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Application of Temperature-Programmed Desorption to the Study of Heteropoly Compounds: Desorption of Water and Pyridine

B. K. HODNETT AND J. B. MOFFAT[1]

Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry,
University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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The behavior of a series of heteropoly compounds during temperature-programmed desorption (TPD) before and after exposure to pyridine has been examined and correlated with structural changes and variations in sorptive capacities of these materials. Representative heteropoly acids and their metallic salts were chosen such that the primary Keggin structure (XM_{12}) was present in each but the series examined included variations in peripheral element, M as Mo or W, in hetero element, X as P or Si, and in cation, H^+, Na^+ or Mg^{2+}. Heteropoly acids of Mo and W desorbed water in two temperature regions; one between 423 and 473°K was assigned to water held in the solid structure by hydrogen bonding and one between 623 and 773°K was assigned to deprotonation of the acid with concurrent nonreductive loss of lattice oxygen, but with retention of the primary Keggin structure. Pyridine sorption by $H_3PW_{12}O_{40} \cdot nH_2O$ was strongly dependent upon pretreatment temperature. Pyridinium ion formation was maximized after pretreatment between 463 and 593°K. In static conditions sorption of pyridine was not inhibited but pyridinium ion formation was when hydrogen-bonded water was still present in the structure. Conversely removal of protons by thermal treatment above 593°K reduced the number of sorption sites. Pyridine was desorbed into the gas phase only in conditions such that more than ca. 1 pyridine molecule had been sorbed per Keggin unit. When smaller quantities were sorbed at 298°K decomposition products only were detected. A model is presented based on correlations between TPD peaks and DTA-measured decompositions.

INTRODUCTION

Recently interest has been increasing in heteropoly compounds as catalysts for the conversion of methanol to hydrocarbons (*1–5*). Many of these studies have concentrated on compounds such as $H_3PW_{12}O_{40}$ or $H_3PMO_{12}O_{40}$, which possess a central Keggin unit (*6*) in which 12 edge-sharing octahedra of oxygen atoms, with a central metal atom, W or Mo, surround and share atoms with the central tetrahedron. Acidic sites on or in these catalysts have been postulated as being involved in the reaction mechanism (*1*). Infrared studies (*7*) of pyridine adsorbed onto $H_3PW_{12}O_{40}$ indicate that the structure formed, i.e., a protonated pyridinium ion, is stable up to at least 620°K; no data were presented for higher temperatures. Since the temperature-programmed desorption (TPD) technique can potentially yield information on both the acid strength distribution of reactive sites and the thermal stability of adsorbed species (*8, 9*), it was decided to apply this technique to the study of heteropoly compounds.

A thermogravimetric study of molybdoheteropoly acids (*10*) concluded that water of hydration was lost after heating to ca. 473°K. Heating between 573 and 623°K provoked total decomposition as in (*9*)

$$H_4[SiMo_{12}O_{40}] \rightarrow SiO_2 + 12\ MoO_3 + 2\ H_2O \quad (1)$$

However, no attempts have been made to determine the relationship between the abilities of heteropoly compounds to sorb bases and their pretreatment conditions. This

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[1] To whom correspondence should be addressed.

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study will concentrate on this relationship using pyridine as base. The TPD behavior of a number of acids will first be presented to evaluate the nature of the residual water content; modifications brought about by sorption of bases will then be considered.

A recent study has reported the testing of metallic salts of $H_3PW_{12}O_{40}$ for methanol conversion to hydrocarbons (*2*). These salts exhibited a wide range of activities and selectivities. The sodium and magnesium salts were chosen for this study since the former exhibited low and the latter high activities and selectivities when tested. In this study the behavior of these salts in TPD experiments were also tested to compare with the acids.

EXPERIMENTAL

Materials. Heteropoly acids used in this study were $H_3PW_{12}O_{40} \cdot nH_2O$ (HPW), $H_3PMo_{12}O_{40} \cdot nH_2O$ (HPMo) (both BDH, AnalaR), and $H_4SiW_{12}O_{40} \cdot nH_2O$ (HSiW) (Baker Analyzed). They were used without further purification except HPMo which was recrystallized from aqueous solution and air-dried, after filtration to remove insoluble residues which formed during storage (*10*). No water-insoluble residues were observed for the tungsten acids. $Na_3PW_{12}O_{40}$(NaPW), $Mg_{3_2}PW_{12}O_{40}$(MgPW), and $(NH_4)_3PW_{12}O_{40}$ (NHW) were prepared following Hayashi and Moffat (*2, 3*). WO_3 was prepared by heating H_3WO_4 at 723°K in air. Pyridine was Baker Analyzed grade and was dried over NaOH or outgassed molecular sieve before use.

