Characterization of Sorbed Intermediates and Implications for the Mechanism of Chain Growth in the Conversion of Methanol and Ethanol to Hydrocarbons 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 conversion of C_1–C_4 alcohols to hydrocarbons over 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$. The C_2–C_4 alcohols undergo Brønsted-acid-catalyzed dehydration by initially the same mechanism as that reported earlier for CH_3OH. Rapid protonation of the sorbed alcohol is followed by thermally induced C–O bond cleavage, and the resulting alkyl cation is stabilized, in varying degree, by neighboring O ions in the Keggin unit. The cycle is completed by deprotonation and olefin desorption, considered to occur preferentially for alkyl intermediates associated with the more basic O ions, i.e., the weaker Brønsted acid sites. For C_2H_5OH, the latter step yields C_2H_4 at 110°–150°C which subsequently plays an important role in chain growth. The olefin readily reacts with sorbed $C_2H_5^+$ in this temperature range to form n-$C_4H_9^+$, which quickly rearranges to i-$C_4H_9^+$. Consistent with its proposed carbenium ion character, the latter species reacts with NH_3 to form the alkylammonium cation, and further rearranges to the tertiary form above ≈200°C. In CH_3OH, the onset of corresponding chain growth (and rearrangement), enhanced by the addition of C_2H_4 is observed at ≈175°C. The carbene (:CH_2) mechanism of initial C–C bond (or C_2H_4) formation from sorbed CH_3^+ is tentatively favored over the onium ylide route. The onset of H-transfer (and carbonization) in conversion of the alcohols under static conditions is observable already at ≈150°C, and becomes extensive at elevated temperature, resulting in essentially paraffins above ≈250°C. Selective suppression of the stretching vibrations of sorbed alkyl intermediates, induced by heating *in vacuo*, is reported. © 1986 Academic Press, Inc.

INTRODUCTION

The conversion of methanol to hydrocarbons is now well established as a viable alternative route to Fischer–Tropsch chemistry in the production of gasoline from coal and other carbon sources, and continues to attract widespread attention. The present state of the art has been described in an excellent review article by Chang (*1*). More recently, the economic feasibility of recovering ethanol from fermentation broths by catalytic conversion to gasoline has also been evaluated (*2, 3*).

Popular catalysts for methanol (and higher alcohol) conversion to date have

been zeolites on account of their "shape-selective" character (*1–3*), but significant interest has also been shown in heteropoly acids and salts, both in this laboratory (*4–7*) and elsewhere (*8, 9*). The effect of chemical composition on both the bulk and surface structure of isomorphous 12-heteropoly compounds has been found to be significant; a systematic correlation existing between monovalent cation size, structural microporosity, and crystallinity (*10*). In order to elucidate the properties of catalytic significance in such compounds, a variety of physicochemical methods have been utilized (*11*), among which Photoacoustic Fourier-Transform Infrared Spectroscopy (PAS-FTIR) has proved valuable. This promising technique, which

offers a means to obtain optical absorption spectra by direct examination of opaque and powdered samples (12), has revealed, among other things, a strong correlation between Brønsted acidity and activity in methanol conversion over 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$, and related salts (13, 14).

One important factor promoting current interest in the process of methanol conversion is the controversy over the mechanism by which chain growth is initiated (1). It now appears generally accepted that methanol undergoes a preliminary dehydration step, and that dimethyl ether (DME), or an equilibrium mixture of methanol and DME acts as the precursor to hydrocarbon formation (4, 9, 15–18). However, a wide variety of mechanisms have been proposed to account for the subsequent step of chain growth, ranging from the condensation of surface alkoxyls (19), to the generation of carbene or carbenoids (15, 20), carbenium ions (9), and onium ylide intermediates (17, 18). Furthermore, the possible role of ethylene, considered the primary olefin product by some researchers (9, 15–17, 21) but not by others (22–24), still remains a matter of conjecture.

Conventional transmission IR spectroscopy has previously been used to investigate methanol conversion over a range of zeolites in their acid (H)-form. Both Ono and Mori (9), and Salvador and Kladnig (25) have observed methoxyl groups on the surface of ZSM-5 and Y-zeolite, respectively, at low temperatures, i.e., 120–150°C. While the former reported only the subsequent removal of methoxyl groups on evacuation at 240°C, the latter observed, on heating up to 280°C in methanol, the retention of methoxyl bands and the development of new bands, tentatively attributed to surface formate. On the other hand, Ceckiewicz (24) investigated the reaction over zeolite T and claimed spectral evidence for sorbed propylene at 400°C. Indeed, the present level of ambiguity is exemplified by the fact that all the aforementioned authors

propose different mechanisms for hydrocarbon formation.

