Thermochimica Acta, 14 (1976) 131–139

A STUDY OF THE THERMAL DECOMPOSITION OF SOME ALKALI METAL DIHYDROGEN PHOSPHATES AND ARSENATES*

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ABSTRACT

The thermal decomposition of a variety of dihydrogen phosphates and arsenates was studied by thermal gravimetry and evolved gas analysis. The dehydration of the phosphates was more complex than that of the arsenates except for the ammonium salts. Arsenic was reduced during the decomposition of $NH_4H_2AsO_4$ with the compensating oxidation of NH_4^+. Trends in the decompositions as a function of alkali metal and deuterium substitution are discussed.

INTRODUCTION

A variety of alkali metal and ammonium dihydrogen phosphates and arsenates are of interest for their electro-optical properties. Some proposed applications in the field of energy research require that the material be stable in very high energy fluxes from the laser beams. It is the purpose of this paper to determine the onset and nature of the thermal decomposition of a number of these crystals.

It is also of interest to investigate the changes in the thermal decomposition as the monovalent ion is varied in such a closely related series of compounds. Similarly, the effects of the substitution of deuterium for hydrogen can be studied for several of the crystals.

Loiacano[1] has utilized differential thermal analysis (DTA) to determine the ferroelectric curie temperatures of these materials but had not continued to temperatures where the materials decomposed. There have been two recent studies on the thermal decomposition of RbH_2PO_4 by Blinc et al.[2], and Erdy et al.[3], but these were not extended to the other materials and hence no comparison regarding the selection of cation, the degree of deuteration, or between phosphates and arsenates could be made.

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*Presented at the 5th North American Thermal Analysis Society Meeting, Peterborough, Ontario, Canada, June 8–14, 1975.

EXPERIMENTAL PROCEDURES

The samples were chips from large single crystals provided by Mr. G. Loiacano of the Isomet Co.

A Perkin-Elmer TGS-1 thermobalance which had been modified to provide a digital output was employed[4]. Samples, 7–21 mg, were heated at 5°C min^{-1} in air to 500°C. Percent weight loss and rate of weight loss were calculated and plotted by a Honeywell 6000 series computer.

An AEI Model MS-10 was used for the evolved gas analysis (EGA) experiments. Samples, 30–100 mg, were heated at 2°C min^{-1} in a fused silica tube. This volume, about 30 cm^3, was connected directly to a turbomolecular pumping system through the mass spectrograph without any variable leaks, capillaries, etc. In the absence of any sample the background pressure was about 2×10^{-8} Torr. At the maximum rate of decomposition, the pressure became as high as 8×10^{-5} ton. The mass range from 12–45 was repeatedly scanned automatically (11.6 min cycle^{-1}). The output signal of the mass spectrometer was conditioned by a Spectrum, Model 1020 active electronic filter and the peaks were then detected and integrated by an Infotronics Model CRS-204 integrator. The peak area and time of the peak were printed and punched on paper tape by a teletypewriter. The timer of the integrator was automatically reset at the beginning of each cycle of the mass spectrometer. The paper tape served as input to the computer which calculated and plotted relative intensity versus temperature for specified mass numbers. Temperature was measured by a Pt–Pt 10% Rh thermocouple touching the sample.

X-ray diffraction data of selected samples were obtained using a GE, Model XRD-3, diffractometer.

RESULTS AND DISCUSSION

Figures 1–4 show typical thermogravimetric (TG) and differential thermogravimetric (DTG) results. The KD*P, where * denotes the substitution of deuterium (Fig. 1), and CD*A (Fig. 2) are selected because they are the crystals of greatest practical interest as well as being typical of the behavior of phosphates and arsenates, respectively. The behavior of the ammonium salts was atypical and hence they are also presented (Figs. 3 and 4). A general summary of the TG and DTG data is given in Table 1.

The phosphates, with the exception of the ammonium salts, exhibit the stepwise loss of weight seen in Fig. 1. The DTG curves all exhibit four peaks but of varying relative heights and areas and at different temperatures. This stepwise weight loss is indicative of the formation of various polymeric intermediates, e.g., $P_2O_7^{4-}$ during the course of dehydration to finally form KPO_3. The X-ray diffraction pattern of the residue from the TG experiment is indicative of KPO_3. A multiplicity of peaks in the DTG curves has also been observed by Erdy et al.[2] and Blinc et al.[3] for RDP.

