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HEATS OF PYRIDINE INTERCALATION WITH α- AND γ-ZIRCONIUM PHOSPHATES

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ABSTRACT

Calorimetric measurements at 25°C were made to determine the thermodynamic quantities for the intercalation of pyridine with α- and γ-zirconium phosphates. These phosphates showed exothermic reactions with $\Delta H^0 = -59.3$ and -21.9 kJ mole^{-1}, respectively. The large difference between the depyridination temperatures for both intercalates is rediscussed with the aid of the ΔG^0 data obtained.

INTRODUCTION

Layered zirconium phosphate (ZrP) is known to behave as an intercalating agent of polar organic substances [1] and as a solid acid catalyst, e.g. for the dehydration of alcohols [2]. ZrP can be obtained in two basic forms: α-ZrP, $Zr(HPO_4)_2 \cdot H_2O$, with an interlayer spacing of 7.6 Å, and γ-ZrP, $Zr(HPO_4)_2 \cdot 2\ H_2O$, with an interlayer spacing of 12.3 Å [3]. Recently, the authors investigated the formation and thermal decomposition behavior of the pyridine intercalates of α- and γ-ZrP [4]. While both host phases intercalate with nearly the same amount of pyridine per formula weight, they show a different tendency for the change in hydration number and interlayer spacing accompanying intercalation. Furthermore, it was found that the depyridination temperature for the γ-intercalate is more than 100°C higher than that for the α-intercalate. In the previous report, the latter observation was explained tentatively in terms of the difference in the structural characteristics of interlayer space for both host matrices. However, another possibility to be suggested may be that the acid strength of γ-ZrP is much higher than that of α-ZrP. Although the second explanation is less likely, no decisive data are available for excluding such an interpretation.

In the present study, the heats of intercalation of pyridine into α- and γ-ZrP as well as the acid strength of both host phases were determined in an attempt to clarify the intercalation behavior in further detail and investigate

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the thermostabilities of the intercalated phases. Information on the acidic properties of α- and γ-ZrP may also contribute to the application of these materials as catalysts or supports in chromatography.

EXPERIMENTAL

Reagents

The α- and γ-ZrP samples used were the same as described previously [4]. Pyridine of reagent grade was dried and distilled prior to use. THAM of reagent grade was further purified by the method of Irving et al. [5], and the 50–100 mesh fraction was used after drying overnight under vacuum. Distilled and deionized water was used throughout.

Calorimetric measurements

A commercial twin type microcalorimeter (Tokyo-riko Model MPC-11) was used. The calorimeter consisted of two 40 cm^3 stainless steel vessels coated with teflon. Each vessel was filled with 19 cm^3 of aqueous pyridine solution with a prescribed concentration. 0.1 g of ZrP was weighed accurately into a thin-walled glass ampoule and 1 cm^3 of water was added to prevent heat of wetting effects. An ampoule containing 1 cm^3 of water was used for reference. After thermal equilibration with stirring at 25.0°C, the two ampoules, immersed in the corresponding vessels, were broken at the same time and the heat evolved on mixing was recorded with an integrator. The internal electrical calibration of the calorimeter was made against the heat of solution of THAM [5]. After the completion of each run, the reaction mixture was centrifuged at the same temperature and the resulting solid was dried in air of $P/P_0 = 0.60 \pm 0.05$ in humidity for one week or more.

Analytical procedure

The pyridine and phosphate concentrations and pH of the supernatants and the TG traces and X-ray diffraction patterns of the solids were determined using the same procedures and instruments as described previously [4]. The contents of pyridine and water in the solids were obtained from the TG and/or solution analysis data.

Measurement of acid strength

The acid strength of the ZrP samples in water was qualitatively measured in the same manner as employed by Namba et al. [6]: 20 mg of the ZrP was put in a flask containing 10 cm^3 of water, 2 drops of 5% ethanol solution of

Hammet indicator ($H_0 = +4.8$, $+3.3$, $+1.5$, -3.0, or -5.6) was added to the suspension, and the mixture was allowed to stand for 24 h at room temperature. The acid strength was determined visually from the color of the indicator. The resulting mixtures were centrifuged and X-ray patterns were taken on the remaining solids dried in air.