Apparatus and procedures for TPD experiments. TPD experiments were carried out on a standard apparatus, details of which have already been presented (*11*). Predried helium was used as carrier gas (70 ml min^{-1}). A fresh charge of catalyst (250 mg) was used for each experiment. The heating rate, β, could be varied between 2.7 and 25°K min^{-1}; 9°K min^{-1} was chosen for standard runs. Primary detection was with the aid of a thermal conductivity detector. In addition a C.E.C. mass spectrometer was attached to the system via a variable leak valve to identify the species contributing to individual peaks. To avoid condensation all piping (stainless steel and glass) was heated above 373°K.

The TPD profile of the unpretreated heteropoly acids could not be determined owing to the large amounts of water which desorbed at room temperature in the helium flow. Several pretreatments were used; 16 h at 298°K or 1.5 h at 393, 463, 593, or 723°K in a helium flow. Catalysts so pretreated were either subjected directly to a TPD experiment or reexposed to water vapor or to various bases. The latter procedure was carried out using two methods depending upon the amount of sorbate used. When small amounts were to be sorbed helium was passed through a saturator which consisted of glass wool which had been soaked in water or pyridine. The temperature of this ensemble, and consequently the pressure of the vapor contained within, was controlled by circulating water through an external jacket. Pulses of the vapor (5 ml contained 5.9 μmol of pyridine or 6.6 μmol of water) could be injected into the helium stream passing over the catalyst via an 8-way valve. A measure of the amount of each pulse sorbed could be obtained from the resultant peak observed with the thermal conductivity detector. The total amount of sorption which occurred was controlled by varying the number of pulses injected. The second method was used when the catalysts were to be exposed to large amounts of sorbate such that the maximum amount of sorption occurred. This involved passing the helium flow from the saturator directly over the catalyst bed until uptake was complete.

The areas under individual water peaks were determined by comparison with a calibration curve constructed from standards injected with a syringe.

Some experiments were also carried out to determine the stability of sorbed pyridine when exposed to a stronger base, i.e., ammonia, at various temperatures. Samples of

HPW were outgassed at 593°K and then exposed to an excess of pyridine at 298°K. The temperature was then raised to 593 or 693°K to desorb loosely held pyridine. A flow of NH_3 in helium (P_{NH_3} = 70 Torr) was passed over the samples at these temperatures and the gas phase monitored. When equilibrium was again established the NH_3 flow was shut off and the TPD profiles run.

Sorption of bases in static conditions. Uptake of pyridine and water by heteropoly acids was measured quantitatively on a quartz spiral spring balance. Various pretreatments were carried out before exposure of the acids to pyridine or water. These were essentially similar to those described above for TPD experiments, i.e., evacuation at 298°K (ca. 10^{-5} Torr) for 16 h or for 1.5 h at 463, 593, or 723°K. Sorption measurements were carried out at 298°K with pyridine at a partial pressure of 15 Torr. Sorption was normally followed until no further increases in weight were observed and this was taken as a measure of the amount of physisorption and chemisorption. The system was then heated and evacuated at 463°K and weight changes recorded. The amounts which remained sorbed were taken as the amounts chemisorbed. In what follows sorption will be expressed as moles of sorbate per mole of acid or as molecules sorbed per Keggin unit (KU), i.e., per PW_{12} unit.

The ability of NH_3 to displace presorbed pyridine from HPW was also tested in static conditions. The amounts of pyridine sorbed and retained by the acid at 593 and 693°K were measured on the spring balance. NH_3 was then introduced at these temperatures and weight changes followed until equilibrium was established. The X-ray diffraction (XRD) patterns of the materials which resulted were also recorded.

Differential thermal analysis. DTA was carried out on a DuPont 900 instrument. A heating rate of 10°K min^{-1} was used. Experiments were carried out in air. No *in situ* pretreatments were done.

