

INTERCALATION OF KETONES IN VANADYL PHOSPHATE AND ISOSTRUCTURAL HOSTS

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The intercalation of acetone and butan-2-one in vanadyl and niobyl phosphates and niobyl arsenate is reported. All intercalates prepared are tetragonal and their basal spacings are close to each other. The intercalates contain one molecule of the ketone per formula unit. The existence of keto-enol tautomerism of guest molecules in interlayer space is assumed.

Key words: Ketones; Acetone; Intercalation; Intercalates; Vanadium; Phosphates; Niobyl phosphates; Arsenates.

Vanadyl phosphate dihydrate $\text{VOPO}_4 \cdot 2 \text{H}_2\text{O}$ and other isostructural layered compounds are able to accommodate some types of organic molecules in the interlayer space¹. Aliphatic alcohols and diols^{2,3}, amines^{4,5}, carboxylic acids⁶, carboxamides⁷, amino acids⁸, and heterocycles^{9,10} belong to the compounds which can be intercalated in such a way. Nevertheless, to the best of our knowledge, intercalation of ketones in these systems has not yet been described even if it is known from the structure of anhydrous VOPO_4 that double-bonded oxygen is able to form donor-acceptor bond to a vanadium atom of the neighboring layer¹¹. In this paper we report on the intercalation of ketones into vanadyl and niobyl phosphates and niobyl arsenate.

EXPERIMENTAL

Vanadyl phosphate dihydrate, niobyl phosphate trihydrate and niobyl arsenate tetrahydrate were synthesized as previously described¹²⁻¹⁴. Intercalates of all hosts with ketones were prepared by a reintercalation reaction. Hosts^{2,3} intercalated with propan-1-ol were prepared in advance and used as a starting material for the reactions with ketones. About 0.25 g of dry

$\text{VOPO}_4 \cdot 2 \text{C}_3\text{H}_7\text{OH}$ in 10 ml of dry ketone was shaken at laboratory temperature for two hours. The solid product was filtered and dried at ambient temperature under nitrogen. The intercalation of acetone and butan-2-one into niobyl phosphate and arsenate was carried out in the same way.

The powder data of the intercalates with a minor excess of the guest were obtained with an X-ray diffractometer (HZG-4, Germany) using $\text{CuK}\alpha 1$ radiation ($\lambda = 0.154051 \text{ nm}$) with discrimination of the $\text{CuK}\beta$ by a Ni-filter. The $\text{CuK}\alpha 2$ intensities were removed from the original data. Silicon ($a = 0.543055 \text{ nm}$) was used as internal standard. Diffraction angles were measured from 3 to 60° (2θ). The obtained data were refined by the least-squares program minimizing $(2\theta_{\text{exp}} - 2\theta_{\text{calc}})^2$. Temperature measurements (from 22 to 240°C) were carried out on a heated corundum plate with a thermocouple¹⁵.

The TGAs of the intercalates were performed with a Derivatograph MOM (Hungary), at 30 – 600°C in air at a heating rate of $5^\circ \text{C}/\text{min}$. The weight of the samples was 100 mg . The composition of NbAsO_4 intercalates was determined by elemental analysis (C, H). For $\text{NbOAsO}_4 \cdot \text{C}_3\text{H}_6\text{O}$ (305.9) calculated: 11.78% C; 1.98% H; found: 12.15% C, 2.05% H. For $\text{NbOAsO}_4 \cdot \text{C}_4\text{H}_8\text{O}$ (319.3) calculated: 15.02% C; 2.52% H; found: 13.96% C, 2.34% H.

Infrared spectra were recorded on a Bio-Rad FTS spectrometer in the range $4\ 000$ – 500 cm^{-1} using a dry KBr powder containing 10% of the intercalate. The resulting reflectance spectra were converted to the Kubelka–Munk format^{16,17}.

RESULTS AND DISCUSSION

Acetone and other ketones cannot be intercalated in anhydrous vanadyl phosphate and also replacement of water molecules in $\text{VOPO}_4 \cdot 2 \text{H}_2\text{O}$ does not lead to a pure intercalate. Therefore propan-1-ol–intercalated vanadyl phosphate was used as a starting material^{2,3}. In such a way, intercalates with acetone and butan-2-one were prepared as yellow powders indicating that there was no reduction of vanadium(V) to vanadium(IV). The attempts to intercalate pentan-2-one, pentan-3-one, and hexan-2-one were not successful.

