SIMULTANEOUS THERMAL/MASS SPECTRAL INVESTIGATIONS OF AMMONIUM EXCHANGED ZIRCONIUM PHOSPHATES AND ZIRCONIUM ARSENATES*

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ABSTRACT

The half- and fully-ammonium ion exchanged forms of α- and γ-zirconium phosphates and of α-zirconium arsenate have been prepared. Their modes of thermal decomposition were studied by thermal methods of analysis, including simultaneous DTA/mass spectrometry. The samples heated to various temperatures were also characterized by X-ray diffraction analysis together with IR spectroscopy. The loss of water and ammonia of the various exchanged samples is compared in terms of the changes taking place in the layer lattice upon heating. The use of DTA/MS for a system involving water and ammonia as volatiles is demonstrated.

INTRODUCTION

Crystalline zirconium bis(monohydrogen *ortho*-phosphate) monohydrate, α-ZrP, and zirconium bis(monohydrogen *ortho*-arsenate) monohydrate, α-ZrAs, are isostructural and possess a layer lattice structure[1]. Zirconium bis(monohydrogen *ortho*-phosphate) dihydrate, γ-ZrP contains an additional water molecule and showed different ion exchange properties[2]. This may be due to the *ortho*-phosphate groups in adjacent layers being opposed and not staggered as in the case of α-ZrP. The stability towards oxidizing conditions, at elevated temperatures, and in the presence of high doses of radiations makes these materials more attractive compared with organic ion exchange materials.

The pH titration curves, where the pH was shown as a function of the amount of base per g of α-ZrP, illustrated that the uptake of sodium and potassium ions occurred in two adjacent steps, as if the two hydrogen phosphate groups in α-ZrP

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have different acidities[1]. In contrast, only one step was found for ammonium ion[3], and it was concluded that the single step was due to the association of ammonia (base) with the hydrogen ions of the α-ZrP through a process involving hydrogen bonding. Preliminary results on the thermal decomposition of fully-ammonium exchanged α-ZrP[4, 5] and half-ammonium exchanged γ-ZrP[6] have been reported, but the exact nature of thermal decomposition is uncertain. This is because the crucial weight loss involves both ammonia and water at the first stage of decomposition. It was therefore decided to investigate the thermal decomposition of various ammonium exchanged forms of α-ZrP, α-ZrAs and γ-ZrP by DTA/MS. In addition to DTA information on the physical nature of the reaction, the mass spectrometer registers simultaneous changes in the m/e ratio of the volatiles. The suitability of this technique has also been demonstrated for investigating a system containing water and ammonia in the present studies.

EXPERIMENTAL

Reagent

All the reagents were of reagent grade. Concentrated ammonia solution was Analar quality.

Instrumentation

DSC and TG analyses were obtained using a Dupont 900 thermal analyser together with a 950 TG cell. The conditions of measurements were those reported earlier[6]. X-ray diffraction patterns were obtained by a Philips X-ray unit, using nickel-filtered Cu K_α radiations. The samples were prepared at various temperatures in the DSC cell. IR spectra were obtained of the heated samples by the KBr disc method. DTA/MS analysis was carried out using a Micromass Quadrupole Q801 mass spectrometer linked to a Stanton 501B DTA unit by a heated capillary. Details of the method and conditions of measurements have been described previously[7]. A computer plotter was used to record peak height against temperature for m/e 16, 17 and 18.

Chemical analysis

This has been described previously[1].

Preparation of ammonium ion exchanged forms

The half- and fully-ammonium ion exchanged forms of α-ZrP and α-ZrAs were obtained as described previously[3, 8]. Monoammonium form of γ-ZrP was also prepared as reported earlier[6]. Diammonium exchanged γ-ZrP was prepared by suspending 300 mg of γ-ZrP in 100 ml 0.1 M ammonium chloride and titrating against 0.1 M ammonia solution, under a flow of nitrogen, to the theoretical exchange value. The pH was not allowed to rise above 7.5 to prevent hydrolysis of the ion exchange

material. The material was filtered, washed with boiled deionized cold water until free of chloride ions, and allowed to air dry.

