\theta = 80^\circ\text{C}$		
			pH <sup>a</sup>	$n(Y):n(V)$	Product	pH <sup>a</sup>	$n(Y):n(V)$	Product	pH <sup>a</sup>	$n(Y):n(V)$	Product
24 h	0	0	2.45	—	—	2.60	0.0746	P	2.65	0.0746	P
	0.2	0.2	2.40	0.0676	P	2.40	0.0709	P	2.45	0.0725	P
	0.4	0.4	2.25	0.0645	P	2.25	0.0658	P	2.35	0.0676	P
	0.6	0.6	2.12	0.0637	P	2.20	0.0645	P	2.30	0.0641	P
	0.8	0.8	2.10	0.0613	P	2.15	0.0606	P	2.20	0.0595	P
	1	1	2.05	0.0606	P	1.90	0.0575	P	1.95	0.0575	P
	2	2	1.80	0.0592	P	1.75	0.0562	HH	1.75	0.0557	HH
	3	3	1.70		+	1.70	0.0559	HH	1.70	0.0556	HH
4 d	0	0	2.50	+	+	2.70	0.0763	P	2.70	0.0758	P
	0.2	0.2	2.35	0.0690	P	2.40	0.0735	P	2.50	0.0746	P
	0.4	0.4	2.25	0.0649	P	2.30	0.0685	P	2.40	0.0704	P
	0.6	0.6	2.20	0.0645	P	2.25	0.0645	P	2.25	0.0667	P
	0.8	0.8	2.10	0.0610	P	2.15	0.0610	P	2.15	0.0606	P
	1	1	2.00	0.0592	P	2.05	0.0578	P	2.00	0.0575	P
	2	2	1.75	0.0588	P	1.75	0.0559	HH	1.75	0.0557	HH
	3	3	1.70	0.0585	P	1.70	0.0560	HH	1.70	0.0562	HH

P — product discussed in the text; + little amount of product; — product is not formed; HH —  $Y(HV_6O_{16})_3 \cdot xH_2O$ ,  $x = 23-25$ .  $n(Y):n(V) = 0.0556$ ; a) pH of solution before the product was separated.

The existence of  $\text{La}_2(\text{V}_{12}\text{O}_{31})_3 \cdot 37\text{H}_2\text{O}$  prepared at room temperature was described in [13]. The published data do not allow to decide whether this vanadate has the same chemical structure as the compound prepared by us.

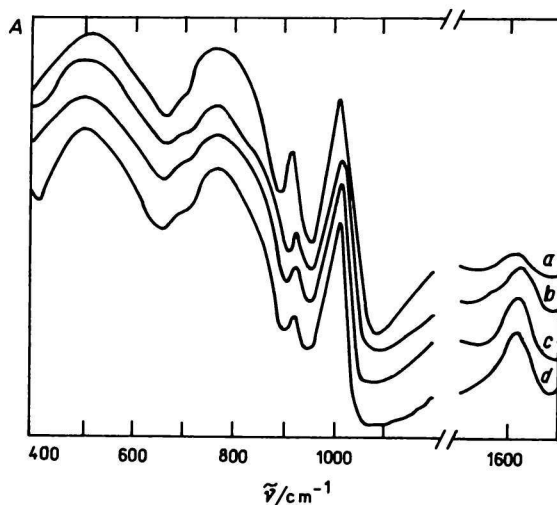


Fig. 1. Infrared spectra of: a)  $\text{NaHV}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$ ; b)  $\text{Ba}(\text{HV}_6\text{O}_{16})_2 \cdot 9\text{H}_2\text{O}$ ; c)  $\text{La}(\text{HV}_6\text{O}_{16})_3 \cdot x\text{H}_2\text{O}$ ; d)  $\text{Y}(\text{HV}_6\text{O}_{16})_3 \cdot x\text{H}_2\text{O}$ .

For further products P (Tables 1 and 2) formed in reaction systems it is characteristic that the  $n(\text{La}(\text{Y})) : n(\text{V})$  ratio gradually decreases with increasing acidity degree. Simultaneously, the characteristic IR absorption of hexavanadates at  $\tilde{\nu} = 980 \text{ cm}^{-1}$  decreases and intensity of the typical band of the protonized product at  $\tilde{\nu} = 920 \text{ cm}^{-1}$  (Fig. 2c, d) increases. The colour of the

Table 3

Interplanar distances

$\text{La}(\text{HV}_6\text{O}_{16})_3 \cdot x\text{H}_2\text{O}$		$\text{Y}(\text{HV}_6\text{O}_{16})_3 \cdot x\text{H}_2\text{O}$	
$d/\text{nm}$	$I_t/\%$	$d/\text{nm}$	$I_t/\%$
1.290	100	1.312	100
0.426	8	0.440	13
0.344	28	0.345	26
0.296	17	0.293	13
0.256	19	0.256	17
0.1916	13	0.1917	18
0.1799	20	0.1798	25
0.1520	10	0.1519	13

products changes from brown-red to dark brown. For this fact we have no unambiguous explanation. The products are either mixtures of  $M^{III}(HV_6O_{16})_3 \cdot xH_2O$  and  $M^{III}(V_6O_{16})_3 \cdot xH_2O$  or compounds of variable composition, obtained as intermediates in formation of the hydrates of hexavanadates.

