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Elucidation of the Mechanism of Dehydration of Methanol over 12-Tungstophosphoric Acid Using Infrared Photoacoustic Spectroscopy

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Photoacoustic Fourier-Transform Infrared Spectroscopy (PAS-FTIR) has been used to study the interaction of CH_3OH with 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) and the related Na^+ salt, in the temperature range 25–150°C. Preliminary catalyst screening using a static reactor demonstrated that under these conditions, dehydration is the exclusive reaction, and indicated that Brønsted acidity is the primary factor in catalyzing this process. Dimethyl ether (DME) is already detectable at 60°C over $H_3PW_{12}O_{40}$, while the Na^+ salt is barely active up to 150°C. PAS-FTIR has revealed that the first step in the mechanism is protonation of sorbed CH_3OH at 25°C to form the $CH_3OH_2^+$ intermediate. The role of the proton is evidently to facilitate the thermally induced cleavage of the C–O bond, which has been identified as the rate-determining step, leading to methylation of the Keggin unit and H_2O formation. The cycle is completed via rapid electrophilic attack at the O atom of physisorbed CH_3OH by the surface CH_3 group, yielding DME and regenerating the proton. Evidence is presented for the partial retention of DME, probably in protonated form, and correlated with the observed reversible inhibition of dehydration by this product.

INTRODUCTION

Heteropoly compounds are finding increasing application as both homogeneous and heterogeneous catalysts in a range of oxidation and acid catalyzed reactions (*1*). In the latter category, the conversion of methanol to hydrocarbons is of particular interest in view of the current energy shortage (*2*), and solid heteropoly compounds show promise as catalysts for this process (*3, 4*). It now appears generally accepted that methanol undergoes a preliminary dehydration step, and that dimethyl ether (DME), or an equilibrium mixture of DME and methanol, acts as the precursor to hydrocarbon formation (*2, 4a*). Several workers (*5, 6*) have shown that dehydration typically proceeds at significantly lower temperatures than hydrocarbon formation and is, therefore, amenable to independent study.

Conventional transmission IR spectroscopy has previously been used to investigate methanol conversion over a range of zeolites in their acid (H)-form (*5–7*). However, despite the proposal by Ono and Mori (*6*) that the mechanism is probably the same over zeolites and heteropoly acids, no direct IR studies have been reported over the latter.

Photoacoustic Fourier-Transform Infrared Spectroscopy (PAS-FTIR) has recently been utilized by the authors to provide information concerning the structure, stability, and acidity of 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$, and related salts (*8, 9*). This rapidly developing technique, which enables direct acquisition of optical absorption spectra from opaque and powdered samples, has revealed a strong correlation between Brønsted acidity and activity in methanol conversion. In this paper, we report the application of PAS-FTIR to examine the preliminary interaction of methanol with 12-tungstophosphoric acid in the tem-

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perature range over which hydrocarbon formation is negligible, i.e., 25–150°C. Results are compared with those for the sodium salt of the parent acid, selected on the basis of its low (and weak) Brønsted acidity and correspondingly poor catalytic activity (*4*, *8*, *9*).

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 equipped with a slightly modified commercial photoacoustic detector. Sample pretreatment, loading, and instrumental conditions were as previously described (*8*), except a lower mirror velocity ($V = 0.02$ cm sec^{-1}) was utilized to give further improvement in spectra quality. 12-Tungstophosphoric acid, $H_3PW_{12}O_{40}$ $29H_2O$ (AnalaR, BDH), was used without further purification. The preparation of the sodium salt (*4a*) (nominal formula $Na_3PW_{12}O_{40} \cdot nH_2O$) and the methylammonium salt (*10*) (nominal formula $(CH_3NH_3)_3PW_{12}O_{40} \cdot nH_2O$) have been described elsewhere. Reagents methanol, CH_3OH (Photrex, J. T. Baker); deuteromethanol, CD_3OH (99.6% isotopic purity, Merck, Sharp & Dohme), dimethyl ether (DME), CH_3OCH_3, and ammonia, NH_3 (anhydrous, 99.99%; Matheson) were subjected to several freeze–pump–thaw cycles to remove contaminant gases prior to use. The methanols were kept dry over activated molecular sieve 3A while DME and ammonia were predried by trap-to-trap distillation. Uptakes were measured volumetrically and expressed, for convenience, as molecules sorbed per Keggin unit ($PW_{12}O_{40}^{3-}$) and/or per proton in the case of the acid.

Qualitative catalytic studies were performed in a static reactor. Samples (typically 1–2 × 10^{-4} mole, preevacuated at 330–350°C) were contacted directly with excess methanol (1–2 × 10^{-3} mole, 80–100 Torr) at the reaction temperature. Dehydration activity was monitored periodically by the trapping of all ambient gas at 77 K, isolation of the condensate, followed by evaporation and selective retrapping of unreacted methanol and product water at −65°C in order to measure product DME.

Desorption of CH_3OH was monitored gravimetrically and the total recovery was confirmed by trapping and volumetric determination at the end of each run. Detailed spectral investigations into the effect of temperature on the "irreversibly sorbed" methanol component were accompanied by trapping and volumetric quantitation of desorbed gases. Following the procedure described above for the estimation of DME, desorbed (unreacted) methanol was distinguished from water by selective trapping of the latter at −20°C, and quantitated after correction for any DME present. After identification of the above three components and confirmation of the absence of hydrocarbons by GLC (*4a*), water was determined by difference.