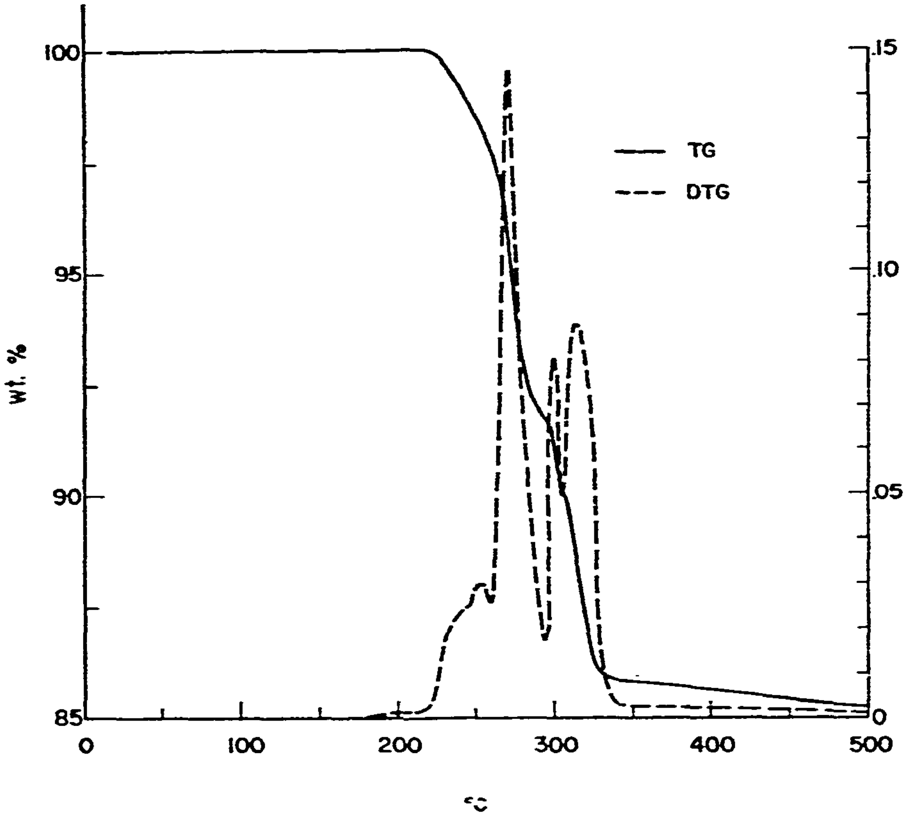

Fig. 1. TG and DTG curves for the thermal decomposition of KD*P, 7.577 mg, 5°C min^{-1}, in air.

TABLE 1

SUMMARY OF TG AND DTG RESULTS

Sample[a]	*Wt.* (*mg*)	*Temperature (°C)*		*% Wt. loss*	
		0.1 wt. % loss	*Max. mg min*$^{-1}$	*At 500°C*	*Theoretical*
KDP	13.124	219	279	13.3	13.2
KD*P (85%)	11.224	233	310	14.3	14.3
KD*P (97%)	7.577	226	274	14.7	14.5
RDP	8.456	216	324	10.0	9.9
ADP	11.338	164	227	32.4	38.3
AD*P (95%)	6.759	179	235	35.8	41.1
KDA	15.063	220	272	9.8	10.0
RDA	15.897	199	245	8.2	8.0
CDA	15.950	149	308	6.9	6.6
CD*A (86%)	21.221	196	296	7.4	7.2
ADA	11.829	180	232	38.4	37.8

[a] K = K$^+$, R = Rb$^+$, C = Cs$^+$, D = ^{1}H$^+$, D* = ^{2}H$^+$, P = PO_4^{3-}, A = NH_4^+ or AsO_4^{3-}, and the quantity in parenthesis is the estimated % of deuteration accompanying the crystal.