RESULTS AND DISCUSSION

It is now known that α-ZrP and α-ZrAs do not undergo ion exchange with ammonium ion but remove ammonia from the system[3, 8]. Thus in the course of forward ion exchange titration a solid solution of α-ZrP (or α-ZrAs) and $Zr(NH_4PO_4)_2H_2O$ (or $Zr(NH_4AsO_4)_2H_2O$) or a pure phase $Zr(NH_4PO_4)_2H_2O$ were obtained. However, a pure half-ammonium exchanged sample, $Zr(NH_4PO_4)$-$(HPO_4)0.3H_2O$ (or $Zr(NH_4AsO_4)$ $(HAsO_4)_2H_2O$) made its appearance if 50%
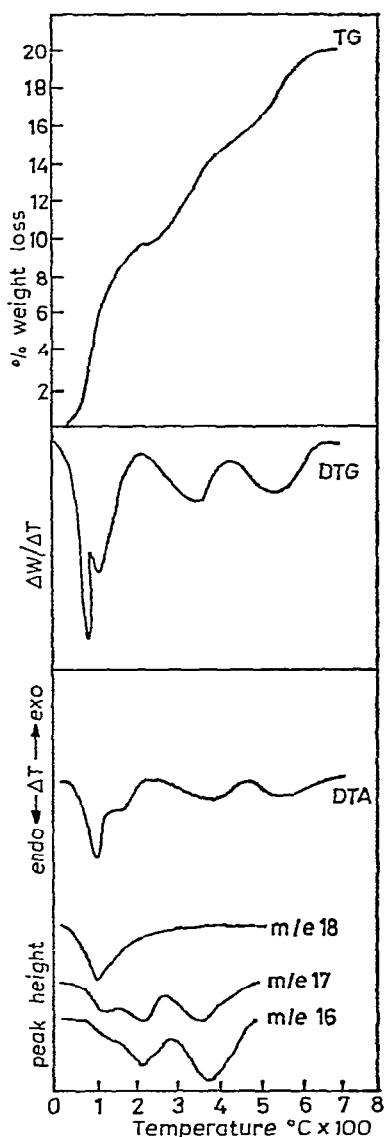

Fig. 1. Thermal and mass spectral analyses of α-$Zr(NH_4PO_4)_2H_2O$.

hydrogen ion loading on to the fully ammonium exchanged form was carried out. In contrast, γ-ZrP produced half- and fully-ammonium exchanged samples in the initial exchange process at 50 and 100% loadings of ammonium ions. This is also supported by the fact that the shape of the DSC curves of the half- and fully-ammonium exchange α- and γ-ZrPs was similar (compare Figs. 1 and 2 of ref. 9, and Figs. 1 and 6 of the present studies). The compositions of the various products were in agreement with the analytical data.