Catalytic Studies

(*a*) *Na^+ salt.* Activity in CH_3OH dehydration over this salt was just detectable at 150°C with a mean conversion rate of ~0.5% per hour. No hydrocarbons were detected by GLC.

(*b*) *$H_3PW_{12}O_{40} \cdot nH_2O$.* In contrast to the Na^+ salt, the threshold temperature for the onset of measurable dehydration activity was found to be as low as ~60°C, and the expected trend of increasing rate with temperature, characteristic of a kinetically controlled reaction, is illustrated in Table 1. However, it can also be seen that the rate fell significantly in the initial stages, suggesting the possibility of the irreversible loss of active sites and/or the inhibition of reaction by product formation. To examine this effect, the DME accumulated after 60 min reaction at 150°C (Experiment (a)) was selectively evacuated at −65°C, and the new rate (in parentheses, at $t = 10$ min) was now close to the initial value. The suppression of activity in the presence of DME was further confirmed in a separate experiment

TABLE 1

Reaction temp (°C)	Conversion (% in reaction time, *t*, min)[a]						
	5	10	15	20	30	45	60
60							2.1
65							3.2
70			2.9			5.0	
80			7.5		11.7		17.2
150(a)[b]	7.0	10.0(12.0)[b]		15.0	18.5		31.3
150(b)[b]		8.0 11.0 9.9 12.7					

[a] Conversion (%) is defined as $[2Q_{\mathrm{DME}}/Q^{\mathrm{init}}_{\mathrm{CH_3OH}} \times 100]$.

[b] See text.

at 150°C, starting with an initial reaction stoichiometry $CH_3OH:DME \simeq 3:1$ ($P \sim 120$ Torr). No high initial dehydration activity was observed and the mean rate was estimated to be ~3% per hour, markedly lower than in Experiment (a).

The effect of H_2O was examined in Experiment (b), in which DME was removed after each (10 min) reaction step. The activity showed no significant trend with accumulation of product H_2O, any variation in rate probably reflecting experimental reproducibility. A similar data set (not shown) as obtained when Experiment (b) was repeated with an initial reaction stoichiometry $CH_3OH:H_2O \simeq 5:1$ ($P \sim 120$ Torr) providing further evidence that H_2O had no significant effect on dehydration activity.

No hydrocarbon products were detected by GLC in any of the above experiments.

Sorption of CH_3OH and Characterization by PAS

a. Na^+ salt. After preevacuation of the solid at 350°C, the uptake of CH_3OH at 25°C was large and rapid (~5 CH_3OH/KU in 5 min), reaching a limit of 6.3 CH_3OH/KU in ~1 h. Upon evacuation for 1 h (with trapping at 77 K), 60–70% of the sorbate was removed from the solid. On heating up to 150°C in static vacuum, the remainder was readily desorbed in ~30 min. No DME was detected in the isolated gas upon cooling to −65°C and GLC analysis confirmed its identity as unreacted CH_3OH. The result is evidently consistent with the previous observation of an extremely low rate of dehydration over this salt.

A typical PAS spectrum of sorbed CH_3OH (3.3/KU) is shown in Fig. 1b. Compared to the spectrum of the preevacuated salt (Fig. 1a), additional bands may be seen at 3560, 2960, 2845, 1470, and 1350 cm^{-1}. Unobscured features of the original salt, e.g., the deformation band of lattice H_2O at 1640 cm^{-1}, and the band envelope characteristic of the Keggin unit below 1100 cm^{-1} (*8*) appear essentially unperturbed. Thus, spectral subtraction in Fig. 1, (b) − (a), normalized at 800 cm^{-1}, yields spectrum (c), which may be considered representative of sorbed CH_3OH alone. The spectrum exhibits features which generally correspond to those reported by Falk and Whalley (*11*) for CH_3OH in a range of physical states, but the combination of details observed here appears unique to the sorbed species. Following these authors, the structured absorption band centered at 3540 cm^{-1} is assigned to the OH stretching vibration (ν_{OH}). In view of its position, intermediate be-

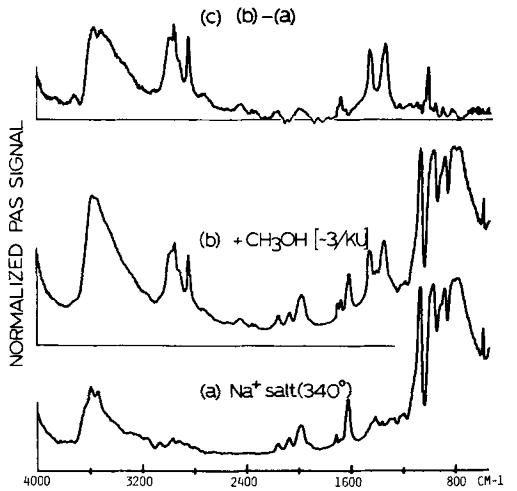


FIG. 1. (a) Na^+ salt of 12-tungstophosphoric acid, preevacuated at 340°C, then (b) exposed to excess CH_3OH at 25°C for 1 h, and reevacuated at 25°C for 10 min; (c) difference spectrum, (b) − (a), normalized at 800 cm^{-1}.

