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Characterization of 12-Tungstophosphoric Acid and Related Salts Using Photoacoustic Spectroscopy in the Infrared Region

I. Thermal Stability and Interactions with Ammonia

J. G. HIGHFIELD AND J. B. MOFFAT[1]

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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Photoacoustic spectroscopy (PAS) has been applied in the infrared region to the characterization of a number of heteropoly compounds which show interesting trends in activity and selectivity in the conversion of methanol to hydrocarbons. From direct studies of powdered catalyst samples, PAS has yielded information concerning the structure, stability, and acidity of 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$, and the respective Al^{3+}, NH_4^+, and Na^+ salts. Results of heating *in vacuo* indicate that the Keggin unit, i.e., the $PW_{12}O_{40}^{3-}$ ion, is stable apart from a small loss of O, up to ~450°C, but the parent acid loses protons, beginning around 400°C. Studies of the sorption of NH_3 show that $H_3PW_{12}O_{40}$ reacts quantitatively to form the NH_4^+ salt and reveal that the salts are nonstoichiometric, existing in partial (Brønsted) acid form. Evidence was found for Lewis acidity in the Al^{3+} salt, and attributed to the presence of the cations. A qualitative correlation of Brønsted acidity with activity is drawn.

INTRODUCTION

Photoacoustic spectroscopy (PAS) is proving an increasingly valuable technique for the investigation of condensed-phase samples. Its calorimetric mode of detection facilitates the acquisition of optical absorption spectra from strongly scattering and/or opaque materials which are difficult to study by conventional photometric methods (*1, 2*). To date, however, there have been relatively few applications of PAS in the field of catalysis or catalyst characterization. This is surprising in view of the fact that such materials are often available as porous, fine powders, a physical state which provides a high thermal transfer efficiency and optimizes the PAS signal for a given absorption strength (*3*). One explanation may lie in the fact that, until very recently, instrumental factors have restricted the use of PAS to the uv–visible, a region in which some success has been achieved (*4–6*) but which yields somewhat limited information as a consequence of the broad, rather featureless absorption bands characteristic of electronic transitions in condensed media. However, since Rockley (*7*) first demonstrated the feasibility of interfacing the PAS cell to a commercial Fourier Transform Infrared (FTIR) spectrometer, in which the throughput (Jacquinot's) advantage of the interferometric system offsets the problem of low source power, the development of PAS–FTIR as a viable technique for midinfrared spectroscopy of powdered samples has been rapid (*8*). Recent catalyst studies, including surface acidity characterization of alumina and silica–alumina (*9*), and the adsorption of CO on Ni/SiO_2 (*10*), illustrate the promise of the technique.

In this paper, we report the application of PAS–FTIR to the characterization of heteropoly compounds which show interesting trends in activity and selectivity in the conversion of methanol to hydrocarbons. The compounds under investigation, selected on the basis of their wide-ranging catalytic properties, include 12-tungstophosphoric

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[1] To whom correspondence should be addressed.

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acid, $H_3PW_{12}O_{40}$, and the respective ammonium, aluminum, and sodium salts of the parent acid (*11–13*). In view of evidence to suggest that methanol conversion over 12-tungstophosphoric acid proceeds via a carbonium ion mechanism (*11*), it was of particular interest to study the acidic properties of these compounds via their interactions with the basic probe molecule ammonia.

EXPERIMENTAL

PAS–FTIR spectra from 4000 to 550 cm^{-1} were recorded at 5 cm^{-1} resolution on a Bomem DA3.02 Fourier Transform infrared spectrometer, utilizing the globar source and KBr beam splitter. The photoacoustic detector module, supplied as a standard accessory by the manufacturer, was used with minor modifications.

Preliminary studies were made using powdered carbon black (Darco, activated carbon, 100–325 mesh, Aldrich Chemical Co.) both to develop the instrumental conditions required for optimum performance and to generate a high-quality reference spectrum for normalization of sample spectra. As the PAS signal is inversely proportional to the modulation frequency (Hz) of the incident radiation (*3*) and the latter is defined by the equation

$$f = 2V\nu \qquad (1)$$

where V is the mirror velocity (cm sec^{-1}) and ν is any particular infrared wavenumber (cm^{-1}) (*14*), the mirror velocity should be kept as low as possible compatible with the alignment stability of the instrument. A good working compromise was found at $V = 0.03$ cm sec^{-1}, resulting in a modulation frequency range of 240–33 Hz over the wavelength region of interest.

In view of the efficiency with which the absorption of radiation by gas-phase contaminants CO_2 and H_2O couples to the microphone (*15*) and the ambiguity in interpretation of spectra after exposure to atmosphere, all samples were isolated *in vacuo* after pretreatment, transferred to the PA cell in a glove box, and ground prior to examination. Helium filler gas was used on account of its reported enhancement of PA sensitivity by a factor of ≈ 2 over air (*3*).