In view of the similarity in product distributions from methanol conversion over zeolites and $H_3PW_{12}O_{40}$, and in their Brønsted acid character, the presumption has been made that a common mechanism may operate in both catalysts (9). However, no direct IR studies have been reported over $H_3PW_{12}O_{40}$. Recently, the authors have elucidated the mechanism of dehydration of methanol over $H_3PW_{12}O_{40}$, using PAS-FTIR, and verified the role of Brønsted acidity in this preliminary step (26). Hence, it was considered of particular interest to extend the investigation to hydrocarbon formation over $H_3PW_{12}O_{40}$ at elevated temperature. Also, in view of evidence that alcohols, in general, show corresponding behavior (15, 16) and the developing interest in ethanol as another potential source of gasoline, it was deemed relevant to broaden the study to include C_2-C_4 alcohols.

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 (13), except a lower mirror velocity ($V = 0.02$ cm sec^{-1}) was utilized to give further improvement in spectral quality. 12-Tungstophosphoric acid, $H_3PW_{12}O_{40}$ · 29H$_2$O (AnalaR, BDH) was used without further purification. Reagents methanol, CH_3OH (Photrex, J. T. Baker); absolute ethanol (Canadian Industrial Alcohols and Chemicals); n-propanol, isopropanol, n-butanol, isobutanol ("Baker-Analyzed," J. T. Baker), tert-butanol (MCB Inc.); isopropylamine (BDH), isobutylamine (Aldrich); ammonia (anhydrous, Matheson), and ethylene (CP cylinder grade Matheson) were subjected to several freeze–pump—thaw cycles to remove contaminant gases prior to use. The alcohols and amines were kept

dry over activated molecular sieve 3A, while ammonia and ethylene were predried by trap-to-trap distillation. Uptakes were measured volumetrically and expressed for convenience as molecules sorbed per Keggin unit ($PW_{12}O_{40}^{3-}$).

Qualitative catalytic studies were performed in a static reactor. Samples (typically $1-2 \times 10^4$ mol, preevacuated at 340—350°C) were contacted directly with excess alcohol ($0.25-2 \times 10^{-3}$ mol, 10–80 Torr) at the reaction temperature. Activity was monitored periodically by GLC analysis of the ambient gas, utilizing the following columns and conditions:

(a) Poropak Q (50–80 mesh, 0.63×50 cm, and 80–100 mesh, 0.63×250 cm, in series) at 120°C for C_1-C_4 alkanes and alkenes; and

(b) 15% squalane on Chromosorb W (0.63×300 cm) and Carbowax 400 on Poracil C (0.63×50 cm) in series at 60°C for Cl–C6 hydrocarbons, ethers, and alcohols. Carrier (He) flow was 30 cm^3 min^{-1} in each case.

Unless otherwise stated, spectral changes were monitored by dosing the alcohols at room temperature, followed by desorption of products into a cold trap (N_2, 77 K) during stepwise heating *in vacuo*. However, it was occasionally of interest to compare spectra obtained as above with those from samples in the static reactor, i.e., subjected to continuous contact with alcohol and any desorbed products, followed by brief (5 min) evacuation at the reaction temperature and analysis as normal.

RESULTS

1. Ethanol

After preevacuation of 12-tungstophosphoric acid at 350°C, the uptake of ethanol at 30°C was significant, typically reaching a limit of ≈ 6 molecules per Keggin unit ($6C_2H_5OH/KU$) in a few hours. Upon evacuation at 30°C (trapping at 77 K), the residual sorbed component reached a limiting value of $\approx 4/KU$, or $1.3/H^+$. The PAS spectrum showed changes (from that of the pre-