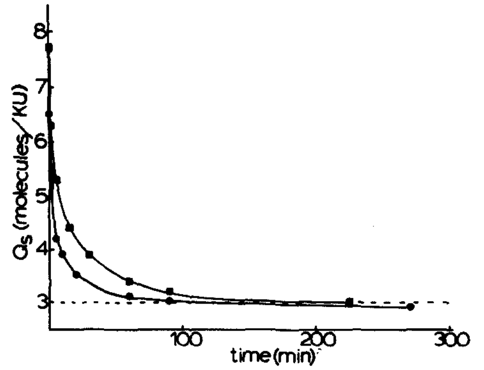


FIG. 2. Typical desorption curves for CH_3OH on 12-tungstophosphoric acid (preevacuated at 330–350°C), dosed in excess at 25°C and evacuated at 25°C.

tween that of gas-phase (~3680 cm^{-1}) and liquid-phase (~3340 cm^{-1}) CH_3OH, it may be inferred that there is only a weak H-bonding interaction. The origin of the doublet structure (3562, 3506 cm^{-1}) in this band is uncertain. A similar splitting has been observed in the corresponding band ($\bar{\nu}_{OH} \approx 3240$ cm^{-1}) in the solid state and attributed to an intermolecular H-bonded zigzag chain structure (*11*), but the wide discrepancy in mean band positions militates against this interpretation. Indeed, as the splitting is still evident at significantly lower CH_3OH loadings (<1/KU), it appears more likely that the effect is intramolecular in origin. The position of the corresponding OH in-plane deformation band ($\delta_{OH} \approx 1360$ cm^{-1}), shifted slightly (~15 cm^{-1}) to higher wavenumbers relative to gas-phase CH_3OH, is also indicative of weak H-bonding (*12*). The bands at ~2950 and 2845 cm^{-1} are assigned to the CH_3 asymmetric and symmetric stretching vibrations, respectively, the structure in the former band being tentatively attributed to Fermi-resonance interaction with an overtone or combination involving CH_3 deformation vibrations. The incompletely resolved doublet at 1460 cm^{-1} is assigned to the asymmetric and symmetric modes of the latter. Interestingly, spectral subtraction has revealed the C–O stretching vibration at 1026 cm^{-1} despite being almost completely hidden under the intense KU absorption. Its lower relative intensity compared to that observed both in PAS (*13*) and literature (transmission) spectra (*11*) of gas- and liquid-phase CH_3OH is probably an artifact associated with the PAS technique, i.e., partial photoacoustic saturation (*9*).

b. $H_3PW_{12}O_{40}$. After preevacuation of the solid at 350°C, the uptake of CH_3OH at 25°C was large and rapid (~4–5 CH_3OH/KU in 5 min), reaching a limit ranging from 6 to 8/KU after 1–2 h, depending on the residual pressure. Typical desorption curves, upon evacuation at 25°C (trapping at 77 K), are shown in Fig. 2. The high initial rate of desorption fell almost exponentially such that after 1–2 h, very little change was observed in the sorbed component, Q_s, amounting to ~3 CH_3OH/KU, or 1 CH_3OH/H^+. The PAS spectrum at this stage (Fig. 3b) shows significant changes from that of the original acid (Fig. 3a). New bands are evident in the region ~1750–1300 cm^{-1}, superimposed on a background continuum similar to that observed previously in the hydrated acid (*8*).

Contemporaneously, the band at 2240 cm^{-1} has almost disappeared while the KU band envelope (below ~1200 cm^{-1}) is relatively unaffected. Assuming the bands from 1750 to 1300 cm^{-1} are deformation vibrations associated with sorbed CH_3OH, it is somewhat surprising that the corresponding stretching vibrations are ostensibly so weak. However, the large bandwidths of the deformation vibrations (at ~1535 and 1405 cm^{-1}; Fig. 3c) show that the sorbate is here subject to strong H-bonding interaction, and as this phenomenon is widely reported to effect greater broadening and shifts in stretching bands (*12*), it is possible that the latter have effectively merged with the continuum. Apart from the obvious spectral differences compared to CH_3OH sorbed on the Na^+ salt (Fig. 1b), additional evidence that these H-bonding effects originate from the association of CH_3OH with the protons of the acid derives from the development of the continuum, which has

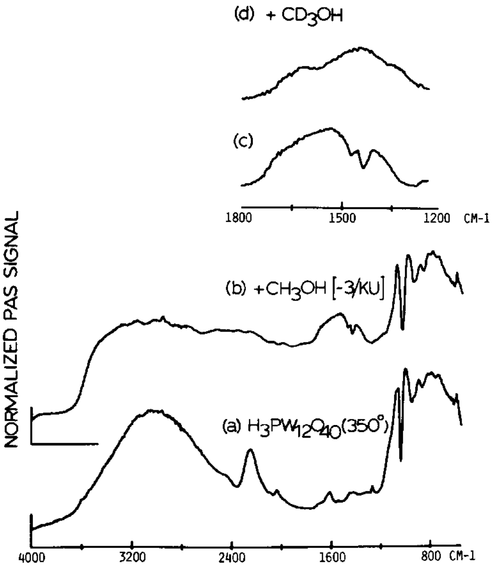
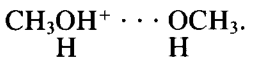


FIG. 3. (a) 12-Tungstophosphoric acid, preevacuated at 350°C, then (b) exposed to excess CH_3OH at 25°C for 1 h, and reevacuated at 25°C for 2 h; (c) detail of (b); (d) corresponding detail of spectrum derived from equivalent treatment of the acid with CD_3OH shown for comparison.