In light of recent evidence (*16, 17*) that some carbons may not provide effective source compensation in the infrared due to incomplete photoacoustic signal saturation, the validity of the reference spectrum generated at standard mirror velocity (0.03 cm sec^{-1}) was checked by comparison with spectra obtained at higher velocities. Continuous deviation from a flat baseline for the carbon/carbon ratioed spectrum was observed at $V = 0.15$ cm sec^{-1} for infrared wavenumbers > 2000 cm^{-1}, indicating complete saturation for modulation frequencies < 600 Hz, i.e., well above the value (240 Hz) corresponding to the highest infrared wavenumber (4000 cm^{-1}) in the spectrum obtained at standard velocity. Thus, after coaddition of ≈ 5000 scans, a reliable reference spectrum was obtained with a S/N ranging from ~150 to 750 over most of the midinfrared region (3600–600 cm^{-1}).

Sample weights ranged typically from 10 to 30 mg and spectral accumulation for 500 scans was routinely performed for good quality results, requiring a data acquisition time of at least 80 min per spectrum. Peak areas were measured reproducibly (±2%) using a planimeter and area ratios were calculated from the means of at least three measurements per peak.

The preparation and physicochemical characterization of the heteropoly compounds under investigation have previously been described (*11–13*). WO_3 was prepared by heating tungstic acid (H_2WO_4, Aldrich Chemical Co.) in air at 400°C for 3 h, while P_2O_5 was obtained directly (J. T. Baker Chemical Co.).

Sample pretreatment was performed on a conventional vacuum system capable of an ultimate dynamic vacuum of 10^{-5} Torr. Reagents ammonia (anhydrous, 99.99%; Matheson) and D_2O (99.7% minimum isotopic purity; Merck Sharp & Dohme) were subjected to several freeze–pump–thaw cycles to remove contaminant gases prior to use; ammonia was also predried by trap-to-trap distillation. Uptakes were measured volumetrically and expressed, for convenience, as molecules sorbed per Keggin unit ($PW_{12}O_{40}^{3-}$ ion) calculated on a dry weight basis. Powder X-ray diffraction data were obtained using a Philips diffractometer (Model PW-1011/60) at 40 kV and 30 mA using Cu*Kα* radiation. Accurate lattice parameters (a_0) were determined using Nelson–Riley extrapolation. Elemental analyses were obtained from Galbraith Laboratories Inc.

RESULTS

1. Structure and Thermal Stability

a. $H_3PW_{12}O_{40}$. Changes in the PAS spectrum of the free acid induced by heating *in vacuo* are illustrated in Fig. 1. The initial spectra are dominated by a featureless background absorption which extends across the entire midinfrared range, its intensity apparently increasing toward the low wavenumber region. At room temperature (Fig. 1a), broad bands assignable to water (≈3200 cm^{-1} (*18*)) and, more specifically, the oxonium ion, H_3O^+ (≈1710 cm^{-1} (*19*)) are evident, together with a group of 5 or 6 bands below 1100 cm^{-1}, albeit poorly resolved, characteristic of the Keggin unit (KU), i.e., the $PW_{12}O_{40}^{3-}$ ion (*20–22*). Assuming an initial molecular formula of $H_3PW_{12}O_{40} \cdot 29H_2O$, the weight loss measured at this stage (≈13%) indicates the retention of ≈4–5 molecules of H_2O/KU, consistent with Keggin's original findings (*23*)). At 200°C (Fig. 1b) the band at 1710 cm^{-1} disappears, leaving a weak residual band at ≈1640 cm^{-1} assignable to the bending vibration of lattice water (*18*). Contemporaneously, weak bands assignable to the corresponding asymmetric and symmetric stretching vibrations (*24*) appear at ≈3060 and 2980 cm^{-1}, and a third band at ≈3160 cm^{-1} which may be the first overtone of the bending fundamental (*25*). The position of the stretching vibrations indicates that some degree of hydrogen bonding is present (*26*). The band at ≈2240 cm^{-1} may also originate from crystal water (≈1–2 molecules/KU by weight loss) as a corresponding band has been observed in hydrates such as $K_2CuCl_4 \cdot 2H_2O$ and assigned to a combination involving bending and librational fundamentals (*25*). The development of structure in the KU bands at ≈1080 and ≈980 cm^{-1} indicates that some distortion of the anion has occurred. Following Rocchiccioli-Deltcheff *et al.* (*22*) the former band is attributed to the triply degenerate asymmetric stretching vibration of the central PO_4 tetrahedron, and the appearance of two new bands at 1120 and 1069 cm^{-1} indicates complete resolution of the degeneracy and implies a lowering of symmetry from T_d to C_{2v} (*26*). A similar splitting has been observed in pyridinium molybdothorophosphate (*27*). The latter band has been assigned to a stretching vibration involving the central W atom and the isolated terminal O (W–O_t) on the periphery of each of the twelve WO_6 coordination octahedra which complete the Keggin unit, on the basis of the shorter length (and implied greater strength) of this bond