Figure 1 shows thermal and mass spectral data of fully-ammonium ion exchanged sample of α-ZrP. Thermogravimetric and DSC curves were identical to those reported by Horseley[4]. The decomposition of this phase took place in three stages. The crucial weight loss in the first stage corresponded to the removal of 1 mole each of water and ammonia molecules commencing at 65°C. The second stage produced a weight loss equivalent to 1 mole of ammonia. This is followed by the loss of 1 mole of water beginning at 475°C due to the condensation of ortho-phosphate to pyrophate. This sequence is shown clearly in the DTG curve. The DTA curves also support TG analysis and result in three endothermic peaks, the first consisting of two overlapping peaks. Mass peaks 18 and 16 were followed as the discriminating peaks for water and ammonia, respectively, since m/e 17 was common to both volatile species. The DTA/MS shows (Fig. 1) an initial decomposition in which water and ammonia are given off simultaneously. These results also depict that partial dehydration proceeds the removal of ammonia. It is, therefore, impossible to obtain the pure anhydrous phase of fully-ammonium exchanged α-ZrP. A mass spectrum above
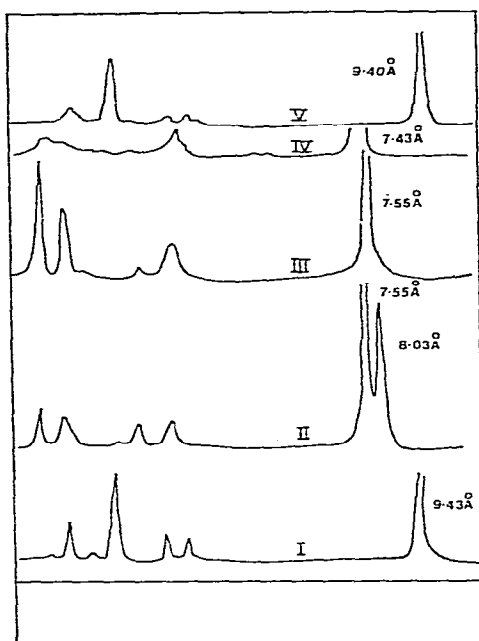

Fig. 2. X-Ray diffraction spectra of α-Zr(NH$_4$PO$_4$)$_2$H$_2$O heated at various temperatures. I, α-Zr(NH$_4$PO$_4$)$_2$H$_2$O; II, α-Zr(NH$_4$PO$_4$)$_2$H$_2$O heated at 250°C under nitrogen; III, α-Zr(NH$_4$PO$_4$)(HPO$_4$); IV, α-Zr(NH$_4$PO$_4$)$_2$H$_2$O heated at 450°C under nitrogen; V, compound IV exposed in the vapours of ammonia.

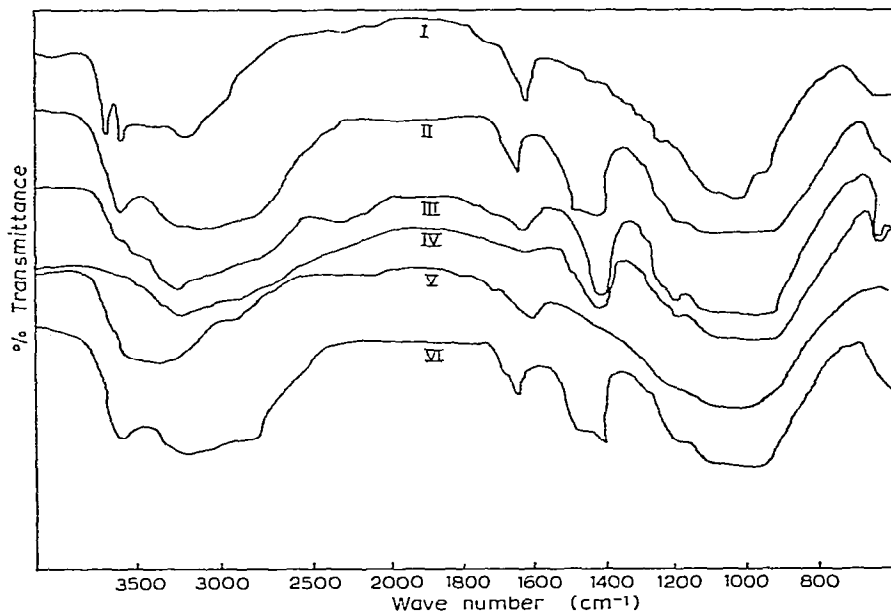Fig. 3. IR spectra of α-Zr(NH₄PO₄)₂H₂O heated at various temperatures. I, α-Zr(HPO₄)₂H₂O at room temperature; II, α-Zr(NH₄PO₄)₂H₂O at room temperature; III, α-Zr(NH₄PO₄)(HPO₄) 0.3 H₂O at room temperature; IV, α-Zr(NH₄PO₄)₂H₂O heated at 250 °C under nitrogen; V, α-Zr(NH₄PO₄)₂H₂O heated at 450 °C under nitrogen; VI, V, equilibrated with ammonia vapours.