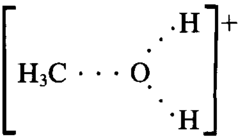
previously been attributed to increased proton mobility (*8*). Similar continua have been reported for Brønsted acids in methanol (*14*) and attributed to an intermolecular interaction of the type



$$\underset{\displaystyle H}{CH_3OH^+} \cdots \underset{\displaystyle H}{OCH_3}.$$

Evidence that the continuum in Fig. 3b originates from a similar interaction in the bulk solid has been found by varying the CH_3OH loadings. At a molar ratio $CH_3OH : H^+ \simeq 2$, the continuum intensifies relative to that in Fig. 3b, whereas at a ratio $\simeq 0.3$, it is virtually absent. However, the characteristic deformation band envelope is still discernible in the latter spectrum (*13*), indicating that this feature owes its origin primarily to an intramolecular H-bonding interaction. The stoichiometry of the "irreversible" uptake (1 CH_3OH/H^+) suggests the formation of the intramolecular complex $CH_3OH_2^+$.

Infrared evidence for the existence of a structure such as



$$\left[H_3C \cdots O \begin{matrix} \cdot H \\ \\ \cdot H \end{matrix} \right]^+$$

may be seen in spectrum c (Fig. 3) and in the corresponding spectrum of sorbed d_3-methanol. Making the simplifying assumption that this molecular ion is effectively an example of a planar $ZXY_2(C_{2v})$ system (Z = CH_3 or CD_3), group theory predicts two active deformation modes (asymmetric and symmetric) in the infrared, involving the ZXY or, in this case, the COH grouping (*15*). This is most clearly illustrated in the case of sorbed CD_3OH (Fig. 3d) which shows a broad band centered at ~1460 cm^{-1}, with a broad shoulder at ~1360 cm^{-1}. By virtue of its higher wavenumber, the former band is tentatively assigned to the asymmetric mode (*15*). The CD_3 deformation and C–O stretching bands almost certainly do not interfere, lying typically below ~1120 cm^{-1} and around 980 cm^{-1}, respectively, while the OH in-plane deformation in CD_3OH ranges from 1500 to 1300 cm^{-1} (depending on its physical state), showing an unstructured band at 1391 cm^{-1} in the liquid (*11*). In view of the well-known susceptibility of OH bands to shifts and broadening via H-bonding, and its similarity to the 1460-cm^{-1} band in $CD_3OH_2^+$, the band at 1535 cm^{-1} in spectrum c (Fig. 3) is assigned to the asymmetric COH deformation in $CH_3OH_2^+$, while the symmetric mode is believed to lie around 1430 cm^{-1} but is obscured by the sharp feature just discernible at 1453 cm^{-1}, characteristic of CH_3 (see below), and the 1405-cm^{-1} band. The discrepancy in position of these bands relative to the equivalent bands in $CD_3OH_2^+$ is not unexpected as a corresponding displacement has been observed in the OH in-plane deformation in the unprotonated species and attributed to coupling, probably with $CH_3(CD_3)$ rocking modes (*11*). The band at 1405 cm^{-1}, asymmetrical in appearance, is believed to be the CH_3 deformation band envelope (symmetric and asymmetric) in $CH_3OH_2^+$. It has been broadened and shifted to lower wavenumbers relative to CH_3OH physisorbed on the Na^+ salt (Fig. 1c), possibly through coupling with the C–O stretching vibration. The C–O bond is almost certainly weakened through protonation at the O atom and its corresponding absorption band would be expected to be broadened and shifted to lower wavenumbers. In accordance with this suggestion, no associated band can be reliably detected below 1100 cm^{-1}, even by subtraction techniques.

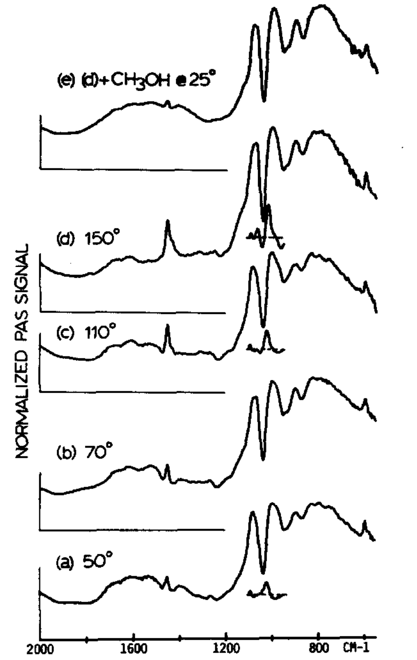


FIG. 4. Effect of stepwise heating *in vacuo* on spectrum of "irreversibly sorbed" CH_3OH on 12-tungstophosphoric acid. (a) 50°C, (b) 70°C, (c) 110°C, (d) 150°C (inset peak obtained by subtraction of spectrum of preevacuated acid (Fig. 3a), normalized at 1080 cm^{-1}), (e) effect of dosing (d) with excess CH_3OH at 25°C and evacuation at 25°C.