RESULTS AND DISCUSSION

The results of pH measurements and X-ray and composition analyses for the intercalated solids of both ZrP agreed well with the previous report [4]. The intercalation processes of pyridine (Py) into α- and γ-ZrP are written as

α-ZrP

$$\mathrm{Zr(HPO_4)_2 \cdot H_2O(7.6\ \AA)} \xrightarrow{\mathrm{Py\ in\ H_2O}} \mathrm{Zr(HPO_4)_{1.55}(PyHPO_4)_{0.45} \cdot 2\ H_2O(10.9\ \AA)} \tag{1}$$

γ-ZrP

$$\mathrm{Zr(HPO_4)_2 \cdot 2\ H_2O(12.3\ \AA)} \xrightarrow{\mathrm{Py\ in\ H_2O}} \mathrm{Zr(HPO_4)_{1.56} \cdot (PyHPO_4)_{0.44} \cdot 0.7\ H_2O(12.3\ \AA)} \tag{2}$$

In eqns. (1) and (2), the interlayer spacing is given in parentheses.

Figure 1 shows the total heat, $-\Delta H_x^0$, evolved on the intercalation of pyridine as a function of the uptake, x, in mole per formula weight of ZrP.

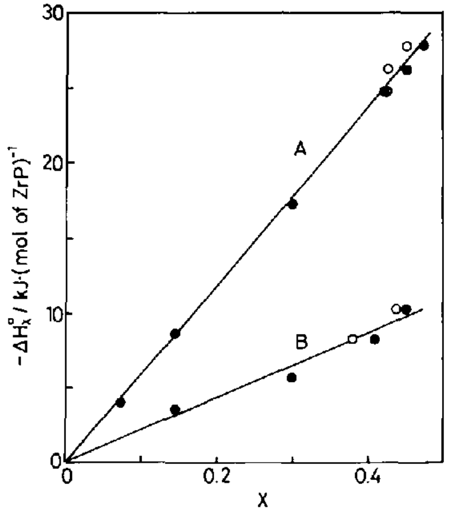

Fig. 1. Heat evolved, $-\Delta H_x^0$, as a function of pyridine uptake, x, for (A) α-ZrP, and (B) γ-ZrP. The x values were determined from the TG (○) or solution analysis (●) data.

TABLE 1

Standard integral functions of pyridine intercalation [a]

Host phase	ΔH^0 (kJ mole^{-1})	ΔS_h^0 (J K^{-1} mole^{-1})	ΔS_g^0 (J K^{-1} mole^{-1})	ΔS^0 (J K^{-1} mole^{-1})	ΔG^0 (kJ mole^{-1})
α-ZrP	-59.3 ± 0.4	−55.9	17.2	−38.7	−47.8 [b]
γ-ZrP	-21.9 ± 0.5	76.2	17.2	93.4	−49.7 [b]

[a] All values are expressed in kJ mole^{-1} of pyridine.
[b] Calculated from the relation $\Delta G^0 = \Delta H^0 - T\,\Delta S^0$.

In both cases, the intercalation is exothermic and the $-\Delta H_x$ vs. x curve gives a straight line. The differential heat of intercalation, $-\Delta \overline{H}_x$, expressed in kJ per mole of pyridine was evaluated from the above data by the least square method. The values of $-\Delta \overline{H}_x$ thus obtained are identical with those for the integral heat of intercalation, $-\Delta H^0$, and the results are listed in Table 1. The ΔH^0 value for α-ZrP will include a positive contribution due to the expansion of the layers, whereas that for γ-ZrP has no such contribution.

The phosphate release accompanying the pyridine uptake was less than 0.095 mmole g^{-1} for α-ZrP and less than 0.025 mmole g^{-1} for γ-ZrP. No data are available for the heat of hydrolysis of α- and γ-ZrP, but heat effects due to the hydrolysis would be negligible because the mole ratio of phosphate released to pyridine taken up is less than 3%.