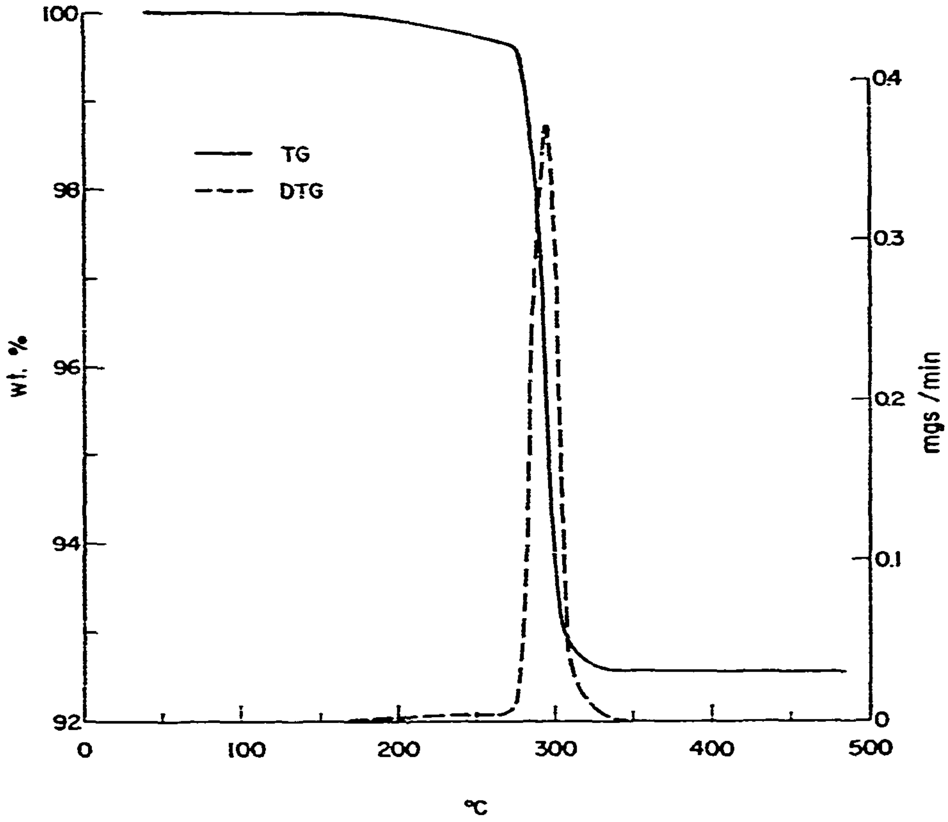

Fig. 2. TG and DTG curves for the thermal decomposition of CD*A, 21.221 mg, 5°C min^{-1}, in air.

Selected EGA data for KD*P (85%) are given in Fig. 5. The resolution is not great enough to show the multiple peaks observed in the DTG curve. There is a large broad peak corresponding to the loss of H_2O, HDO and D_2O. Relative intensity is normalized by setting the maximum number of counts from the integrator during each experiment equal to 100. In Fig. 5 the mass 17 peak (OH^+) is plotted as indicative of the undeuterated evolution and mass 20 peak (D_2O^+) for the deuterated evolution. Masses 18 and 19 would be subject to uncertainties regarding their origin due to mixed isotopes of hydrogen.

There appears to be a slight tendency in Fig. 5 for the natural water to evolve before the heavy water. This is consistent with the generally lower temperatures associated with the onset of weight loss as given in Table 1. The weight loss for the partially deuterated sample of KD*P checks well with the estimate of 85% substitution from the manufacturer. The temperatures corresponding to the decomposition are lower in the EGA experiments than for the TG work because the former are performed in vacuum while the latter are in air.