Heating under static vacuum caused significant spectral changes which showed an interesting correlation with the composition of the desorbate. At 50°C, CH_3OH (0.1/H^+) and H_2O (0.1/H^+) were detected in the cold trap and the PAS spectrum (Fig. 4a) revealed the selective loss of the broad bands at 1535 and 1405 cm^{-1} and the development of a sharp band at 1453 cm^{-1}, whose position lies in the range expected for the CH_3 symmetric deformation in the CH_3O group (*11, 16*). Up to 70°C (Fig. 4b), this band continued to develop at the expense of the other two and a small quantity of DME (~0.04/H^+) was recovered in addition to CH_3OH and H_2O (~0.20/H^+, and ~0.16/H^+) was recovered in addition to CH_3OH and H_2O (~0.20/H^+, and ~0.16/H^+, cumulative totals, respectively). Up to 150°C, this spectral trend continued (Figs. 4c,d) with the original bands (at 1535 and 1405 cm^{-1}) finally disappearing and a shoulder at ~1435 cm^{-1} becoming evident as the 1453-cm^{-1} band intensified. No additional recovery of CH_3OH was observed and DME comprised an increasing fraction of the total product. At this stage, however, the quantity of "residual CH_3" on the solid was estimated (from material balance) to be ~0.5 CH_3/H^+, or still roughly half the initial loading. Furthermore, the DME/H_2O product ratio (~1 : 3) was markedly below the stoichiometric ratio for sustained dehydration (1 : 1). Further spectral evidence for thermally activated dissociation of the C–O bond in the $CH_3OH_2^+$ complex, with concomitant formation of a surface methoxy group, was obtained by subtraction of the room-temperature spectrum (Fig. 3c) from that of the heat-treated sample at each stage. The progressive development of a band at 1022 cm^{-1} (inset, Fig. 4) suggested the increasing formation of a metal alkoxide-type structure. The C–O stretch in transition metal methoxides is reported to lie typically in the region 1100–1000 cm^{-1} (*17*) and, more specifically, appears at 1070 cm^{-1} in $W(OCH_3)_6$ (*18*).

After exposure of the sample (150°C pretreatment, Fig. 4d) to excess CH_3OH at 25°C for 5 min, a significant amount of DME (~0.2/H^+, or ~0.6/KU) was recovered, showing that the active intermediate in CH_3OH dehydration has already been produced in the thermal pretreatment step, and that it reacts rapidly with CH_3OH in a subsequent step. However, warming up to 50°C produced only a slight increase (0.02/H^+) in the yield of DME, indicating that a certain fraction of the "residual CH_3" was markedly less reactive to CH_3OH. The PAS spectrum after 25°C exposure (Fig. 4e) confirmed this suspicion in revealing incomplete removal of the 1453-cm^{-1} band, along with regeneration of the broad envelope characteristic of $CH_3OH_2^+$.

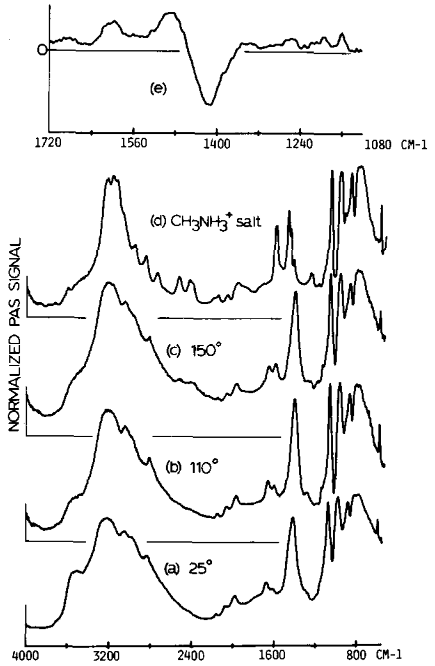


FIG. 5. Effect on the spectrum of preheating "irreversibly sorbed" CH_3OH on 12-tungstophosphoric acid prior to addition of NH_3 (~1.1/H^+). (a) At 25°C, (b) and (c) at 100°C, (d) $CH_3NH_3^+$ salt (preevacuated at 215°C) for comparison, (e) difference spectrum, [(c) − NH_4^+ salt spectrum; (see Fig. 5d in Ref. (*8*)], normalized at 1080 cm^{-1}.