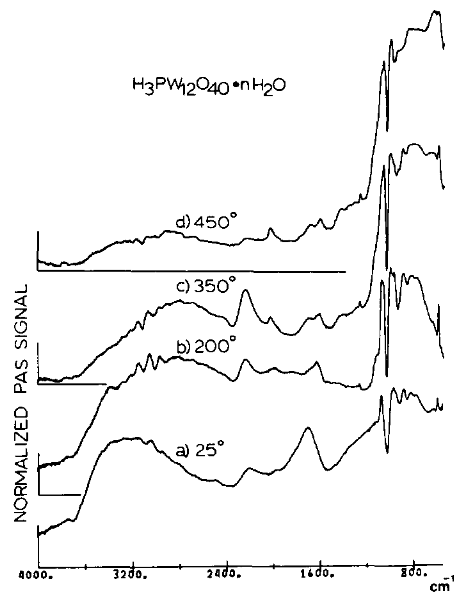

FIG. 1. Effect of heating $H_3PW_{12}O_{40} \cdot nH_2O$ *in vacuo* (temp °C).

(*22*). Despite the evident distortion of the primary structure, the XRD pattern shows that the secondary (bulk) structure is still cubic with a lattice parameter $a_0 = 12.11$ Å, a value in close correspondence with that reported by Keggin (*23*). On further heating (Figs. 1c and d) the band at 2240 cm^{-1} appears first to intensify (350°C) and then disappears, indicating possibly complete loss of lattice water by 450°C. Similarly, the progressive attenuation of the background absorption is believed to result from the loss of water and/or protons. The phenomenon of continuous absorption in the ir has been observed by several workers and related to proton mobility in adsorbed layers on solid surfaces (*28*). Supporting evidence for the occurrence of a similar effect, originating in the bulk in this case, derives from changes in the spectrum upon absorption of ammonia (see later). The KU bands broaden but remain recognizable despite the development of absorption below 1000 cm^{-1}, indicating partial decomposition (the PAS spectrum of WO_3 shows a band in this region). Above 500°C, a broad absorption appears, initially at high frequency, which develops and extends progressively across the spectrum with temperature until all detail is obscured. Contemporaneously, the sample is observed to change color from white through dark blue to black, an effect which probably results from reduction of W(VI), presumably via oxygen removal and the development of mixed-valence absorption as in the tungsten bronzes (*29*). Consistent with this interpretation, similar behavior is observed in WO_3.

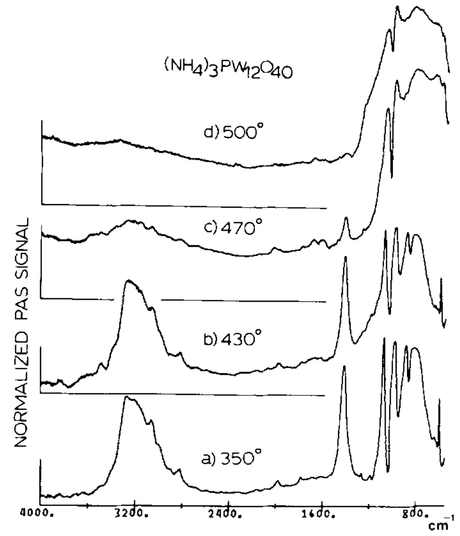

FIG. 2. Effect of heating $(NH_4)_3PW_{12}O_{40}$ *in vacuo* (temp °C).

b. $(NH_4)_3PW_{12}O_{40}$. The PAS spectrum of the ammonium salt hardly changes on heating up to 350°C and hence serves as a useful reference spectrum (Fig. 2a). Obvious differences are observed between this and corresponding spectra for the parent acid. The background absorption is much weaker and strong new bands, diagnostic of the NH_4^+ ion, are evident at ≈3200 and 1420 cm^{-1}. By analogy with the data of Wagner and Hornig for NH_4Cl (*30*) these bands are assigned to the triply degenerate asymmetric stretching (ν_3) and bending (ν_4) fundamentals, respectively. The appearance of several bands in the region 3300–2800 cm^{-1} is not considered to arise from a lowering of the site symmetry of the NH_4^+ ion below T_d nor to the presence of ions in two or more crystallographically distinct sites, e.g., as in $(NH_4)_3AlF_6$ (*31*) as a corresponding structure would be expected in ν_4, which is not observed. Following the above authors, these bands are assigned to combinations and overtones as 3280 cm^{-1} ($\nu_1 + \nu_5$), 3220 cm^{-1} (ν_3), 3060 cm^{-1} ($\nu_2 + \nu_4$), and 2820 cm^{-1} ($2\nu_4$), where ν_1 is the symmetric stretching fundamental, ν_2 is the doubly degenerate bending fundamental, and ν_5 is a lattice mode. Particularly striking features in this spectrum are the good resolution and absence of structure in the KU bands, indicating an undistorted anion, i.e., T_d symmetry. The secondary structure is also well ordered as the XRD pattern is sharp and intense, confirming that this salt is isostructural with $H_3PW_{12}O_{40}$ (cubic) but with a smaller lattice parameter, $a_0 = 11.71$ Å, a value comparable to that reported for the Mo-containing analog ($a_0 = 11.666$ Å, ASTM 9-412). The P–O and W–O_t stretch-