500 °C could not be obtained owing to the limitation of operating the DTA cell beyond 500 °C. It has been noticed in the exchange process between α-ZrP and ammonia, that both the protons of α-ZrP possessed the same pK value towards ammonia. Thus both ammonium ions of α-Zr(NH₄PO₄)₂H₂O should take part in the first stage of decomposition. This would result in a mixture of 50% each of Zr(HPO₄)₂ and Zr(NH₄PO₄)₂ after the first decomposition stage. Horseley[4] postulated that the product at this point was a half-ammonium exchanged zirconium phosphate (anhydrous). In an attempt to clarify the situation, X-ray diffractograms and IR spectra of the heated samples were obtained (cf. Figs. 2 and 3). Figure 2(II) is similar to the α-Zr(NH₄PO₄)(HPO₄)0.3H₂O reported earlier[3]. This shows that the resulting product at 250 °C was neither the anhydrous phase of half-ammonium exchanged zirconium phosphate nor the solid solution of the two phases. This is supported by α-Zr(NH₄PO₄)(HPO₄) not producing a line of interlayer distance 8.03 Å (see Fig. 2(III)). The phase at 250 °C is therefore α-Zr(NH₄PO₄)(HPO₄)0.3H₂O and is again reflected in the IR spectra (Fig. 3(III and IV)). The mass spectral results together with thermal analysis seem to indicate that only ammonia removal took place at the second stage of decomposition. Thus the two losses of ammonia at different temperatures could be seen to be due to the presence of two different sites of ammonium ions. This can be seen from Fig. 4 of the α-Zr(NH₄PO₄)₂H₂O cavity formed by the two adjacent layers which locates the position of ammonium ions at two different sites[10]. The interesting observation in the present studies was the fact that if the product, after heating α-Zr(NH₄PO₄)₂H₂O to 450 °C, was equilibrated with (i) aqueous ammonia,
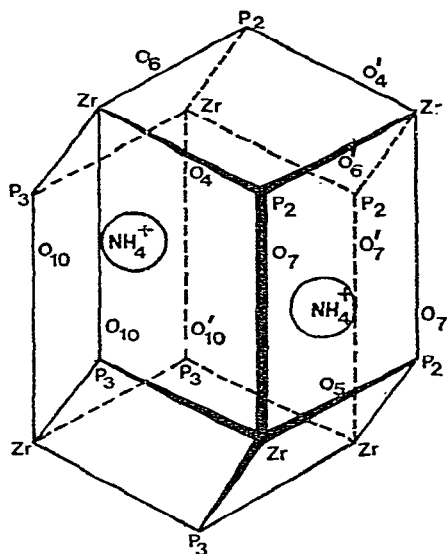
362

Fig. 4. Idealized picture of a cavity formed by two adjacent layers showing the approximate locations of ammonium ions. Reprinted with permission from Journal of Physical Chemistry, copyright by the American Chemical Society.