To provide further characterization of the sorbed species, a series of experiments were performed in which CH_3OH was presorbed at 25°C, evacuated with or without heating as above, and then exposed to NH_3 in slight excess of stoichiometric (typically 1.1 NH_3/H^+) over a range of temperature. The uptake of NH_3 at 25°C, after preexposure to CH_3OH at 25°C, was initially thought to be below stoichiometric (0.7/H^+) but GLC analysis showed the identity of the residual gas to be CH_3OH, evidently displaced by the incoming base. The PAS spectrum (Fig. 5a), with strong bands characteristic of the NH_4^+ ion at ~3200 and 1420 cm^{-1}, resembled that observed previously in the absence of presorbed CH_3OH (*8*). However, the broad band at ~3540 cm^{-1} appeared to correspond to the OH stretching band of physisorbed CH_3OH, as seen in the Na^+ salt (Fig. 1c). It was also significant that the band envelope centered at 1520 cm^{-1}, characteristic of presorbed CH_3OH (Fig. 3c), disappeared along with the continuum. When the order of exposure was reversed in a separate experiment, a virtually identical spectrum (to Fig. 5a) was obtained, thereby confirming the origin of the 3540-cm^{-1} band. Thus, the ready displacement of CH_3OH by NH_3, with accompanying formation of NH_4^+, substantiates the view that the alcohol is initially H-bonded to the proton, remaining in undissociated form at 25°C, probably as $CH_3OH_2^+$. Heating up to 150°C caused no change in the NH_4^+ bands, but resulted in attenuation of the 3540-cm^{-1} band and further recovery of displaced (probably weakly H-bonded) CH_3OH. No evidence was found for dehydration activity in this step. The effect of heating presorbed CH_3OH up to 150°C, prior to exposure to NH_3 at 100°C, produced interesting trends in the PAS spectrum (Figs. 5b,c). The 3540-cm^{-1} band became progressively less intense, the structured N–H stretching band at ~3200 cm^{-1} became sharper, and a band developed at 1610 cm^{-1}. As the uptake of NH_3 was observed to be very close to stoichiometric (3.0 ± 0.1 NH_3/KU), with little or no displacement of CH_3OH into the gas phase, these spectral trends must be related to the pretreatment step, which effectively reproduced the changes already seen in the previous experiment (Figs. 4a–d). This result provides strong supporting evidence that $CH_3OH_2^+$ dissociates on heating to yield chemisorbed methyl and/or methoxy groups, some of which are highly active intermediates in the dehydration process. The PAS reference spectrum of $(CH_3NH_3)_3PW_{12}O_{40}$ (Fig. 5d) provides an additional clue as to the nature of the intermediate. The most distinctive differences between the spectra of the $CH_3NH_3^+$ and NH_4^+ salts are the sharper N–H stretching band envelope, the presence of the NH_3^+ degenerate and symmetrical deformation at 1610 and 1490 cm^{-1} (*19*) (the latter probably overlapped by CH_3 deformation bands), and the absence of the N–H deformation at 1420 cm^{-1} in the former. Clearly, spectra b and c in Fig. 5, show a progressive resemblance to the $CH_3NH_3^+$ salt, although the 1420-cm^{-1} band remains a dominant feature, and subtraction of the NH_4^+ salt spectrum from Fig. 5c (normalized at 1080 cm^{-1}) yields a revealing difference spectrum of the deformation region (Fig. 5e). The two bands characteristic of the NH_3^+ group are clearly evident while the negative band at 1420 cm^{-1} implies that the NH_4^+ ion loading is below 3 NH_4^+/KU, despite the volumetric evidence for stoichiometric uptake of NH_3. These results demonstrate that the CH_3 group, probably existing in surface methoxy form, behaves in a manner similar to that expected for the methyl carbonium ion, CH_3^+, upon exposure to NH_3 (with which it would be expected to undergo rapid reaction to form the $CH_3NH_3^+$ ion), and further suggest that its creation is accompanied by removal of a proton. More quantitative support for this interpretation has been obtained from estimates of the amounts of both cations present, i.e., $CH_3NH_3^+$ and NH_4^+, according to Fig. 5c. The former, calculated from the peak area ratio A_{1610}/A_{1080} relative to that of the $CH_3NH_3^+$ salt (assuming full stoichiometry in the reference and no serious saturation effects (*8, 9*)), was found to be 0.55 $CH_3NH_3^+$/KU, or ~20% of the total cation loading. The latter, obtained similarly from A_{1420}/A_{1080} (*8*) after correction for the minor (~10%) contribution from overlapping $CH_3NH_3^+$ deformation bands, was found to be 2.37 NH_4^+/KU, or ~80% of the total cation loading. These self-consistent estimates, which are considered reliable as they were obtained independently, reveal the equivalence between CH_3^+ ion creation and proton elimination with clear mechanistic implications. Perhaps of equal significance is the striking consistency between the amounts of DME and $CH_3NH_3^+$ ion produced on exposure of identically treated samples to CH_3OH (as described earlier) and NH_3, respectively, which suggests that the active intermediate in CH_3OH dehydration is indeed the CH_3^+ ion. Spectral evidence that CH_3OH and NH_3 react with the same intermediate was obtained by subsequent exposure of the sample yielding DME (by preexposure to CH_3OH at low temperature, Fig. 4e) to NH_3. The spectrum resembled closely Fig. 5a, in showing NH_4^+ ion formation and displaced CH_3OH, and the subtraction technique (as in Fig. 5e) failed to reveal any bands characteristic of the $CH_3NH_3^+$ ion (*13*).