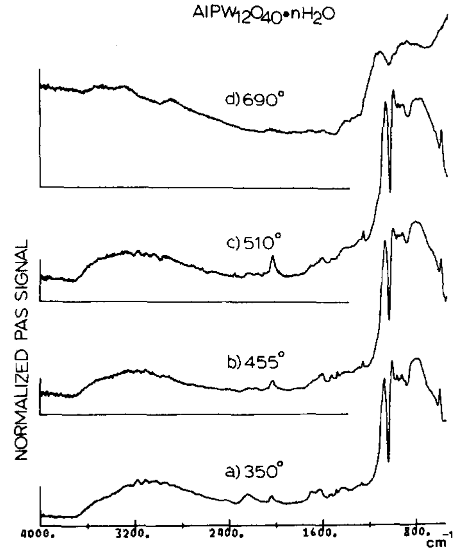

FIG. 3. Effect of heating $AlPW_{12}O_{40} \cdot nH_2O$ *in vacuo* (temp °C).

ing bands are at 1083 and 987 cm^{-1}, respectively, while the other three bands are assigned, after Rocchiccioli-Deltcheff *et al.* (*22*), as 891 cm^{-1}, stretching of W–O–W bridges between corner-sharing WO_6 octahedra; 815 cm^{-1}, stretching of W–O–W bridges between edge-sharing octahedra; and 596 cm^{-1}, P–O bend. The absence of any distinct absorption features at ≈2240 and ≈1640 cm^{-1} indicates that little or no lattice water is present. As the ammonium salt is heated (Figs. 2b–d), there is a progressive loss of bands due to the NH_4^+ ion (beginning above ≈450°C) and a broadening and shifting of the KU bands (P–O stretch to lower, W–O stretches to higher frequencies). However, even at 500°C the detail remaining in the spectrum indicates some retention of the anion structure, despite the appearance of a shoulder at 1260 cm^{-1} and an increase in background absorption below ≈1200 cm^{-1}, both features characteristic of WO_3.

c. $AlPW_{12}O_{40}$. PAS spectra of the aluminium salt show the KU bands as expected (Fig. 3a) and also the presence of residual lattice water, as indicated by the broad bands at ≈3200, 2240, and 1640 cm^{-1}. The KU bands, albeit broader, show a general correspondence with those of the ammonium salt but with distinct shifts and splitting in the high-frequency W–O bands (1018, 977, and 932 cm^{-1}), indicating some degree of anion distortion. Peaks in the XRD pattern are not as sharp and intense as for the previous compounds but confirm that the solid has a cubic structure with a lattice parameter a_0 = 12.135 Å. On heating, most of the lattice water is lost by ≈450°C but the KU appears stable even above 500°C (Figs. 3b and c). However, more severe treatment (690°C, Fig. 3d) causes complete breakdown, the broad P–O stretching band at ≈1140 cm^{-1} resembling that seen in $AlPO_4$ (*32*), a possible decomposition product. A notable feature of this spectrum is the limited development of the background absorption consistent with the green appearance of the sample, implying that the presence of Al^{3+} may inhibit the reduction of W(VI) in the KU and/or WO_3.

d. $Na_3PW_{12}O_{40}$. The PAS spectrum of the sodium salt (200°C, Fig. 4a) is striking in its detail. The strong, sharp bands at 3590, 3537, and 1640 cm^{-1} are assigned to the stretching [asymmetric (ν_1) and symmetric

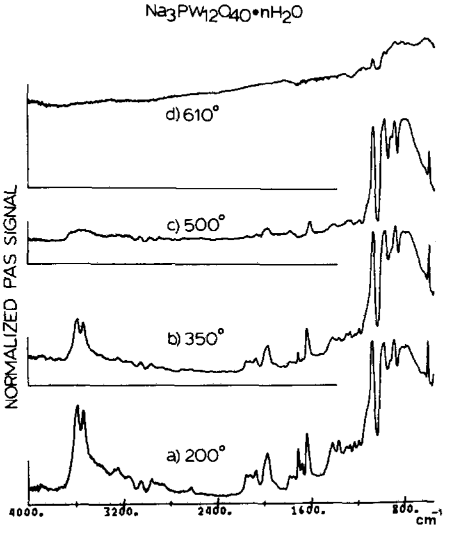

FIG. 4. Effect of heating $Na_3PW_{12}P_{40} \cdot nH_2O$ *in vacuo* (temp °C).