evacuated acid) roughly corresponding to those observed with methanol (26), i.e., new bands in the deformation region, $\approx 1700-1200$ cm^{-1}, superimposed on a sloping background continuum, the intensity of which increased toward lower wavenumbers. By analogy with CH_3OH, the stoichiometry of the "irreversible" uptake suggested the formation of the intramolecular complex $C_2H_5OH_2^+$, while the background continuum was attributed to intermolecular interactions of the type $C_2H_5OH^+ \cdots OC_2H_5$. The PAS spectrum over the major region of interest, i.e., 1800–1000 cm^{-1}, is shown in Fig. 1b. The broad band centered at ≈ 1520 cm^{-1} is believed to correspond to a band similar in appearance at 1535 cm^{-1} in $CH_3OH_2^+$, attributed to the asymmetric COH deformation (26). The bands at 1445 and ≈ 1390 cm^{-1} appear to correspond to the asymmetric and symmetric deformation, respectively, of CH_3 (attached to carbon), while the shoulder at ≈ 1465 cm^{-1} is characteristic of the CH_2 deformation (27). Assignment of the weaker
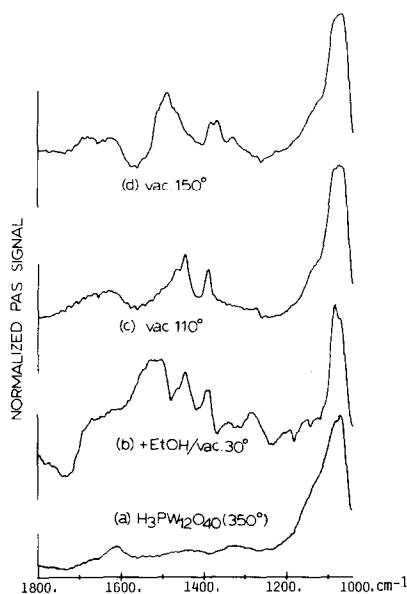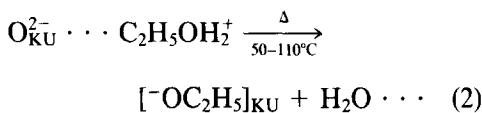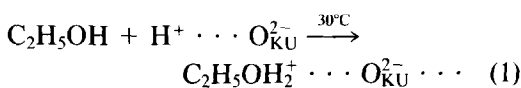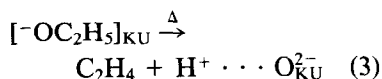

FIG. 1. (a) $H_3PW_{12}O_{40}$, preevacuated at 350°C; (b) exposed to ethanol (excess) and evacuated at 30°C for 2 h; (c) further evacuation up to 110°C for 2 h; (d) further evacuation up to 150°C for 2 h.
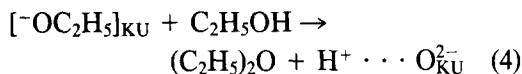
bands in the region 1350–1150 cm^{-1} is uncertain but they are believed to be associated with intermolecular H-bonded alcohol species as they were preferentially removed upon gentle heating *in vacuo*. By 40–50°C, the 1520-cm^{-1} band was already weaker and had completely disappeared after evacuation for 2 h at 110°C (Fig. 1c), while the bands at 1465, 1445, and 1387 cm^{-1} remained essentially unchanged. Similar bands at 1470, 1445 and 1375 cm^{-1} have been reported by other workers in W(OC$_2$H$_5$)$_6$ (*28*). The contemporaneous removal of a broad, albeit weaker, absorption centered at ≈1420 cm^{-1} was also discernible, this band being attributed to the symmetric COH deformation in C$_2$H$_5$OH$_2^+$. Analysis of the trap contents showed that C$_2$H$_4$ already comprised roughly half the total desorbate, the remainder consisting of C$_2$H$_5$OH, H$_2$O, and a small amount (10 mol%) of (C$_2$H$_5$)$_2$O. However, material balance indicated that there was still a significant sorbed component, ≈2C$_2$H$_5$/KU, at this stage. Thus, decomposition of C$_2$H$_5$OH is evidently initiated by protonation, followed by dehydration (via C–O bond cleavage) with concomitant ethylation of the solid, viz.