The intercalates prepared were well crystalline and their diffractograms showed a series of relatively sharp $(00l)$ reflections (Fig. 1). The a parameter of the tetragonal lattice was determined from the position of the (200) line for vanadyl phosphate and from the positions of the (110) and (200) lines for niobyl compounds. The presence of these lines indicates that a preferred orientation is minimized. The (hkl) lines were not found in the intercalates. The presence of the $(hk0)$ and the absence of the (hkl) reflections in the intercalates is characteristic of a turbostratic structure. In this structure, the original tetragonal layers of the hosts are retained but shifted in the directions of the x and/or y axes. The lattice parameters are given in Table I. The c parameters of both acetone and butan-2-one intercalates are close to each other. The longer chain of butan-2-one does not cause an increase in basal spacing compared with acetone. From that it can be inferred that the alkyl

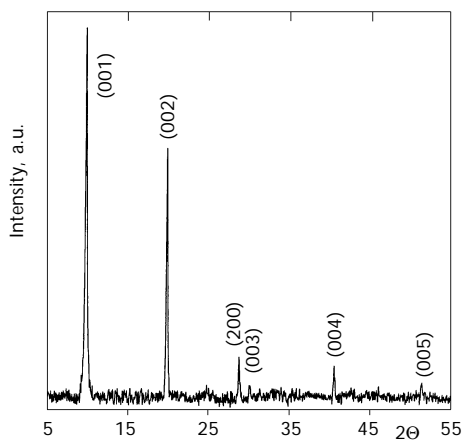
chains are parallel with the host layers. If the alkyl chain is longer than four carbons, no intercalate is formed, probably for steric reasons.

The composition of the vanadyl and niobyl phosphate intercalates was determined by thermogravimetric analysis. Guests are released in one step; the total weight losses correspond to the stoichiometric ratio x given in Table I. Thermogravimetry is not suitable for determination of the composition of NbOAsO_4 intercalates because this host is decomposed at about $500\text{ }^\circ\text{C}$: As(V) is reduced to As(III) by the rest of the organic guest during heating and the As_2O_3 formed escapes³. Therefore, the composition of these intercalates was determined by elemental analysis. As follows from the results obtained, the intercalates most probably contain one molecule of ketone per formula unit.

TABLE I
Lattice parameters and the guests content in the intercalates prepared

Intercalate	a , nm	c , nm	x
VOPO_4 + acetone	0.621	0.893	1.05
VOPO_4 + butan-2-one	0.621	0.900	0.88
NbOPO_4 + acetone	0.646	0.892	0.98
NbOPO_4 + butan-2-one	0.647	0.898	1.00
NbOAsO_4 + acetone	0.665	0.893	1.04
NbOAsO_4 + butan-2-one	0.667	0.898	0.91

FIG. 1
Diffractogram ($\text{CuK}\alpha$) of acetone-intercalated VOPO_4



The intercalates prepared are more stable in air than alkan-1-ol and alkane-1,2-diol intercalates. In the case of the VOPO_4 intercalate with acetone, the lines of the dihydrate appear in the diffractogram after more than one hour whereas these lines are observed after several minutes in the VOPO_4 intercalate with propan-1-ol. The NbOPO_4 and NbOAsO_4 intercalates are generally less stable than that of VOPO_4 . A surprisingly high thermal stability was found for VOPO_4 intercalate with acetone, which is stable up to 130°C . This indicates a very strong interaction between the host and guest species.

An IR spectrum of the butan-2-one intercalate (b) together with that of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (a) is given in Fig. 2. The peaks in the region from 500 to $1\,100\text{ cm}^{-1}$ correspond to vibrations of the PO_4 tetrahedron (557 , 926 , and $1\,084\text{ cm}^{-1}$), vanadyl group ($1\,003\text{ cm}^{-1}$), and to a lattice vibration (685 cm^{-1}). A very intensive peak of the carbonyl group in the intercalate is shifted to lower wavenumbers ($1\,690\text{ cm}^{-1}$) in comparison with its position in pure butan-2-one. This indicates a strong interaction of carbonyl oxygen with vanadium atom of the host layer. A broad band in the region from $2\,900$ to $3\,600\text{ cm}^{-1}$ suggests the existence of OH groups in the compound studied. The OH-group vibrations can be explained either by the presence of water in the interlayer space or by keto-enol tautomerism of the guest molecules. The presence of water in the intercalate is not probable because both the propan-1-ol intercalate and butan-2-one used as starting materials were anhydrous. Moreover, the band in the intercalate is broader and more complex compared with that in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. The band at $1\,644\text{ cm}^{-1}$ in the intercalate can be assigned to vibration of the C=C bond in the enol form

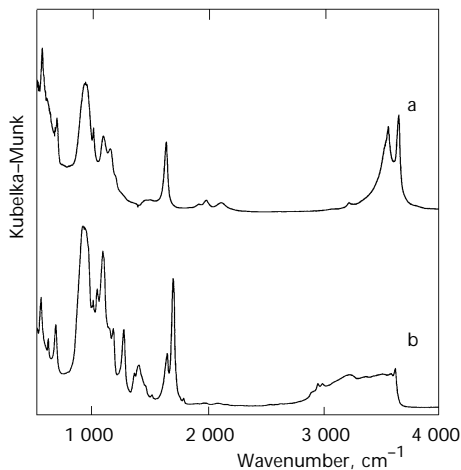


FIG. 2
IR spectra of vanadyl phosphate dihydrate (a)
and butan-2-one-intercalated vanadyl phosphate (b)

of the guest. The formation of the enol form can be caused by the acid character of the host layers. The existence of keto–enol tautomerism and the arrangement of the guest molecules in the intercalate is under investigation.

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