(ν_3)] and bending (ν_3) fundamentals of water, respectively. However, bands in the range ≈2200–1200 cm^{-1} are somewhat more difficult to assign. In view of the fact that this salt was prepared from the bicarbonate (*12*) it is possible that some bands may originate from contamination by HCO_3^-, or the more thermally stable CO_3^{2-} ion. The marked suppression of bands at 1715, 1680, 1420, and 1365 cm^{-1} on heating to 350°C (Fig. 4b) suggests their common origin in the latter species. The unperturbed CO_3^{2-} ion (D_{3h}) shows a doubly degenerate stretching vibration in the range 1500–1400 cm^{-1} which is split by unidentate (C_s) or bidentate (C_{2v}) coordination, the degree of splitting being greater in the latter case (*18*). By analogy with the findings of Bertsch and Habgood (*33*) in studies of CO_2 adsorption on alkali metal X-zeolites, the 1715, 1365 cm^{-1}, and 1680, 1420 cm^{-1} pairs are tentatively ascribed to bidendate CO_3^{2-} species having different strengths of coordination. The band at 1975 cm^{-1} is assigned to the first overtone of the P–O stretching fundamental, as a band appears around 2000 cm^{-1} in the spectra of all samples under investigation. The structured band centered at 2120 cm^{-1} is associated with lattice water as its intensity increases (together with those already assigned to it) when water is reabsorbed at 150°C. In view of its position, this band is tentatively ascribed to combination (difference) vibrations such as $\nu_1 - \nu_2$ and $\nu_3 - \nu_2$. The features in the KU band envelope resemble quite closely those of the ammonium salt and, hence, analogous peak assignments can be made. The XRD pattern confirms that the salt is cubic with a lattice parameter (a_0 = 11.94 Å) lying between those of the ammonium salt and parent acid. The anion structure appears quite stable with temperature. Up to 500°C (Fig. 4c), the only significant changes in this region are the development of shoulders at 1005 and 925 cm^{-1} on the two higher frequency W–O absorption bands. On further heating, the background absorption due to reduction of W(VI) develops progressively such that above 600°C (Fig. 4d) spectral detail is almost completely obscured and firm conclusions regarding anion stability are, unfortunately, precluded. However, on closer inspection, the tips of the intense peaks at 1083, 985, and 891 cm^{-1} are still present, indicating that the KU may still be intact but for some loss of oxygen.

2. *Acidity Characterization*

2a. Ammonia on $H_3PW_{12}O_{40}$. After pre-evacuation at 200°C, the uptake of NH_3 was large and rapid at room temperature, approaching ≈5 molecules/KU in 5 min. However, a significant fraction desorbed on heating in static vacuum above 150°C. To obtain a more accurate measure of the irreversibly sorbed component, smaller quantities of NH_3 were dosed stepwise at 150°C. Above 3 molecules/KU no further uptake occurred, implying penetration of NH_3 into the bulk and the formation of a stoichiometric salt, i.e.,

$$3NH_3 + H_3PW_{12}O_{40} \rightarrow (NH_4)_3PW_{12}O_{40} \quad (1)$$

Changes observed in the PAS spectrum of $H_3PW_{12}O_{40}$ upon stepwise addition of NH_3 provide strong support for this interpretation (see Fig. 5). With the development of bands (at ≈3200 and 1420 cm^{-1}) characteristic of the NH_4^+ ion and sharpening of the KU bands, the spectrum ultimately resembles that of the bulk salt (Fig. 2), notwithstanding the weak bands at 1700–1600 cm^{-1} suggestive of residual lattice water. Additional support derives from XRD which confirms that the cubic structure is retained and that the lattice parameter shrinks to that of the ammonium salt (a_0 = 11.71 Å). The progressive loss of the background continuum provides strong evidence that this feature owes its origin to the presence of mobile protons (see earlier). Little or no evidence can be seen for coordinately bound NH_3, indicating the absence of Lewis acidity (*34*).

In view of the strong interaction of NH_3 with $H_3PW_{12}O_{40}$ and the associated formation of a single new species, i.e., the NH_4^+

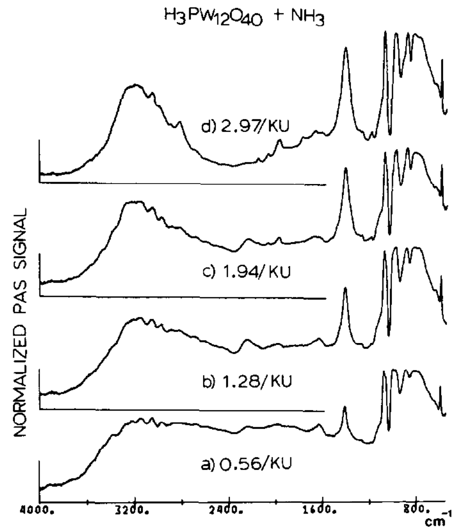

FIG. 5. Effect of dosing NH_3 (molecules sorbed/KU) stepwise at 150°C on $H_3PW_{12}O_{40}$ (preevacuated at 200°C).