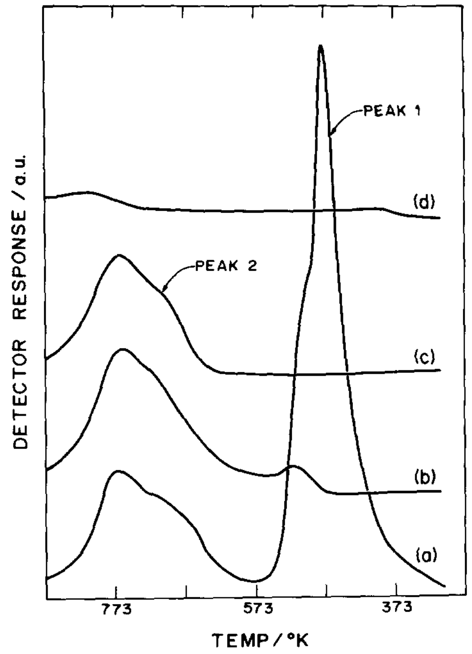

FIG. 1. Influence of pretreatment temperature on the TPD profile of HPW; pretreatment temperatures: (a) 298, (b) 463, (c) 593, (d) 723°K.

XRD. X-Ray powder diffraction patterns were recorded with the aid of a Phillips Model PW-1011/60 diffractometer using Cu*Kα* radiation filtered through nickel. X-Ray patterns were recorded immediately after various heat pretreatments for 1.5 h in air at 463, 593, 723, or 773°K.

RESULTS AND DISCUSSION

TPD of Water from Heteropoly Acids and Their Salts. The TPD profiles of HPW, obtained after various pretreatments are presented in Fig. 1. The sample pretreated at 298°K exhibited two peaks; one centered around 473°K (peak 1) with an unresolved shoulder on the high temperature side; the second was a very broad asymmetrical peak centered around 773°K (peak 2). Mass spectrometric analysis indicated that these peaks were due entirely to water. Their basic shapes were not changed by varying the helium flow rate or the heating rate. Integration for the area of peak 2 yielded values of 1.3–1.4 water molecules desorbed per K.U. The corresponding value for peak 1 was 6.5. Owing to problems of readsorption

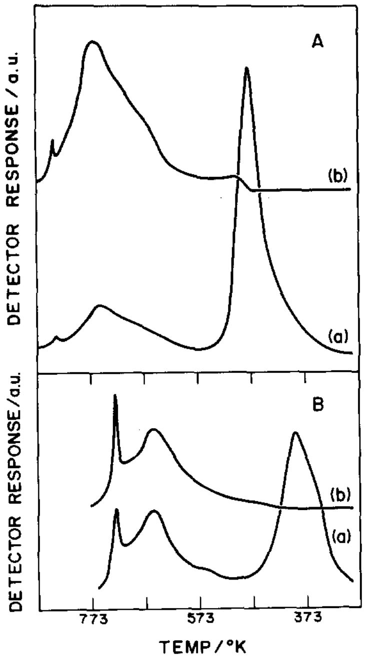

FIG. 2. (A) TPD of HSiW after pretreatments at (a) 298 and (b) 463°K. (B) TPD of HPMo after pretreatments at (a) 298 and (b) 393°K.

and subsequent unreliability reported for activation energies for desorption from porous solids determined from TPD data (*12*, *13*), no such values will be reported here.

Outgassing at 463 or 593°K essentially removed peak 1 but had no effect on peak 2. No peaks were observed after outgassing at 723°K. A final point to note is that extremely large amounts of water were desorbed from the unpretreated acid at room temperature under the influence of the helium flow. This phenomenon corresponds to the efflorescence reported for the fully hydrated acid (*10*) and the water thus evolved was too abundant to be resolved from the other peaks.

Water desorbed during outgassing at 463 or 593°K could be replaced by contacting the acid with water vapor at 298°K but outgassing at 723°K destroyed the catalyst's ability to reform its original TPD behavior.

HPMo and HSiW showed similar behavior to HPW in that after pretreatment at 298°K peaks were observed in two temperature ranges, as shown in Fig. 2. These will again be referred to as peaks 1 and 2. In addition, for these two acids a very sharp peak (peak 3) was observed at the high temperature side of peak 2. This was identified by mass spectrometric analysis as due to water. Integration of the total area of the upper temperature peaks (i.e., peaks 2 and 3) yielded values of 1.9 water molecules desorbed per HSiW unit (Fig. 2A) and 1.5 per H_3PMo_{12} unit (Fig. 2B). The absolute positions of the peaks for HSiW were almost identical to those observed with HPW, which contrasts sharply with HPMo. This behavior points to the peripheral metallic element as being of primary importance in determining the TPD behavior.

Additional observation indicated that as the heating rate was reduced, peaks 2 and 3 tended to separate with peak 2 moving toward lower temperatures. In these conditions the (3 : 2) area ratio became progressively smaller until peak 3 was almost absent for the lowest heating rate used.