$$C_2H_5OH + H^+ \cdots O_{KU}^{2-} \xrightarrow{30°C}$$
$$C_2H_5OH_2^+ \cdots O_{KU}^{2-} \cdots \quad (1)$$

$$O_{KU}^{2-} \cdots C_2H_5OH_2^+ \xrightarrow[50-110°C]{\Delta}$$
$$[^-OC_2H_5]_{KU} + H_2O \cdots \quad (2)$$

where O_{KU}^{2-} is a formalized representation of an O ion in the Keggin unit. This process is clearly analogous to that already described for CH$_3$OH (*26*) and suggests that alkylation of the catalyst may be a vital intermediate step in the dehydration of alcohols in general. To complete the catalytic cycle, two routes are open:
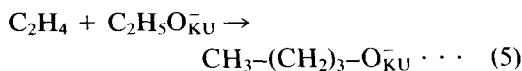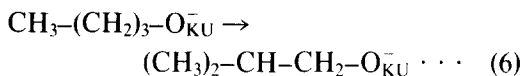
$$[^-OC_2H_5]_{KU} \xrightarrow{\Delta}$$
$$C_2H_4 + H^+ \cdots O_{KU}^{2-} \quad (3)$$

and/or

$$[^-OC_2H_5]_{KU} + C_2H_5OH \rightarrow$$
$$(C_2H_5)_2O + H^+ \cdots O_{KU}^{2-} \quad (4)$$

In this case, olefin production is favored, probably on account of the facile character of step (3) and the efficient removal of most of the physisorbed, or weakly chemisorbed, alcohol by evacuation prior to the generation of the alkoxyl intermediate.

The effect of heating up to 150°C is illustrated in Fig. 1d. The bands due to –C$_2$H$_5$ have been replaced by new bands at ≈1490, 1385, 1365, and 1330 cm^{-1}. The apparent splitting of the CH$_3$ symmetrical deformation into two bands of roughly equal intensity is a well-known resonance effect diagnostic of the geminal dimethyl grouping (CH$_3$)$_2$C, the degree of splitting increasing with narrowing of the bond angle between the geminal CH$_3$ groups (*29*). The weak band at 1330 cm^{-1} is characteristic of the C–H deformation while the strong band at 1490 cm^{-1} is assigned to the CH$_3$ asymmetric bend although it normally appears in the region 1470–1460 cm^{-1} for compounds in the free state (*29*). Hence, spectral evidence has been obtained for both chain growth and chain branching in an unexpectedly low temperature range, 110–150°C. As no corresponding process was observed in CH$_3$OH under similar experimental conditions (*26*), this result implies the operation of a mechanism specific to the present system. In view of the strongly electrophilic character of the sorbed ethyl species (H$^+$ effectively having been replaced by C$_2$H$_5^+$) chain growth may be anticipated via its interaction with C$_2$H$_4$, which is evidently diffusing out of the bulk and, hence, readily available for reaction. However, the formation of a branched chain alkyl species cannot easily be envisaged in a single step, a more likely explanation being that chain growth and rearrangement occur consecutively, e.g.,

$$C_2H_4 + C_2H_5O_{KU}^- \rightarrow$$
$$CH_3-(CH_2)_3-O_{KU}^- \cdots \quad (5)$$

$$CH_3-(CH_2)_3-O_{KU}^- \rightarrow$$

$$(CH_3)_2-CH-CH_2-O_{KU}^- \cdots \quad (6)$$

The chain length C_4 is implicit in this mechanism, although the IR data has not distinguished between the isopropyl and isobutyl groupings at this stage (see later).

Supporting evidence for chain growth/rearrangement was obtained by analysis of the trapped material desorbed in the higher temperature range, i.e., above 110°C. This consisted primarily of C_2 hydrocarbons ($C_2H_6 : C_2H_4 \simeq 2:1$) together with small amounts of C_3 and C_4, a product distribution similar to that reported by other workers (30). Material balance indicated the retention of ≈ 0.5 C_4H_9/KU or alternatively 0.7 C_3H_7/KU. More direct evidence for the occurrence of chain growth and rearrangement as consecutive steps was obtained in a separate experiment in which the surface ethoxyl was generated at $\approx 100°C$ as before, and then exposed to excess C_2H_4 at this temperature for several hours. The PAS spectra (Figs. 2a–c) clearly show the development of absorption around 1470 cm^{-1}, characteristic of CH_2, with only very slight rearrangement as suggested by the development of weak bands at ≈ 1365 and ≈ 1330