The onset of weight loss is taken as the beginning of decomposition. Using the departure of the DTG curve from the baseline was considered too subjective and

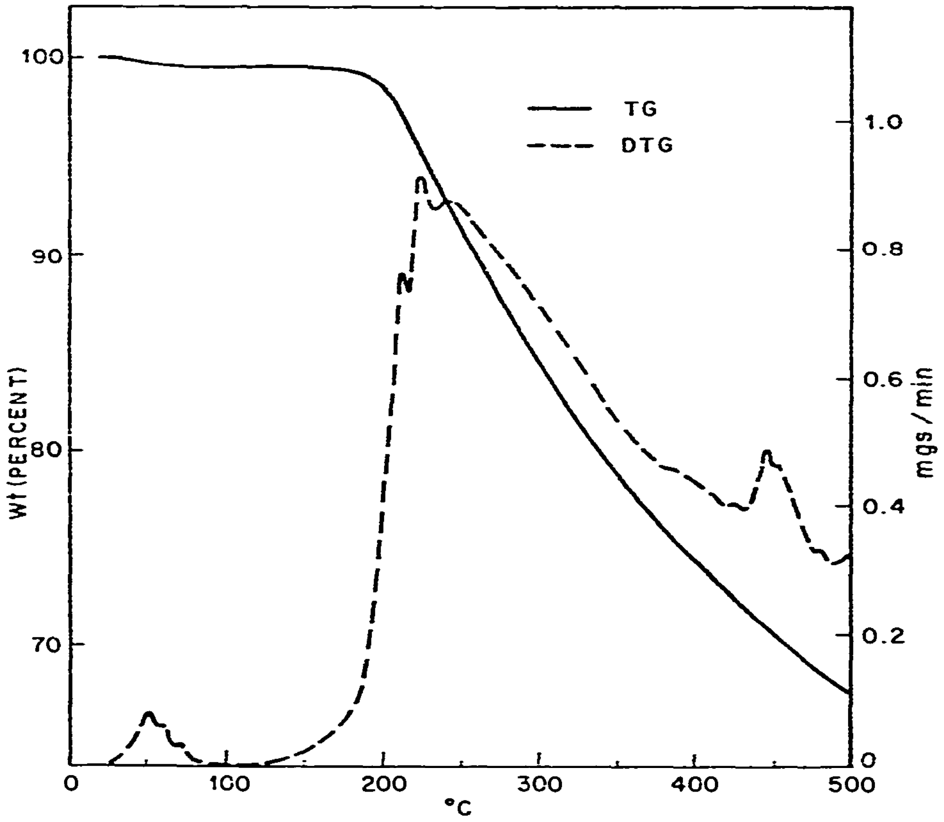

Fig. 3. TG and DTG curves for the thermal decomposition of ADP, 11.338 mg, 5°C min^{-1}, in air.

therefore the temperature at which 0.1% weight loss occurred was tabulated in Table 1 as indicative of at least the relative order of stabilities and the upper limit for the thermal stability of the particular crystal. Other factors, however, such as loss of transparency, probably create problems before this temperature is reached. There do not appear to be consistent trends in stability amongst the various cations. In addition, the relative order depends upon whether the temperature of the onset or of the rate of maximum weight loss is used.

Figure 2 indicates that the decomposition of the arsenates is much simpler. The DTG curve exhibits a single relatively symmetric peak. The temperature region associated with the decomposition is also much narrower. In this case the weight loss is less sensitive to the degree of deuteration because of the much greater mass of Cs compound to K.

As mentioned earlier the ammonium salts are atypical. There is, of course, a much greater weight loss as shown in Fig. 3 and Table 1 due to the evolution of NH_3 as well as H_2O. This loss takes place over a wide range of temperature but commences earlier. The loss below 100°C in Fig. 3 is attributed to surface moisture and is not considered in determining the values in Table 1. The EGA results in Fig. 6 indicate