Figure 3 presents the TPD profiles for NaPW and MgPW. Very little molecular

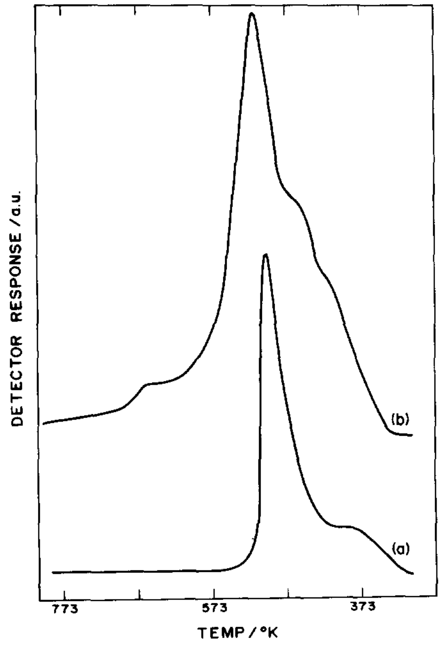

FIG. 3. TPD of (a) NaPW and (b) MgPW. Pretreatments were at 298°K for 2 h.

water was desorbed from these salts at 298°K. However, they both exhibited peaks due to water close to 470°K. An important feature was the total absence of desorption of water above 673°K.

DTA. DTA showed two general features; endotherms below 673°K and exotherms above. The main features are summarized in Table 1. The exotherms probably correspond to decompositions to the constituent oxides and the endotherms below 473°K correspond to loss of water of crystallization (*14*).

XRD analysis. Figure 4 outlines the XRD patterns obtained for HPW after various heat pretreatments in air. The pattern for the unpretreated free acid was not reproducible as reported previously (*15*), presumably due to loss of water by efflorescence (*10*) or provoked by the X-ray beam. A feature of the results was the pronounced broadening of the lines on heating between 463 and 593°K; some additional lines also appeared at $2\theta = 19, 21.5$, and $25°$, as indicated by the asterix in Fig. 4b. After heating to 723°K these lines became more pronounced. The peak at $2\theta = 25°$ seemed to shift to 24.5° and a new peak appeared at $2\theta = 26.2°$. Reexposure of the acid, pretreated at 593°K, to water vapor at 298°K caused the reappearance of the XRD pattern observed after outgassing at 463°K but the lines were noticeably less intense. Decomposition of HPW to its constituent oxides, i.e., WO_3 and P_2O_5 (only the former was detected by XRD), occurred after heating to 773°K (Fig. 4d).

TABLE 1

DTA of Heteropoly Acids and Their Salts

Sample	Endotherms (°K)		Exotherms (°K)
HPW	383	553	888
HPMo	393	435	713, 733
HSiW	398	553	803
NaPW	—	593	848
MgPW	—	—	893
HPW + pyridine[a]	448		830

[a] Sample pretreated at 463°K then exposed to pyridine vapor at 298°K.

Origin of Water Desorbed from the Unperturbed Acids and Salts

The position of peak 1 for each of the acids studied here is consistent with the type of multiple hydrogen bonding interactions between the acid and molecular water, which has been proposed in the literature (*16*). The fact that the peripheral element was dominant in determining the position of peak 1 (compare Figs. 1 and 2) is suggestive of these interactions taking place on the outsides of the Keggin structures, buffered from the influence of the heteroatom.

The higher desorption temperatures associated with peaks 2 and 3 imply stronger interactions in these cases. The fact that peak 2 was absent from the stoichiometric salts suggests that it must have been associated directly with the protons of the acid.

The results presented above, based on peak area measurements from TPD profiles

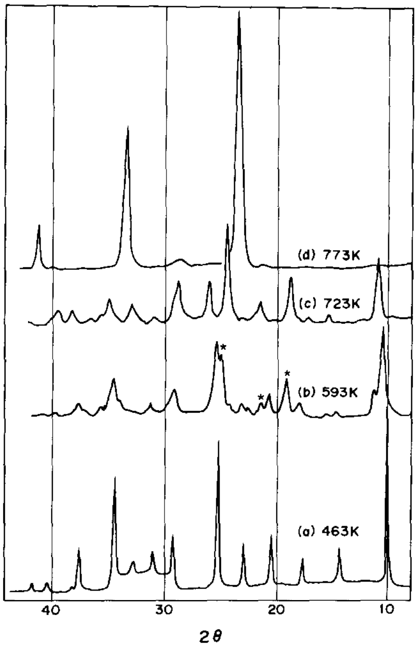

FIG. 4. XRD patterns for HPW pretreated in air for 90 min at (a) 463, (b) 593, (c) 723, (d) 773°K.