ion, under the conditions described, this reaction serves as a useful model system to assess the quantitative capabilities of PAS–FTIR. On account of the influence of experimental variables, e.g., instrumental conditions, and particle size and thermal properties of the sample, absolute signal intensity is not particularly useful and some form of internal standardization is required. By analogy with other workers (*9*) the ratio of the integrated intensities of bands selected for the analyte and reference provides a parameter which, in principle, may be used for quantitative correlation. In the heteropoly compounds under examination, the P–O stretching fundamental at ≈1080 cm^{-1} appears to be most suitable as a reference band, notwithstanding its triply degenerate character and tendency to show structure in the parent acid. It is strong, reproducible in position and the best-resolved of all the bands in the KU envelope, hence facilitating good baseline estimation. For the NH_4^+ ion, the bending fundamental at 1420 cm^{-1} was preferred in view of its definition and position, having a low probability of interference from other bands, unlike the corresponding stretching vibration at ≈3200 cm^{-1}. The calibration curve for the peak area ratio A_{1420}/A_{1080} plotted versus sorbed NH_3 (molecules/KU) is presented in Fig. 6. The graph shows good linearity with possibly a slight negative deviation on approaching formation of the stoichiometric salt, indicating almost complete absence of photoacoustic signal saturation. This encouraging result led to initial application of the method to provide more diagnostic information concerning the thermal stability of $H_3PW_{12}O_{40}$ and the loss of background absorption on heating. The PAS spectra of $H_3PW_{12}O_{40}$ heated to 450°C (Fig. 1d) and dosed with NH_3 to form the stoichiometric salt (Fig. 5d) show almost equivalent background absorption, suggesting that if this feature originates from the protons, then heating to 450°C apparently causes their removal, possibly by the reaction

$$H_3PW_{12}O_{40} \xrightarrow[\text{vacuum}]{\Delta} H_{3-x}PW_{12}O_{40-x/2} + \frac{x}{2}H_2O \quad (2)$$

On dosing excess NH_3 onto the acid (pretreated at 450°C) and evacuation at 250°C,

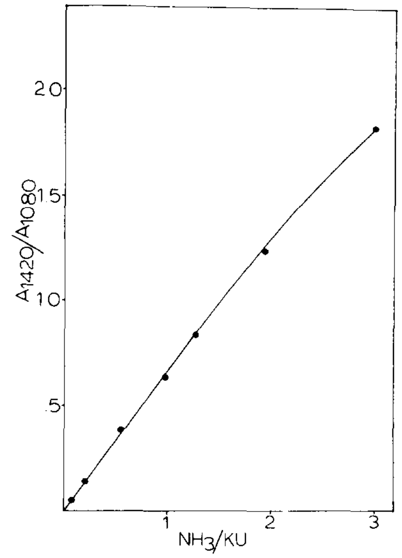

FIG. 6. Calibration curve of peak area ratio A_{1420}/A_{1080} versus sorbed NH_3 (molecules/KU) on $H_3PW_{12}O_{40}$.

the band at 1420 cm^{-1} due to NH_4^+ ion formation is still present but the area ratio A_{1420}/A_{1080} indicates the retention of only $\approx 1H^+$/KU, consistent with the above interpretation.

2b. Ammonia on the heteropoly salts. On comparison of relative peak heights in the PAS spectra of the ammonium salt with that obtained by dosing NH_3 on $H_3PW_{12}O_{40}$, it was suspected that this salt might be substoichiometric. When peak area ratios were measured and reference made to the calibration curve, this was indeed found to be the case, values falling typically around 2.4–2.6 NH_3 molecules/KU, implying precipitation in partial acid form. When the NH_4^+ salt was exposed to excess NH_3 at 250°C, after preevacuation at 350°C, the irreversible uptake (after evacuation at 150°C) was 0.4 molecules/KU, indicating absorption up to (almost) stoichiometric. The PAS spectra confirmed that only the NH_4^+ ion was formed and that the change in the peak area ratio A_{1420}/A_{1080} was consistent with the volumetric uptake.