The acid strength of α-ZrP determined by the conventional method agreed qualitatively with that of γ-ZrP, as shown in Table 2. The X-ray patterns of ZrP samples equilibrated with the Hammet indicator solution showed no trace of intercalated phases, except for very small peaks of α-ZrP complexes with Methyl Red ($H_0 = +4.8$) and Butter Yellow ($H_0 = +3.3$) whose interlayer spacings are 16.7 and 16.8 Å, respectively. This means that the acid

TABLE 2

Acid strength of α- and γ-ZrP in water [a]

	H_0				
	+4.8	+3.3	+1.5	−3.0	−5.6
α-ZrP	+	+	−	−	−
γ-zrP	+	+	−	−	−

[a] +, Acidic color; −, basic color.

strength determined in the present study is concerned substantially with the POH sites on the surface of the ZrP crystals. An earlier study on the acidity of α-ZrP suggested that there is no appreciable difference between the acidities of the interlayer and surface POH sites [7]. On the basis of this suggestion and the above data, it seems reasonable to assume that the interlayer POH sites in α- and γ-ZrP have similar acid strengths. This contrasts strikingly with the finding that the heat of intercalation of pyridine for α-ZrP is 2.7 times larger than that for γ-ZrP. For the interpretation of these observations, it will be instructive to compare the Gibbs free energies, ΔG^0, for both intercalation reactions.

As in cation exchange reactions [8,9], the entropy change for the pyridine intercalation reaction from aqueous solution on a host phase may be expressed as

$$\Delta S^0 = \Delta S_h^0 + \Delta S_g^0 \tag{3}$$

and

$$\Delta S_g^0 = S_{g(i)}^0 - S_{g(h)}^0 \tag{4}$$

Here ΔS_h^0 represents the entropy difference between the final and initial forms of the host phase and ΔS_g^0 or $(S_{g(i)}^0 - S_{g(h)}^0)$ the difference in the entropies of the guest molecule, i.e. pyridine, in the intercalated and hydrated state.

Values of ΔS_h^0 reflect (i) changes in hydration accompanying the intercalation reaction and (ii) the differences in the lattice distortion of the two forms of the host phase. During the uptake of one mole of pyridine through reactions (1) and (2), α-ZrP takes up 2.2 moles of water and γ-Zrp releases 3.0 moles of water. As discussed by Clearfield and Kullberg on the $Na^+ - H^+$ exchange reaction in α-ZrP [9], uptake of water must result in a decrease in entropy while release of water results in an entropy increase. The entropy change accompanying the uptake or release of water can be regarded as being approximately equal to that due to the binding of water on freezing or release of water on fusion. No data are available for evaluating the entropy change due to the expansion of the layers from 7.6 to 10.9 Å during the intercalation process for α-ZrP. Such a lattice expansion, however, will probably make a much smaller contribution to ΔS_h^0 than that due to the solid–liquid transformation of water. Thus, the approximate values of ΔS_h^0 on pyridine intercalation can be evaluated from 25.4 J K^{-1} $mole^{-1}$ for the entropy of fusion of ice at 25°C [9].

It is likely that, as a first approximation, the entropy of pyridine in the intercalated state falls to the same level as in the solid state. Then, the value of the difference $(S_{g(h)}^0 - S_{g(i)}^0)$ is equal to the sum of the entropy of fusion, ΔS_f^0, and entropy of solution, ΔS_s^0. Values of the entropy of pyridine in the solid and liquid state are available in the literature [10]. The extrapolation of the solid-entropy data to 25°C yields 39.3 J K^{-1} $mole^{-1}$ for the entropy of fusion at 25°C. The value of ΔS_s^0 at 25°C for pyridine is -56.5 J K^{-1} mole^{-1} [11]. The negative value for the sum $(\Delta S_f^0 + \Delta S_s^0)$ means that the entropy level of pyridine in the solid state is higher than that in the hydrated state at the same temperature. This is not surprising because the pyridine molecules are highly hydrated in aqueous solution through the formation of hydrogen bonding to water molecules, resulting in an increase in the rigidity of the system [11].

The thermodynamic quantities thus obtained are summarized in Table 1. It is apparent that the large difference between the ΔH^0 values for both ZrP species is ascribed to their opposite change in hydration number accompanying the intercalation. The close agreement of the ΔG^0 values is consistent with the fact that the α- and γ-intercalates have nearly the same amount of pyridine and also suggests that there is little difference between the thermodynamical stabilities of both intercalates at 25°C. Thus, it is reasonable to conclude that the marked difference between the depyridination temperatures for both intercalates would be caused by the desorption of water during the heating process. This supports the previous explanation [4] that the α-intercalate is stabilized by the introduction of interlayer water into the vacant space between the guest molecules, while the high stability of the γ-intercalate is because the pyridine molecules fit the interlayer space and are strongly held without any reinforcement by water molecules.

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