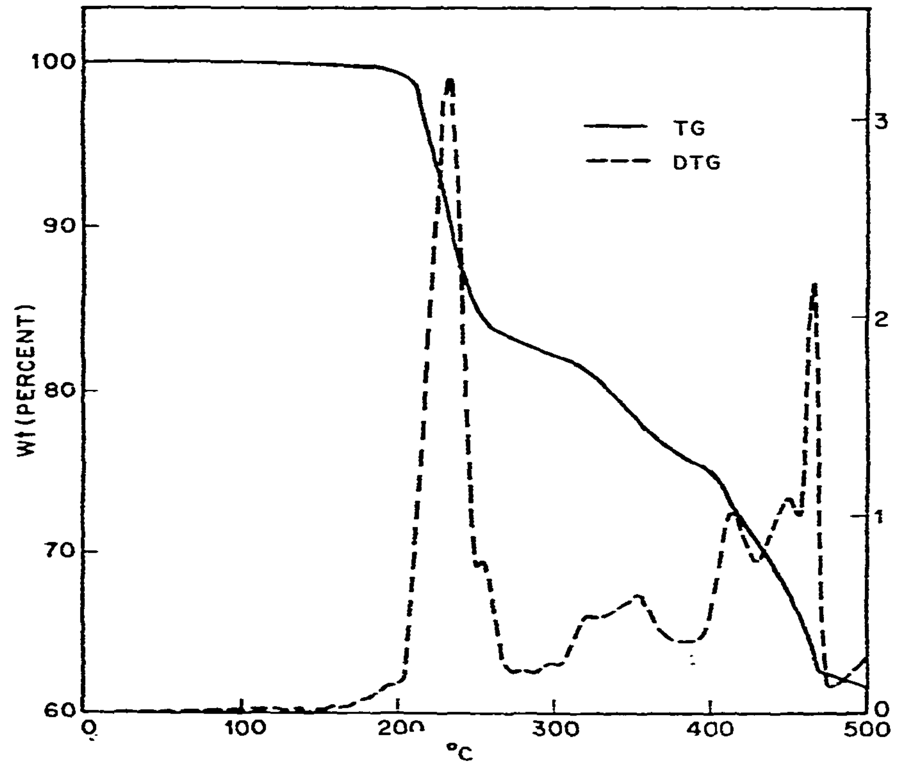

Fig. 4. TG and DTG curves for the thermal decomposition of ADA, 11.829 mg, 5°C min^{-1}, in air.

that NH_3 is evolved first. The mass 16 peak rather than 17 is used to avoid the contribution due to OH. About half of the NH_3 is evolved in a relatively rapid burst while the second half is evolved slowly over a broad range of temperature. The H_2O on the other hand tends to evolve in a single broad peak skewed towards high temperatures. The sum of these two effects produces the generally smooth DTG peak in Fig. 3. Again the temperatures are lower for the EGA results in vacuum.

The decomposition of ADA proves to be the most interesting. Contrary to the other arsenates studied, As^{5+} is reduced to As^{3+}. The theoretical weight loss in Table 1 is for a final product of As_2O_3. This value of 37.8% corresponds well with the final minimum in the DTG curve (Fig. 4) at about 475°C. Such a reduction poses several questions. Why does this reduction not occur during the decomposition of the alkali metal arsenates and is O_2 evolved or the NH_4^+ oxidized? If the reduction takes place with the evolution of O_2, then the stability of the alkali metal ortho-arsenates must be the result of some crystalline energy stabilization in these solids compared with H_3AsO_3.

EGA results in Fig. 7 indicate that O_2 is not evolved but that the NH_4^+ is oxidized to N_2 at higher temperatures. In general terms the decomposition can be described by eqns (1) and (2).