To illustrate the value of NH_3 as a probe of residual Brønsted acidity in the heteropoly salts and the quantitative capabilities of PAS–FTIR, the above data is compiled (Table 1) together with corresponding results for the aluminum and sodium salts and comparison of the adjusted molecular formulae, as determined by NH_4^+ ion formation (assuming charge balance by the respective cations), with those calculated from the elemental analyses (assuming charge balance by protons). Inspection of Table 1 reveals that all the compounds under examination exist in partial acid salt form, the deviation from formal stoichiometry being particularly large for the aluminum salt. Except in the last case, volumetric data were quantitatively consistent with these estimates, indicating no association of NH_3 in unprotonated forms, a deduction supported by the absence of relevant bands in the PAS spectra. The aluminum salt absorbed ≈ 2.9 NH_3 molecules/KU, only about half of which formed the NH_4^+ ion. Inspection of the PAS spectrum (Figs. 7b,c) reveals new features at 1372, 1332, 1305 (medium, shoulders), 1285 (sharp, intense), and 685 cm^{-1}, none of which are assignable to NH_4^+. However, bands lying in the regions 1350–1200 and 900–600 cm^{-1} commonly appear in the spectra of metal–ammine complexes, being assigned to the nondegenerate symmetric deformation and rocking mode, respectively, of coordinated NH_3 (*35*). Perhaps more pertinent, the former assignment has been given to a band at ≈ 1230 cm^{-1} which appears when γ-Al_2O_3 is exposed to NH_3, being considered to derive from coordination to surface Al^{3+} ions (*36*). Eischens and Pliskin (*37*) have remarked that the symmetric deformation

TABLE 1

Nominal molecular formula	Residual proton content (H^+/KU) by PAS[a]	Adjusted molecular formula		
		As prepared[b]	Calculated from NH_4^+ formation[c]	Calculated from elemental analysis[d]
$(NH_4)_3PW_{12}O_{40}$	0.40	$(NH_4)_{2.4}H_{0.6}PW_{12}O_{40}$	$(NH_4)_{2.6}H_{0.4}PW_{12}O_{40}$	$(NH_4)_{2.6}H_{0.4}PW_{12}O_{40}$ [2.6% N]
$AlPW_{12}O_{40}$	1.45, 1.25	—	$Al_{0.55}H_{1.35}PW_{12}O_{40}$	$Al_{0.58}H_{1.26}PW_{12}O_{40}$ [0.55% Al]
$Na_3PW_{12}O_{40}$	0.32	—	$Na_{2.68}H_{0.32}PW_{12}O_{40}$	$Na_{2.88}H_{0.12}PW_{12}O_{40}$ [2.25% Na]

[a] Estimated from NH_4^+ formation (A_{1420}/A_{1080}).

[b] Calculated from NH_4^+ initially present.

[c] Assumed complete.

[d] Values in brackets are the means of duplicates.

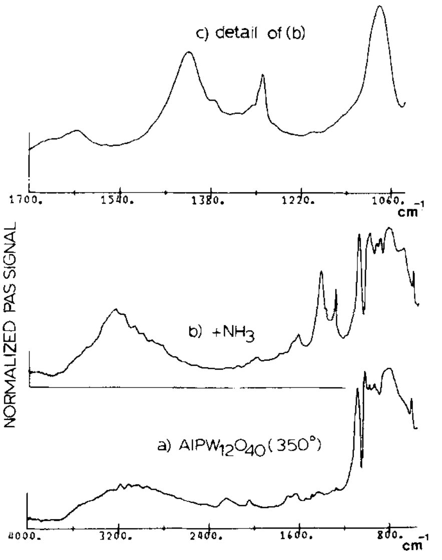

FIG. 7. (a) $AlPW_{12}O_{40}$ preevacuated at 350°C; (b) exposed to excess NH_3 at 250°C and evacuated at 150°C; and (c) spectral detail of (b) with wavenumber scale expanded for clarity.

band is quite sensitive to the strength of the coordinative bond and its position may provide a measure of the relative (Lewis) acid strength of the adsorption sites on a catalyst. Hence, in this case the structure observed in the region 1380–1280 cm^{-1} may represent a range of coordinative bond strengths between NH_3 and Al^{3+} ions in the bulk. Calculation indicates that each Al^{3+} ion is surrounded, on average, by ≈ 2.5 NH_3 molecules, this coordination number perhaps being controlled by steric factors. In view of its association in two distinct forms, i.e., protonated and coordinated, an indication of their relative bond strengths was obtained by dosing NH_3 in smaller quantity (0.3 molecules/KU). The NH_4^+ ion was formed selectively to the exclusion of the coordinated species, no bands appearing in the region 1380–1280 cm^{-1}.

DISCUSSION

The results obtained in this initial study on heteropoly compounds illustrate the promise of PAS–FTIR for catalyst characterization. PAS spectra have revealed that the absorption band envelope characteristic of the Keggin structure is unique to each compound and, hence, of analytical value. The band positions for the parent acid, and the NH_4^+ and Na^+ salts appear to correlate satisfactorily (± 10 cm^{-1}) with the corresponding values determined by other workers using conventional transmission spectroscopy, the reported variation among the latter being typically in the above range (*20, 38*). The absence of band broadening and shifts during the early stages of heat treatment suggest that the $PW_{12}O_{40}^{3-}$ ion is stable, apart from a small loss of O, at least up to 450°C, a temperature well above that typically used in methanol conversion, i.e., 350°C (*11–13*). However, $H_3PW_{12}O_{40}$ evidently loses protons *in vacuo*, beginning around 400°C, a result which finds support from independent studies using temperature-programmed desorption (*39*). This may provide an explanation for the marked influence exerted by the pretreatment conditions on the catalytic behavior of this compound in methanol conversion (*11*). If protons are lost by reaction with O atoms of the Keggin unit to form H_2O, as proposed, then activation in H_2 may be expected to inhibit this process by competing with protons for O. Accordingly, treatment in H_2 at 450°C results in a yield of hydrocarbon products greater than that obtained after similar treatment in He, and far superior to that obtained after heating in air at 400°C.