FIG. 3. (a) $H_3PW_{12}O_{40}$, preevacuated at 350°C and exposed to excess isopropylamine at 100°C [3.1/KU, irreversibly sorbed]; (b) $H_3PW_{12}O_{40}$, preevacuated at 350°C and exposed to excess isobutylamine at 100°C [3.0/KU, irreversibly sorbed]; (c) difference spectrum; (d) exposed to NH_3 at 100°C [3.0/KU irreversibly sorbed] minus spectrum of stoichiometric NH_4^- salt (see (13)).
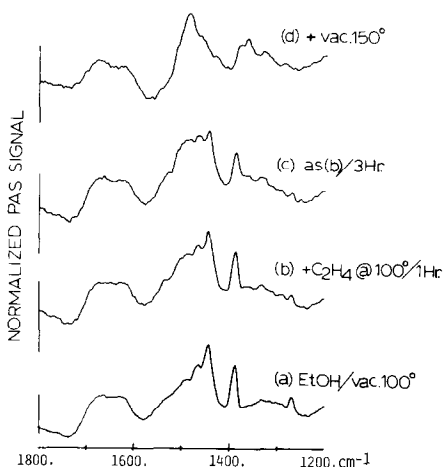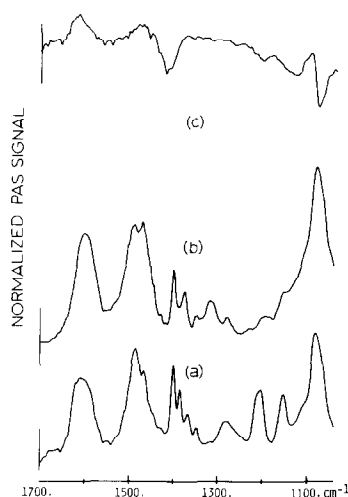

FIG. 2. (a) $H_3PW_{12}O_{40}$ (preevacuated at 350°C) exposed to ethanol at 25°C and evacuated at 100°C for 1.5 h; (b) as (a) exposed to C_2H_4 ($P \approx 80$ Torr) at 100°C for 1 h; (c) as (b) exposed to C_2H_4 for a further 2 h; (d) as (c), evacuated at 150°C for 2.5 h.

cm^{-1}. Further heating up to 150°C (Fig. 2d) generated the characteristic spectrum of the "iso" species, as observed earlier. To confirm the positively polarized character of the sorbed alkyl species and to provide supporting evidence that the observed IR spectrum derives from the isobutyl (rather than isopropyl) grouping, the system was exposed to NH_3 in an attempt to form the alkyl ammonium cation, as observed previously with the sorbed methyl intermediate (26). Reference spectra of the $(CH_3)_2CH$ $CH_2NH_3^+$ and $(CH_3)_2CHNH_3^+$ salts, obtained by dosing stoichiometric amounts of the respective amine onto the acid, were found to show broad similarities but with some significant differences in the region 1700–1155 cm^{-1} (Figs. 3b,a). Both exhibit the NH_3^+ degenerate and symmetric deformation at ≈ 1605 and 1490 cm^{-1}, respectively, and the split CH_3 symmetric mode in the region 1400–1350 cm^{-1}. However, the CH deformation at ≈ 1320 cm^{-1} in the isobutylamino group (its normal position) is shifted to ≈ 1280 cm^{-1} in the C3 analog, pre-

sumably due to the influence of the neighboring NH_3^+ group. More significantly, the latter spectrum exhibits strong bands at 1205 and 1155 cm^{-1} which cannot be readily assigned but appear to correspond to similar bands in liquid isopropylamine at 1170 and 1130 cm^{-1}, being absent in isobutylamine (31). After sorption of 3.0 NH$_3$/KU at $\approx$100°C (limiting uptake) on the catalyst (alkylated at 150°C), the PAS spectrum was dominated by the intense NH$_4^+$ deformation at 1420 cm^{-1}, as expected, but the NH$_3^+$ degenerate deformation at 1605 cm^{-1} was also prominent. Subtraction of the NH$_4^+$ salt spectrum (26) (normalized at 1080 cm^{-1}) also revealed the NH$_3^+$ symmetric deformation at $\approx$1480 cm^{-1} and the substoichiometric NH$_4^+$ loading, but no bands were discernible at 1205 and 1155 cm^{-1} (Fig. 3c).