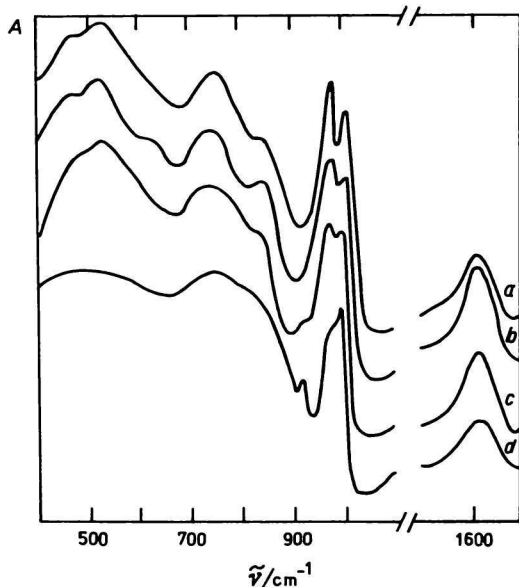


Fig. 2. Infrared spectra of: a)  $BaV_6O_{16} \cdot 5H_2O$ ; b)  $La_2(V_6O_{16})_3 \cdot 25H_2O$ ; c) product P with  $n(Y):n(V)$  ratio 0.0763; d) product P with  $n(La(Y)):n(V)$  ratio 0.0575.

In the products formed in both systems at  $60^\circ C$  and  $Z = 0.0$ , the  $n(La(Y)):n(V)$  ratio corresponds mostly to the values characteristic of hexavanadates. The products show IR spectra (Fig. 2c) exhibiting in certain regions a relation to the spectra of  $M^{II}_2V_6O_{16} \cdot xH_2O$  and  $M^{III}V_6O_{16} \cdot xH_2O$ , respectively.

The brown-green products obtained at  $40^\circ C$  and higher  $Z$  contain 1.29–2.54% V(IV). In other products vanadium(IV) was not proved by the method used. Probably, the reason why no pure La(Y) hexavanadates were formed in the systems mentioned above is that pH was low (1.7–2.8) in the whole  $Z$  range. Therefore, some other reaction systems with increased pH were investigated in which La(Y) acetates, instead of nitrates, were used in preparation of starting solution of vanadate. In such reaction systems, in comparison with those mentioned above, the acetate ions were present as well. A red-brown compound was isolated from the lanthanum system at pH 3.6,  $Z = 1.82$ , reaction time 4 d and  $\theta = 60^\circ C$ . In agreement with its IR spectrum (*cf.* Fig. 2a and 2b) characteristic of hydrates of hexavanadates, as well as with the results of chemical analysis we have formulated the compound as  $La_2(V_6O_{16})_3 \cdot 25H_2O$ ;  $w_i(\text{calc.})$ : 11.52% La, 38.00% V, 18.66%  $H_2O$ ;  $w_i(\text{found})$ : 11.55% La, 37.99% V, 18.67%  $H_2O$ .

At  $Z > 1.82$  the products P and at lower  $Z$  an unidentified yellow compound containing 24.46 % V and 29.87 % La were formed. The powder diffraction pattern of the latter one showed that it is X-ray amorphous.

The attempts to prepare  $Y_2(V_6O_{16})_3 \cdot xH_2O$  from the yttrium system were not successful. At  $Z > 0.6$  (pH 3.4), the products P were formed and at lower  $Z$ ,  $YVO_4$  was identified as admixture. This difference in comparison with lanthanum vanadates can be explained so that  $YVO_4$  is formed at lower pH than needed for  $LaVO_4$ , due to the chemical properties of yttrium and lanthanum.

Our study of the influence of investigated factors on the composition of products formed in the described reaction systems showed that optimum temperature for formation of both types of vanadates investigated is higher than 40 °C. As concerns the optimum acidity degree of the reaction solution, the vanadates with the  $n(La(Y)):n(V)$  ratio 1 : 18 are formed at higher  $Z$  whereas the hydrate of lanthanum hexavanadate requires lower  $Z$  and longer reaction time.

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