support the findings of Ref. (*10*) and suggest that (1) the 6–7 hydrate of HPW is formed after outgassing in helium at 298°K and (2) above 473°K 1.5 water molecules per K.U. could be desorbed. The latter number and these measured for HPMo and HSiW suggest that this loss of water involved a deprotonation of the catalyst with concurrent loss of lattice oxygen. An important point to note is that the XRD analysis of HPW, which had been pretreated at 723°K (Fig. 1(d)) in order to remove peak 2, indicated that it had not decomposed to its constituent oxides as suggested by Eq. 1 (*10*). This finding has been confirmed by ir measurements carried out under very similar conditions. Rather, these results suggest that HPW is capable of losing some lattice oxygen without collapse of its primary Keggin structure, as indicated by ir data, but with some slight rearrangement of its secondary structure, as indicated by the XRD data. Thus

$$H_3PW_{12}O_{40} \rightarrow PW_{12}O_{38.5} + 1.5\ H_2O \quad (2)$$

can be postulated to explain peak 2.

Both HPMo and HSiW exhibited a third peak (peak 3) in their TPD profiles in appropriate conditions. The position of peak 3 for HPMo coincides exactly with its thermal decomposition (*10, 14*) measured by DTA (Table 3); peak 3 for HSiW occurs at 843°K whereas its decomposition was measured by DTA at 803°K. This evidence would suggest that, at least, in the former case, peak 3 was associated with decomposition of the Keggin structure; the observed peak may then have resulted from an accelerated desorption–expulsion of some of the proton-related water which remained in the structure up to the temperature at which decomposition occurred. This type of peak was not observed for HPW since its decomposition temperature, 888°K, by DTA is well separated from the end of the tail of peak 2 in its TPD profile; the water associated with peak 2 had fully desorbed below 873°K. Further evidence that this hypothesis is valid was seen in the behavior of the intensity ratios of peaks 2 and 3 for both HPMo and HSiW; as the heating rate was lowered the separation between peaks 2 and 3 increased, water desorbed in peak 2 at lower temperatures whereas peak 3 remained uneffected thus the area ratios (3 : 2) fell sharply for both acids.

As to the structure which forms during pretreatment of HPW between 593 and 723°K some correlations can be drawn with the DTA and TPD analysis. This structure only began to appear at a temperature higher than that at which the last endotherm was observed by DTA. It should be noted that peak 2 of the TPD profile of HPW began to evolve at this temperature. When HPMo and HSiW were pretreated in similar circumstances, i.e., at a temperature above the last DTA endotherm such that peak 2 of their TPD profile began to appear, very similar XRD patterns were observed. Similar patterns have also been reported by Misono *et al.* (*15*) for heat-treated HPMo. Thus a structure may be tentatively proposed which involves some reorganization of the solid due to loss of protons via Eq. (2) without decomposition of the primary Keggin unit (*6*).

As the next step in our study of these compounds it was logical to use the model of the free acids developed above to investigate the interactions of basic probe molecules such as pyridine and ammonia.

TPD of heteropoly acids exposed to pyridine. Figure 5 presents TPD profiles for HPW which had been pretreated in helium at 463°K and into which various amounts of pyridine had been sorbed at 298°K using the two methods described in the experimental section. The number of pyridine pulses was varied between 2 and 20 for traces (a)–(d). In practice the first 10 pulses were totally sorbed by the standard charge of catalyst and close to 90% of pulses 10 to 20 could also be sorbed in the conditions of the experiment. Assuming that complete sorption had occurred the following amounts of pyridine were sorbed per K.U.: (a) 0.15, (b) 0.38, (c) 0.75, (d) 1.5. Trace (e) of Fig. 5

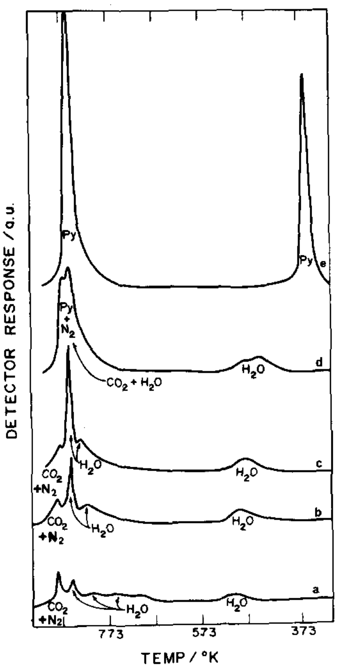

FIG. 5. Influence of number of pyridine pulses (5.9 mol per pulse) sorbed onto HPW at 298°K; number of pulses: (a) 2, (b) 5, (c) 10, (d) 20, and (e) sample saturated. Pretreatment was at 463°K.