(ii) anhydrous liquid ammonia, or (iii) exposed in the atmosphere of gaseous ammonia, it converted to α-Zr(NH$_4$PO$_4$)$_2$H$_2$O. This has been confirmed by X-ray differaction and IR analyses (Figs. 2 and 3). The decrease in the first interlayer distance upon heating may be due to the fact that the lattice collapse upon loss of ammonia and water. However, it increased if the ζ-ZrP was equilibrated with ammonia. The thermal decomposition scheme of the α-Zr(NH$_4$PO$_4$)$_2$H$_2$O can be represented as is shown in (1).
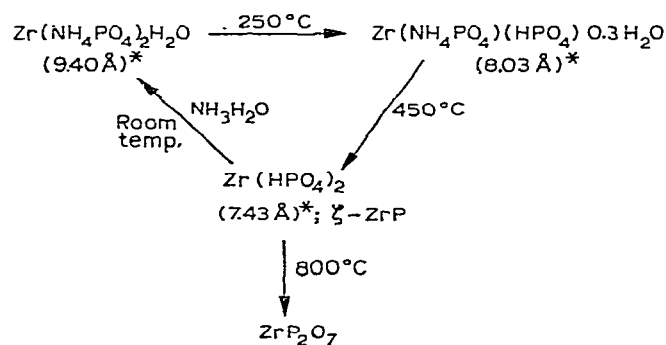
The thermal decomposition of fully-ammonium exchanged zirconium arsenate (Zr(NH$_4$AsO$_4$)$_2$H$_2$O) and γ-zirconium phosphate (Zr(NH$_4$PO$_4$)$_2$H$_2$O) followed the same route and were essentially parallel in nature to α-Zr(NH$_4$PO$_4$)$_2$H$_2$O (cf. Fig. 5 and ref. 9, Fig. 2). The condensation of γ-P-OH groups to pyrosphosphate started at the same temperature as in the case of α-ZrAs. The essential difference of the thermal decomposition reactions between α-Zr(NH$_4$PO$_4$)$_2$H$_2$O and α-Zr(NH$_4$-

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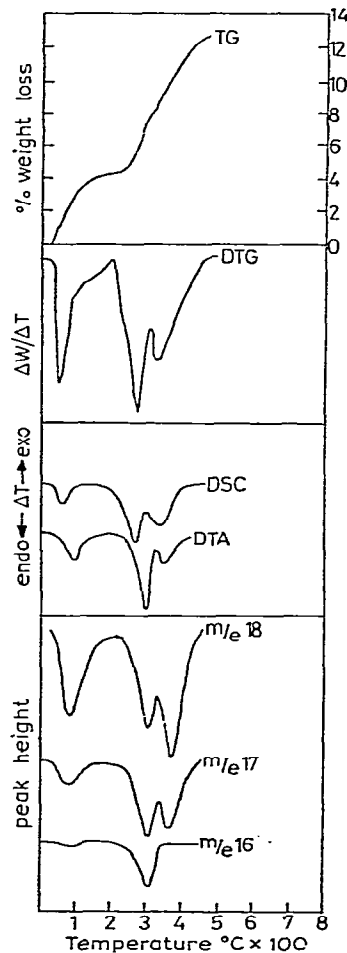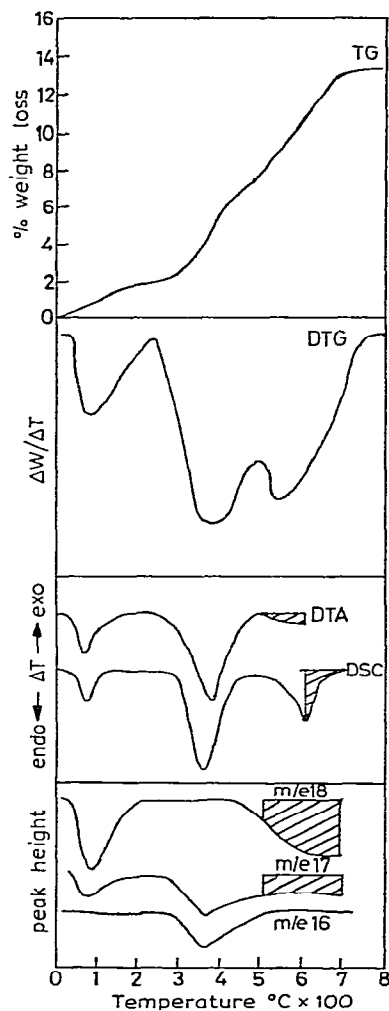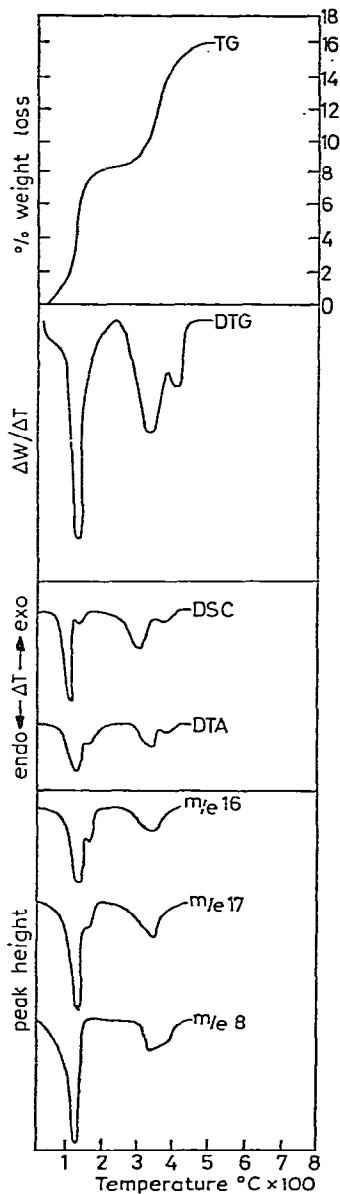* Numerals in parentheses represent the first interlayer distance of the materials.