Perhaps the most important aspect of this study as regards catalysis is the discovery that all the salts possess varying amounts of Brønsted acidity. Hence, the development of preparational methods which allow control over the cation/proton ratio would be of particular value in fundamental studies into the influence of this ratio and the effect of the cation (in different salts at equivalent proton concentration) on the activity and selectivity in methanol conversion. Certainly, the evidence obtained here indicates that there is at least a qualitative correlation of activity with Brønsted acidity as recently suggested from estimates of partial charge on the oxygen atoms of the Keggin unit (*12*). The agreement between the molecular formulae calculated from NH_4^+ ion formation and by elemental analysis is relatively good and serves to confirm the reliability of the PAS method developed here for quantitative work. Thus, the Al^{3+} and NH_4^+ salts show significant deviation from formal stoichiometry and are known to exhibit high activities in the conversion of methanol to hydrocarbons. The Na^+ salt, however, shows a degree of nonstoichiometry similar to that of the NH_4^+ salt, but is only slightly active, behaving essentially as a dehydration catalyst (*12*). This result may indicate that only a small fraction of the protons in the Na^+ salt are accessible for catalytic purposes, a reasonable conclusion in view of their large surface area difference (~5 and 150 $m^2 g^{-1}$ for Na^+ and NH_4^+ salts, respectively). Compared to the Al^{3+} salt, the somewhat lower yield of hydrocarbons over $H_3PW_{12}O_{40}$ appears to stem from the selectivity of the free acid (carbonization being prevalent (*11*)) rather than to any intrinsic difference in activity. Poisoning of the activity of the NH_4^+ salt by prior exposure to NH_3 (*13*) can now be readily understood, NH_3 simply reacting with residual protons to form the stoichiometric salt. Additional evidence that Brønsted acid sites are primarily responsible for methanol conversion over heteropoly compounds (and ZSM-5 zeolites) stems from the hydrocarbon product distribution, which implies that this reaction proceeds via a carbonium ion mechanism (*11–13, 40*). The spectroscopic evidence from this work indicates that Lewis acidity is neither present (with one exception) nor evidently required for this reaction. It is interesting to note that the Al^{3+} salt, which is shown here to possess both Brønsted (H^+) and Lewis (Al^{3+}) acid centers, also produces about half the hydrocarbon yield of the NH_4^+ salt under equivalent reaction conditions (*12, 13*) despite the large difference (×30) in their surface areas (5 $m^2 g^{-1}$ for the Al^{3+} salt). Its special catalytic behavior may be related not only to the presence of Lewis acid sites, but also to the greater accessibility of protons in the bulk. The reported ionic radii of Al^{3+} (0.53 Å) and NH_4^+ (1.50 Å) (*41*), the cation/anion ratios in the respective salts (0.6 Al^{3+}/KU; 2.5 NH_4^+/KU) and their lattice parameters [a_0 = 12.135 Å (Al^{3+}); a_0 = 11.71 Å (NH_4^+)] all indicate that there is greater (cation) space available in the former salt to facilitate bulk diffusion by reactants and products within a certain size range. However, until information has been obtained concerning their respective Brønsted acid strength (best probed using a weaker base such as pyridine (*34*)), the origin of their selectivity differences (the NH_4^+ salt producing more paraffinic products) remains speculative. Nonetheless, the distinction between surface and bulk selectivity has been recognized by other workers, who observed the recovery of diethyl ether and ethylene, respectively, from the dehydration of ethanol over $H_3PW_{12}O_{40}$ (*42*).

The ease of penetration of NH_3 into the bulk of $H_3PW_{12}O_{40}$ and its related salts, as inferred from Brønsted acidity determinations and assuming a homogeneous distribution of protons, is a remarkable property which may be characteristic of heteropoly compounds in general. From molecular size considerations, methanol (and its likely intermediate dimethyl ether (*11*)) may be expected to show diffusional behavior lying between that of NH_3 and a larger base such as pyridine. Hence, study of the effects of selective poisoning (*34*) using such basic probe molecules should elucidate the role played by the bulk; assess the influence, if any, of Lewis acidity (as in the Al^{3+} salt) and correlate any associated trends in the product distribution, e.g., the interstitial space in the bulk may exert control over the molecular size of products by analogy with the "shape-selective" character of the ZSM-5 zeolite catalyst (*43*).

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