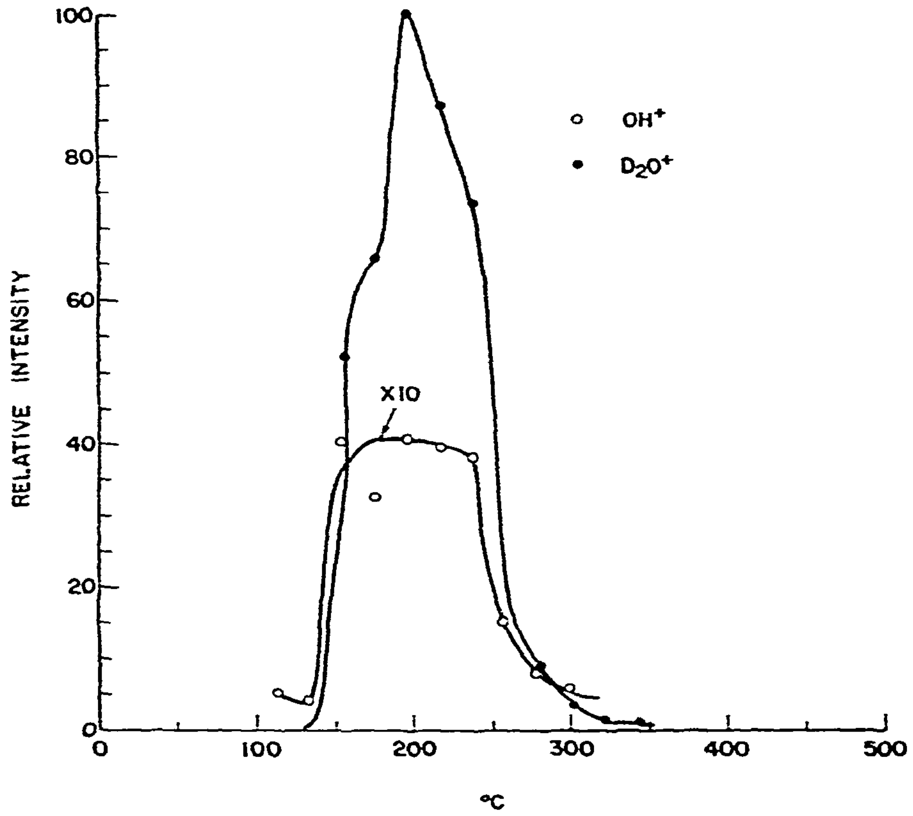

Fig. 5. EGA curves for the thermal decomposition of KD*P (85% substitution), 78 mg, 1 °C min^{-1}, in vacuum.

$$6NH_4H_2AsO_4 \rightarrow 2(NH_4)_2H(AsO_3)_3 + 2NH_3 + 6H_2O \quad (1)$$

$$2(NH_4)_2H(AsO_3)_3 \rightarrow 3As_2O_3 + 2N_2 + 9H_2O \quad (2)$$

These equations correspond to overall reactions above and below ~165 °C, respectively. The theoretical weight loss for eqn (1) is 14.9% which agrees well with the first peak in the DTG curve (Fig. 4). The actual formula shown for the intermediate composition in eqns (1) and (2) is not meant to imply any particular structure or bonding but simply represents a stoichiometric assemblage. The reason that the other arsenates did not undergo reduction is due to the fact that the associated cations (K, Rb, or Cs) were not readily oxidized.

CONCLUSIONS

1. The thermal dehydration of KDP, KD*P, and RDP occurred in a poorly resolved stepwise fashion suggesting various polymeric intermediates.