corresponds to HPW which was exposed to an excess of pyridine. The results of mass spectrometric analysis are indicated under each individual peak of Fig. 5. Clearly two limiting cases can be identified; that in which pyridine was the major species desorbed (trace (e)) and that where products which could have arisen from the decomposition of sorbed pyridine, i.e., CO_2, N_2, and H_2O, were desorbed (traces (a)–(c)). Trace (d) would then seem to represent a case intermediate between these two extremes.

Figure 6 presents TPD profiles for HPW which had been pretreated to temperatures of up to 723°K and exposed to pyridine at 298°K; either 0.38 pyridine molecules per K.U. for Fig. 6A or an excess for Fig. 6B. Behavior closely analogous to that outlined in Fig. 5 was again observed. Large amounts of pyridine were desorbed from HPW outgassed at 463 or 593°K. However, in all other cases some or all of the peaks previously associated with decomposition products (cf. Fig. 5), could be detected. These peaks became more pronounced

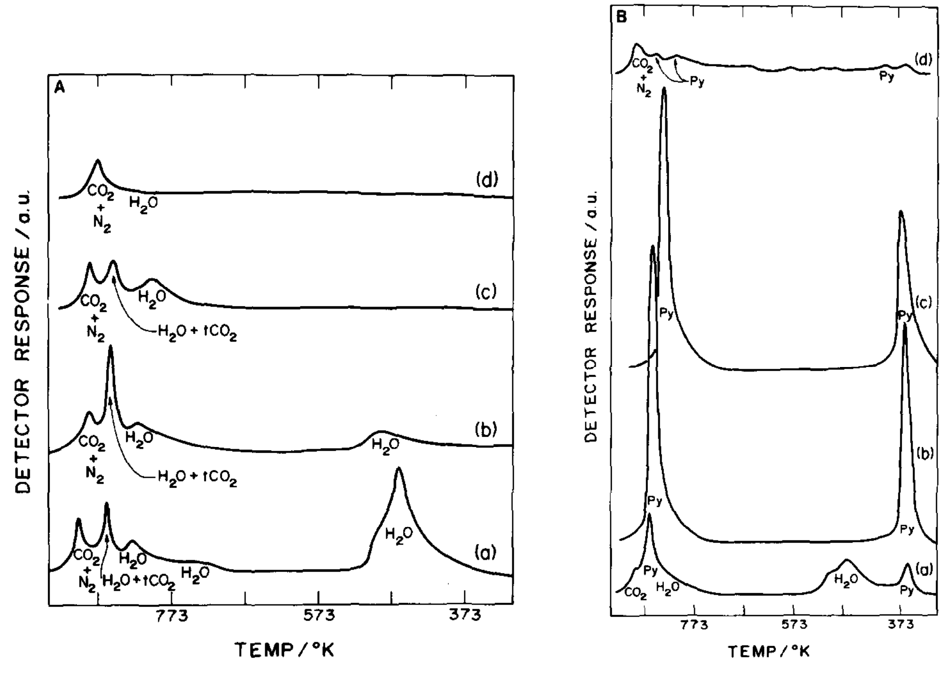

FIG. 6. Influence of pretreatment temperature on subsequent desorption of pyridine from HPW. (a) 298, (b) 463, (c) 593, (d) 723°K. (A) Exposure to 0.38 pyridine molecules per K.U. at 298°K. (B) Saturated with pyridine at 298°K.

when the amount of desorbable material was reduced either by deliberate control of the amount available for sorption, as in Fig. 6A, or through thermal modification of the sorptive behavior of the heteropoly acid as in Fig. 6B, traces (a) and (d). In addition, there was a general tendency for peak maxima to shift toward lower temperatures as the outgassing temperature of HPW was increased. No change was observed in the area of the high temperature pyridine peak as the heating rate was changed.

When NaPW and MgPW were exposed to pulses of pyridine at 298°K, after pretreatment at 463°K, very little sorption was observed in these conditions and their TPD profiles exhibited only residual traces of water at ca. 473°K originating from the peaks shown in Fig. 3.