DISCUSSION

The experimental correlation between Brønsted acidity and catalytic activity in the overall process of methanol conversion to hydrocarbons over zeolites (*2, 5, 6*) and heteropoly compounds (*4, 6, 8*) is already well established. However, the specific role(s) played by such active sites is still the subject of much controversy (*2*). The catalytic data obtained in the present work on 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$, and the Na^+ salt of the parent acid has clearly demonstrated the link between Brønsted acidity and the dehydration of methanol to dimethyl ether over heteropoly compounds. Spectral studies by PAS have revealed, in some detail, the mode of interaction of CH_3OH with $H_3PW_{12}O_{40}$ at room temperature, the thermal stability of the sorbed species so formed, and the nature of the active intermediate produced by such treatment. Based on an overview of all relevant data, the following reaction mechanism is proposed for the dehydration of

CH_3OH over $H_3PW_{12}O_{40}$:

$$CH_3OH + H^+ \cdots O_{KU}^{2-} \xrightarrow[\text{fast}]{25^\circ C} CH_3OH_2^+ \cdots O_{KU}^{2-} \quad (1)$$

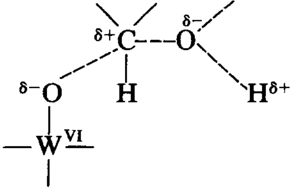
$$\left[\begin{array}{l} CH_3OH_2 + \xrightarrow[\text{slow}]{50\text{–}150^\circ C} CH_3^+ + H_2O \quad (2) \\ CH_3^+ + O_{KU}^{2-} \xrightarrow[\text{fast}]{} CH_3O_{KU}^- \quad (3) \end{array}\right]$$

$$CH_3O_{KU}^- + CH_3OH \xrightarrow[\text{fast}]{25^\circ C} CH_3OCH_3 + H^+ \cdots O_{KU}^{2-} \quad (4)$$

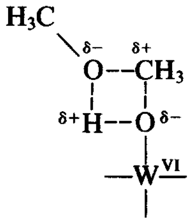
where O_{KU}^{2-} is a simplified representation of an O ion in the Keggin unit.

This mechanism is similar to that proposed for CH_3OH dehydration over H-Y zeolite by Salvador and Kladnig (*5*) but with some differences in detail. In step (1), CH_3OH is rapidly bound to the catalyst via a strong H-bonding interaction with the proton, forming the molecular ion $CH_3OH_2^+$. To postulate the existence of this species is certainly not new. It has been implicated in the mechanism of proton exchange on SiO_2, based on NMR relaxation and dielectric absorption data (*20*), and cited by Salvador and Kladnig as a short-lived intermediate in methoxylation of the SiO_2 surface. However, the IR spectroscopic characterization work presented here provides, perhaps, the most substantial evidence to date for its existence as a stable intermediate in a catalytic system. A similar IR band envelope in the region 1600–1400 cm^{-1}, characteristic of $CH_3OH_2^+$ (cf. Fig. 3c), has previously been reported for CH_3OH on H-T zeolite at 25°C (*7*), but the author attributed this to what is referred to as "surface methoxylation" with the concomitant production of H_2O. In the present work, the effects of thermal treatment and displacement of CH_3OH by NH_3 militate strongly against surface methylation at 25°C over $H_3PW_{12}O_{40}$, except perhaps to a very slight extent as indicated by the weak band at 1453 cm^{-1} in Fig. 3c. The detection and identification of $CH_3OH_2^+$ is evidently facilitated here by the unique conditions existing in the system under investigation. First, despite $CH_3OH_2^+$ being relatively acidic ($pK_a \approx -2$ to -4 (*21*)), the extremely high acidity of preheated $H_3PW_{12}O_{40}$ (*4a, 22*) should ensure almost quantitative protonation of a stoichiometric dose of CH_3OH under equilibrium conditions, as is observed. Second, the high $[CH_3OH_2^+]/[CH_3OH]$ ratio, together with steric and electrostatic restrictions imposed on alcohol and cation mobility, respectively, in the bulk solid would be expected to inhibit proton-exchange processes and thereby restrict the associated development of an unacceptably strong background continuum (*21*). Kampschulte-Scheuing and Zundel (*14*) have shown that in solutions of *p*-toluene sulfonic acid in CH_3OH, the continuum arising from formation of intermolecular complexes such as $(CH_3OH)_2H^+$ ultimately obliterates the absorption features of the solvent, and thus precludes any possibility of band analysis.

The dissociation of $CH_3OH_2^+$ (step (2)) is identified as the rate-determining step in the dehydration reaction, requiring temperatures greater than ~50°C. The role of the proton is evidently to weaken the C–O bond sufficiently, via complex formation, to induce cleavage by mild thermal activation. Although (2) and (3) have been written as consecutive steps, from energetic considerations, a concerted process may be favored, in which a neighboring oxygen ion in the Keggin unit assists in methanolic C–O bond cleavage by electron donation to the carbon, which probably bears a significant partial positive charge in the protonated complex, e.g., as shown below:



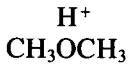
Whichever route is followed, the overall result is one of surface methylation and the production of H_2O. The dehydration cycle is then completed by a rapid reaction between the surface methoxy group and physisorbed CH_3OH, producing DME and regenerating the proton (step (4)). The methoxy C–O bond is considered to be polarized such that the carbon atom bears a partial positive charge, leading to electrophilic attack at the most basic center, i.e., the methanolic O. Assisted cleavage of the methanolic OH bond via H-bonding interaction, either with the methoxy O, as shown below, or neighboring O ions, may also be envisaged.