Fig. 5. Thermal and mass spectral analyses of α-Zr(NH₄AsO₄)₂H₂O.

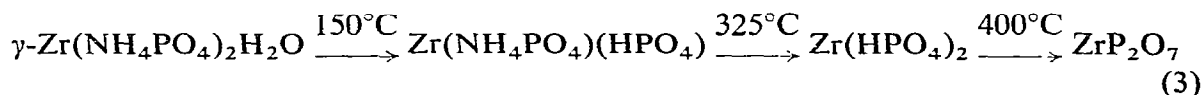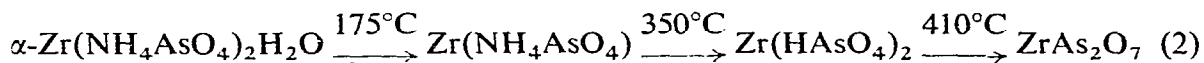Fig. 6. Thermal and mass spectral analyses of α-Zr(NH₄PO₄)(HPO₄) 0.3 H₂O.

Fig. 7. Thermal and mass spectral analyses of α-Zr(NH₄AsO₄) (HAsO₄)H₂O.

$AsO_4)_2H_2O$ (or γ-$Zr(NH_4PO_4)_2H_2O$) is the fact that the removal of the second mole of ammonia took place at a higher temperature and is distinctive in the former case. In the latter cases the removal of ammonia is followed immediately by the condensation. The difference in their decomposition temperatures may be due to the difference in the basicity of phosphate and arsenate groups. The decomposition temperature of ammonium salts is inversely proportional to the basicity of the anion bases in the salts[11]. Moreover, α-ZrP is much more thermally stable than γ-ZrP[4].

Figures 6 and 7 show thermal mass spectral results of the half-ammonium

exchanged samples of α-ZrP, α-ZrAs, respectively. Figure 1 of ref. 9 is comparable with half-ammonium exchanged zirconium arsenate (Fig. 7). The anhydrous samples gave results which were virtually the same as those samples obtained after the first step of decomposition of $Zr(NH_4MO_4)_2H_2O$; where M = P or As.

The various steps of thermal decomposition of ammonium exchanged α-ZrAs and γ-ZrP can be represented as in eqns. (2 and 3).

$$\alpha\text{-}Zr(NH_4AsO_4)_2H_2O \xrightarrow{175°C} Zr(NH_4AsO_4) \xrightarrow{350°C} Zr(HAsO_4)_2 \xrightarrow{410°C} ZrAs_2O_7 \quad (2)$$

$$\gamma\text{-}Zr(NH_4PO_4)_2H_2O \xrightarrow{150°C} Zr(NH_4PO_4)(HPO_4) \xrightarrow{325°C} Zr(HPO_4)_2 \xrightarrow{400°C} ZrP_2O_7 \quad (3)$$

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We thank the American Chemical Society for permission to reproduce Fig. 4.

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