Displacement of presorbed pyridine by ammonia. When $NH_{3(g)}$ at 593 or 693°K, was passed over HPW onto which pyridine had been presorbed to saturation levels, pyridine was evolved into the gas phase and when the TPD profiles were subsequently run neither pyridine nor its decomposition products were detected; the profiles observed resembled that of NHW as shown in Fig. 7.

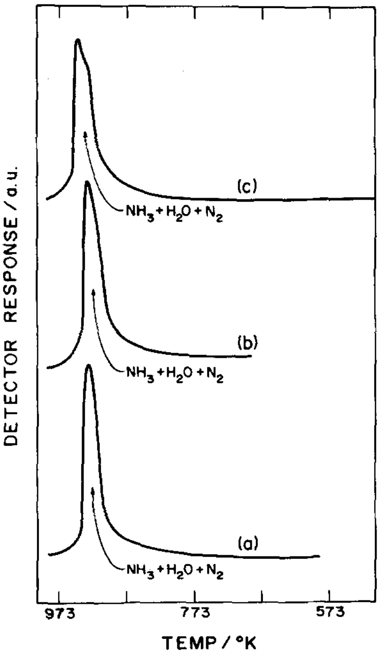

FIG. 7. TPD of HPW which was saturated with pyridine at 298°K, then exposed to $NH_{3(g)}$ at (a) 593 and (b) 693°K. Trace (c) is the TPD profile for NHPW.

TABLE 2

Uptake of Pyridine by HPW, NaPW, and MgPW at 298°K

Sample	Pretreatment temp. (°K)	Pyridine sorption[a] (mol K.U.$^{-1}$ total)	
HPW	298	5.7	—[c]
HPW	463	6.2	(2.9)
HPW	593	6.5	(2.4)
HPW	723	1.4	(0.7)
NaPW	463	13.7	(0.2)[b]
MgPW	463	0.40	—[c]

[a] Amount irreversibly sorbed at 463°K.

[b] Amount irreversibly sorbed after outgassing at 598°K.

[c] Not measured.

Sorption of pyridine in static conditions. Uptake of pyridine at 298°K by HPW, NaPW, and MgPW is summarized in Table 2. This study was undertaken to obtain a more quantitative measure of the capacity of these materials for sorption of pyridine. The data which relate to the free acid show a change in behaviour as a function of pretreatment temperature. The amount of irreversibly sorbed pyridine could not be determined for the sample outgassed at 298°K as heating to 463°K would have provoked loss of both water and pyridine. The amount of irreversibly held pyridine was at a maximum for samples outgassed between 463 and 593°K and the sample outgassed at 723°K sorbed much less pyridine at 298°K. The magnesium salt showed very little affinity for pyridine sorption. By contrast up to 13.7 pyridine molecules per K.U. were taken up by the sodium salt, all of which could be removed below 593°K.

Some additional experiments were carried out to test the ability of NH_3 to displace presorbed pyridine from HPW in static conditions. Weight changes recorded after exposure of the pyridine saturated acid to $NH_{3(g)}$ at 593 and 693°K indicated that displacement was quantitatively complete and the XRD pattern of the recovered material was identical to that recorded for APW (*3*). However, large amounts of pyridine were sorbed in these conditions, which is consistent with literature reports (*7*), but contrasts with the TPD experiments (Fig. 6B, trace (a)). DTA of a sample of HPW which was exposed to pyridine vapor until it had sorbed to its maximum capacity exhibited a very broad peak centered at ca. 830°K.

Nature of the Interaction of Pyridine with Heteropoly Compounds

The data presented in Table 2 concerning the influence of pretreatment temperature on pyridine sorption in static conditions and on the TPD of pyridine from HPW (Figs. 5 and 6) may be interpreted in terms of the model of the free acids presented above. The observed drop in pyridine uptake, after pretreatment at 723°K, can be assigned to a lack of protons within the heteropoly structure with which strong interactions can occur. Thus irrespective of the amount of base to which 723°K pretreated HPW was exposed, i.e., 0.38 mol per K.U. or to saturation (Fig. 6), the sizes of the peaks associated normally with strongly interacting pyridine were always much less intense than for the corresponding samples pretreated at lower temperatures. Further evidence that protons are needed for strong interaction was the analogous behavior of the sodium and magnesium salts which did not exhibit any TPD peaks due to desorption of pyridine or related species. Although large amounts of pyridine could be sorbed at 298°K by the sodium salt (Table 2), desorption occurred at low temperatures.

The absence of peaks at low temperatures for samples which were not presaturated with pyridine suggests a preference for interactions with strong acid sites in these conditions.