Strong evidence for the polar nature of the methoxy C–O bond derives from the fact that it reacts rapidly with NH_3 to form the $CH_3NH_3^+$ ion. Indeed, from electrostatic considerations, the surface methyl group would ultimately be expected to behave like a methyl carbonium ion, CH_3^+, as the charge imbalance created by the loss of protons in step (2) cannot be compensated by increasing the valency of the W^{VI} or P^V atoms in the Keggin unit. The infrared data tends to support this view insofar as the methoxy C–O band at 1022 cm^{-1} lies ~50 cm^{-1} below the corresponding band in $W(OCH_3)_6$ (*18*). In addition, the absence of any significant erosion of the three W–O stretching bands (below 1000 cm^{-1} (*8*)) or any obvious increase in absorption in the region 600–550 cm^{-1} (characteristic of the W–O stretch in W^{VI}-alkoxides (*18*)), as the methoxy C–O band develops (see Fig. 4), suggests that the integrity of the Keggin unit is maintained. There is a systematic shift (of 10–20 cm^{-1}) to higher wavenumbers of all the W–O bands (Figs. 3c, 4a–d) but this effect is believed to originate from anion–anion repulsive interactions, which would be expected to increase as the cation size decreases (*23*), i.e., as H_2O is lost from the $CH_3OH_2^+$ ion. This interpretation is supported by the fact that the W–O band positions approach those observed for the preevacuated acid, the greatest discrepancy being in the terminal W–O stretch (*8*), at 1000 cm^{-1} (Fig. 4d) and 1010 cm^{-1} (Fig. 3a), respectively.

The equivalence between the number of surface methoxy groups and the number of protons lost suggests that possible side reactions between adjacent OCH_3 groups to give DME do not occur to any significant degree. Catalytic and infrared data support this view as the loss of protons and O_{KU} implicit in this mechanism would ultimately be expected to manifest itself in irreversible loss of activity and degradation of the Keggin unit, neither of which is observed. In addition, the appearance of only one methoxy C–O stretching band and two CH_3 deformation bands indicates the equivalence of these groups, and militates against the cleavage of the C–O bond in one, and the W–O bond in the other, as would be required in such a reaction scheme. Hence, the relatively small amount of DME recovered from *in vacuo* thermal treatment of the "irreversibly sorbed" CH_3OH component is considered to have arisen from the interaction of methoxy groups with CH_3OH desorbed from the weaker acid sites in the catalyst.

Information regarding the nature of the "unreactive residual CH_3" (described earlier) may be gained from the infrared spectra. The sharp band at 1155 cm^{-1} (in Figs. 5b and c) is in the region expected for the asymmetric C–O–C stretch in DME (*24*). The fact that this band only appears on addition of NH_3 is good evidence that a certain fraction of the product DME is bound in protonated complex form, probably at the strongest acid sites, as governed by the relative electronegativity of the O atom in the original methoxy groups (*25*). By analogy with the $CH_3OH_2^+$ ion, the C–O stretching band in



$$CH_3\overset{H^+}{O}CH_3$$

would be expected to be broadened and shifted to lower wavenumbers, relative to physisorbed DME, and therefore obscured by the intense KU bands. In view of the similar basicities reported for CH_3OH and DME (pK_a of protonated form $= -3.83$ (*26*)), equilibration with a large excess of CH_3OH may be required to displace this strongly bound DME. The apparent ease of recovery of DME created at 25°C (step (4)), as indicated by its quantitative correspondence with $CH_3NH_3^+$ ion formation, suggests that the active sites involved are of relatively low acid strength on the basis of the mechanism described earlier. Alternatively, the variety of orientations conceivably open to the sorbed CH_3OH may increase the range of O atoms available for donor bonding interaction with the alcoholic H. The involvement of the most basic O, resulting in formation of the least acidic OH group, would facilitate cleavage of the alcoholic OH bond and the subsequent desorption of DME. Recent theoretical calculations (*25*) indicate that the unshared terminal O atoms are the most basic in the peripheral WO_6 octahedra of the Keggin unit.

The reversible inhibition of CH_3OH dehydration by DME and the lack of influence of H_2O can be readily understood in light of the foregoing evidence. DME competes with CH_3OH for the active sites, i.e., available protons, and forms a complex which is apparently more thermally stable. The sensitivity of the reaction rate to initial accumulation of DME indicates that this molecule is sorbed preferentially, i.e., it is more basic than CH_3OH, implying that the more acidic pK_a (-4.5) quoted for $CH_3OH_2^+$ by Weston *et al.* (*27*) is probably quite accurate.

The very low activity of the Na^+ salt, i.e., over two orders of magnitude lower than $H_3PW_{12}O_{40}$ (based on initial rate), is at first sight surprising as previous work (*8, 9*) has shown that the salt exists in partial Brønsted acid form with an adjusted molecular formula $Na_{2.7}H_{0.3}PW_{12}O_{40}$, and its surface area is similar to that of the acid (*4a,b*). However, in view of the mechanism established over $H_3PW_{12}O_{40}$, the discrepancy can be attributed to the lower strength of acid sites in the salt ($pK_a > -3$, Ref. (*4b*)). The equilibrium concentration of the primary intermediate $CH_3OH_2^+$, at room temperature (and hence the rate of surface methylation on heating) would be expected to be rather low, a prediction supported by the ready desorption of CH_3OH and the absence of IR bands characteristic of the protonated complex.

In conclusion, the work reported here has elucidated the role played by Brønsted acidity in the dehydration of CH_3OH over these heteropoly compounds, and has indicated that a certain range of acid strength may be required for optimum catalyst performance.

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