2. The thermal dehydration of KDA, RDA, CDA, and CD*A was simpler without even partially resolved steps.

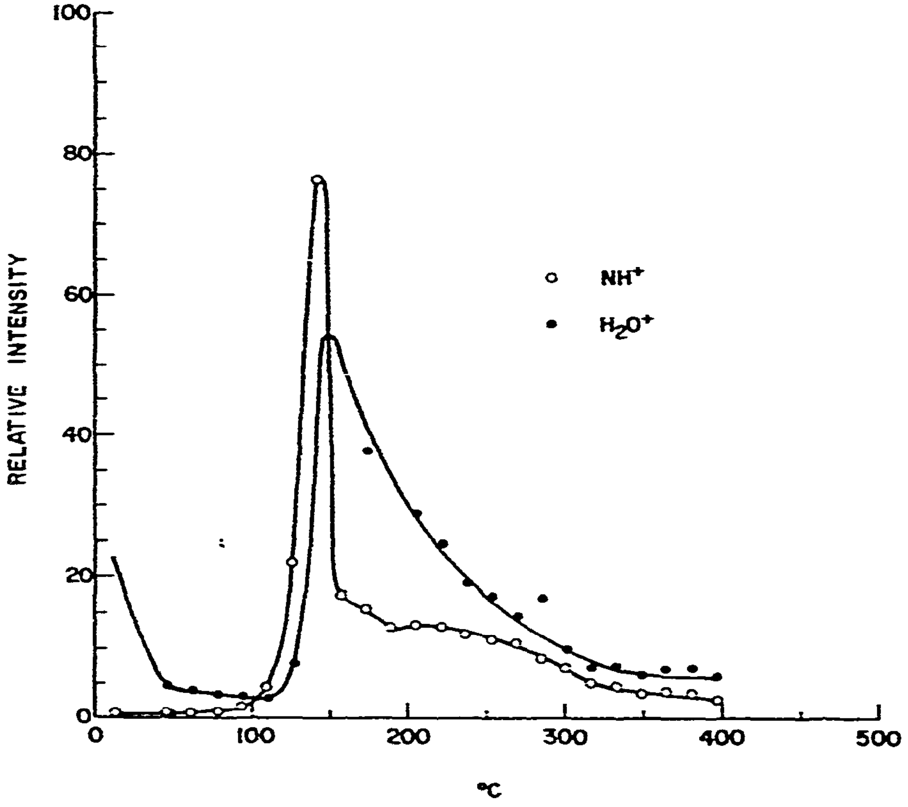

Fig. 6. EGA curves for the thermal decomposition of ADP, 31 mg, 1 °C min^{-1}, in vacuum.

3. The temperature at which the dehydration commenced (loss of 0.1 wt. %) seemed to decrease with increasing ionic radius of the alkali metal, however, the peak temperatures in the DTG curves did not exhibit a similar trend.

4. There was a slight tendency for H_2O to evolve at lower temperature than D_2O for incompletely substituted KD*P. The degree of substitution could be established from the total weight loss.

5. The decomposition of ADP took place over a wide temperature range. The NH_3 tended to evolve slightly before the H_2O.

6. A reduction of As^{5+} to As^{3+} occurred during the decomposition of ADA. At temperatures below ~165°C NH_3+H_2O are evolved while above this temperature N_2 and H_2O are evolved. This indicated that reduction of the As^{5+} is accomplished by the oxidation of NH_4^+ rather than the liberation of O_2. This explains then why the alkali metal arsenates did not undergo a similar reduction.

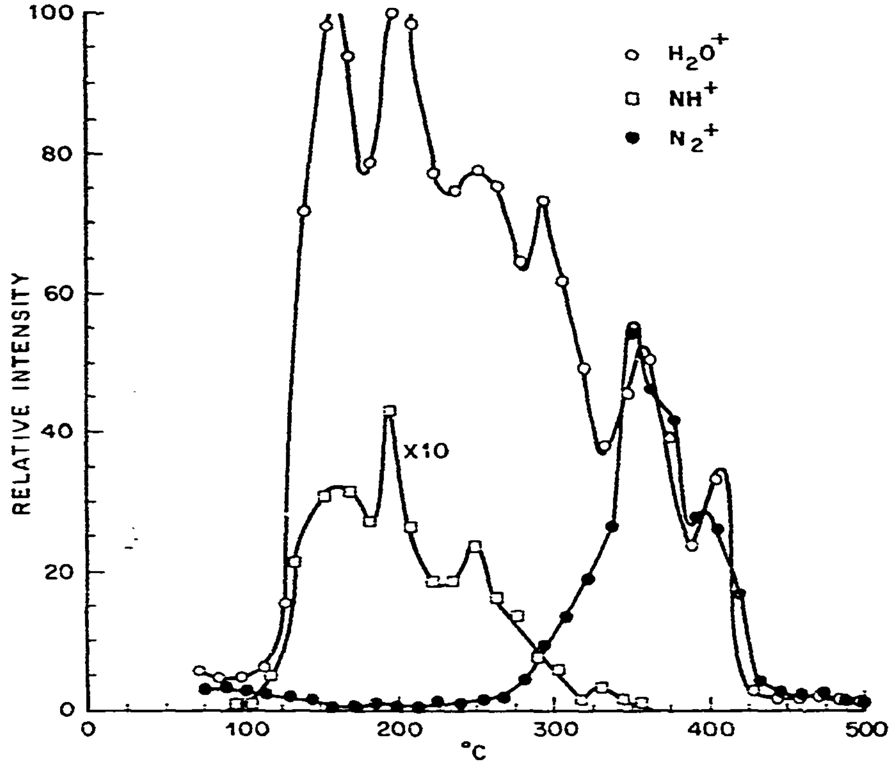

Fig. 7. EGA curves for the thermal decomposition of ADA, 89 mg, 1 °C min^{-1}, in vacuum.

ACKNOWLEDGMENTS

The author is grateful to Mr. G. M. Loiacano for providing the crystals and suggesting the study and to Messrs. Loiacano and D. W. Johnson, Jr. for helpful discussions.

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