The discrepancy observed between the amount of pyridine uptake in static conditions (Table 2) and the amount desorbed in TPD (Fig. 6B, trace (a)), after pretreating HPW at 298°K, may be explained in two ways. The first is that sorption after this pretreatment was more efficient in static than in dynamic conditions. The second is that pyridine was unable, at 298°K, to displace water which was hydrogen-bonded to the protons after outgassing at this temperature. It should be recalled that the amount of pyridine irreversibly adsorbed could not be measured in static conditions for samples pretreated at 298°K.

The relative proportions of the peaks associated with pyridine desorption, observed above 773°K, changed markedly as the amount of adsorbed pyridine varied. The absolute size of the lowest of these peaks (due to water) did not change as a function of the amount of pyridine adsorbed but shifted to slightly higher temperatures (from 810 to 820°K) and eventually became obscured by stronger peaks. This peak is possibly associated with the free acid perturbed by the presence of pyridine.

The two other peaks, i.e., at 850°K (due to water with traces of CO_2) and at 880°K (due to CO_2 and N_2) can be correlated, respectively, with the DTA measured decomposition temperatures of the pyridinium salt and the free acid (Table 1). Thus the increase in intensity of the peak at 850°K with increased sorption of pyridine and the concurrent reduction of the peak at 880°K can be interpreted in terms of increased formation of pyridinium salt at the cost of the free acid. The observation of decomposition products at low exposures to pyridine can be interpreted in terms of a limited availability of lattice oxygen for this reaction. Finally, the ease with which pyridine was displaced by ammonia at 593 and 643°K argues against an entrapment–decomposition mechanism to explain the formation of oxidized products.

Examination of Fig. 6 reveals that as the pretreatment temperature was increased the peaks observed above 773°K tended to shift toward lower temperatures. A tentative explanation of this effect is to propose that the various temperature pretreatments promote the formation of germination points for the eventual high temperature decompositions in an analogous manner to that in which the formation of surface defects can act as germination points for the reduction of simple metal oxides (*19*).

On the basis of the foregoing analysis it is not possible to come to any conclusions concerning the acid strength distribution of HPW from these results since desorption peaks coincided with decomposition temperatures of the heteropoly compounds and make it more likely that the peak positions reflect these events rather than desorption from acid sites.

Measurements for pyridine uptake in static conditions indicate that the total uptake at 298°K was always twice the amount irreversibly sorbed irrespective of the residual proton content (Table 2). Other sources (*6, 18*) suggest that when HPW is exposed to an excess of pyridine (i.e., greater than 3 mol per K.U.) the infrared bands associated with the pyridinium ion are strongly attenuated until the excess pyridine is removed. This suggests that in conditions where HPW was presaturated with pyridine a transformation occurred during temperature programming which involved formation of pyridinium ions on the one hand and desorption of loosely bound pyridine on the other. The fact that no change occurred in the size of the pyridine desorption peak which occurs at 850°K, i.e., that associated with pyridinium ion formation, as a function of heating rate implies either that pyridinium ion formation was complete at the temperature at which desorption of physisorbed pyridine occurred, i.e., at 373°K, or that desorption of this portion of the sorbed pyridine and pyridinium ion was a simultaneous process. The fact that the total uptake of pyridine at 298°K in static conditions was always twice the amount irreversibly sorbed points toward a mechanism similar to that already proposed by Misono *et al.* (*7*). Their mechanism involved dimer formation between strongly held pyridinium species and a sorbed pyridine molecule. To explain our results more satisfactorily it is assumed that below ca. 373°K the N---H$^+$---N interactions are equivalent and quite labile. This is in accord with the apparent ease with which pyridine can move through this system at 298°K. This concept of two-way approach by the base to the proton can also be useful in explaining the mechanism of displacement of pyridine by ammonia observed at high temperatures.

CONCLUSIONS

TPD is a useful technique for characterizing the nature of water which desorbs from heteropoly acids, i.e., whether molecular water which hydrogen bonds to protons or water derived from the reaction of protons with lattice oxygen in a deprotonation process. The useful temperature range for catalysis can also be checked very quickly by this technique. The sorptive capacity of heteropoly acids toward pyridine depends strongly upon pretreatment conditions; after thermal treatment at 723°K HPW is essentially deprotonated but retains the primary Keggin unit. However, little interaction with pyridine occurs which contrasts sharply with the behavior after treatment at lower temperatures. Pyridine only desorbs from HPW without decomposition provided more than 1 pyridine molecule per K.U. is sorbed, below this value decomposition to CO_2, H_2O, and N_2 occurs.

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