The effect of stepwise heating *in vacuo* up to 300°C of 12-tungstophosphoric acid previously exposed to ethanol is shown in Fig. 4. Little spectral change was observed up to 205°C but at 250°C (Fig. 4b), the 1490-cm^{-1} band diminished, absorption developed at $\approx$1350 cm^{-1} and a weak band developed at 1280 cm^{-1}. By 300°C (Fig. 4c), the original bands had disappeared, and a major new band was evident at $\approx$1355 cm^{-1}, together with a shoulder at $\approx$1380 cm^{-1}. The tert-butyl (t-Bu) grouping is generally reported to show a CH$_3$ symmetric deformation split by resonance into two bands at $\approx$1365 and 1380 cm^{-1} (the former band being roughly twice as intense as the latter), and a skeletal vibration at $\approx$1250 cm^{-1} (32). Other workers have observed bands at 1360(s), 1378(m) and 1231(s) cm^{-1} in WO(O–t–Bu)$_4$ (28). The thermally activated rearrangement of isobutoxyl to the tert-butoxyl form is entirely consistent with the proposed electrophilic character of the sorbed alkyl intermediate, insofar as it behaves like a carbenium ion in its reaction with NH$_3$. An additional spectral trend observed during heating above 150°C was the systematic development of a flat background continuum, consistent with the observed blackening of the solid, indicative of
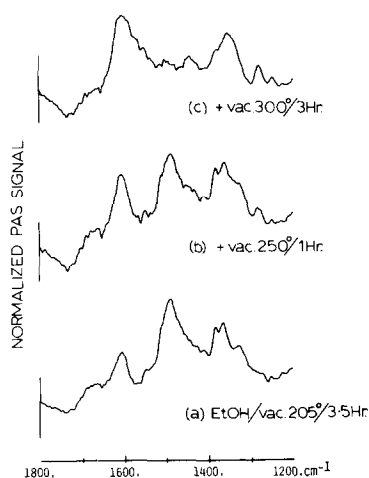

FIG. 4. (a) H$_3$PW$_{12}$O$_{40}$ (preevacuated at 350°C) exposed to ethanol (excess) at 25°C and evacuated up to 205°C for 3.5 h; (b) further evacuation up to 250°C for 1 h; (c) further evacuation up to 300°C for 3 h.

carbon deposition. The concomitant formation of saturated hydrocarbons, which would be expected to accompany carbonization (1), was verified by GLC. After desorption at 205°C, the products recovered were in the order C$_2$H$_4$ > n-C$_4$H$_{10}$ $\approx$ C$_3$H$_8$ > i-C$_4$H$_{10}$ > C$_2$H$_6$. Above 250°C, the order had changed to C$_3$H$_8$ > n-C$_4$H$_{10}$ $\approx$ C$_2$H$_6$ > C$_2$H$_4$, possibly due to consumption of the reactive olefin. Sustained catalysis in excess C$_2$H$_5$OH at 200, 250, and 300°C resulted in virtually identical PAS spectra and product distributions, at the respective temperatures, to those already described.

2. C$_3$ and C$_4$ Alcohols

(a) C$_3$ alcohols. The sorption of n-C$_3$H$_7$OH and i-C$_3$H$_7$OH at 25°C into H$_3$PW$_{12}$O$_{40}$ was significant, albeit somewhat slower and less extensive than for C$_2$H$_5$OH. Limiting uptakes, in the range 3–4/KU, were reached after $\approx$5–10 h exposure, the rate of sorption being initially greater for i-C$_3$H$_7$OH, possibly due to the higher vapor pressure employed. Upon evacuation at 25°C, the "irreversible" uptake was similar for both, $\approx$2.5/KU, and their PAS spectra (Figs. 5d,e) were dominated by features characteristic of protona-
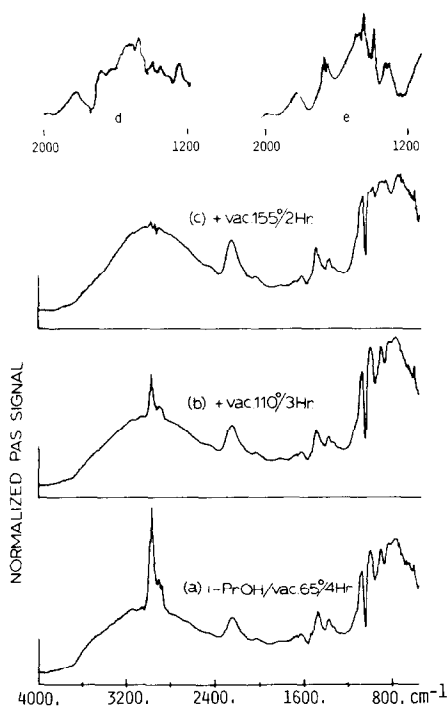
FIG. 5. (a) $H_3PW_{12}O_{40}$ (preevacuated at 350°C) exposed to isopropanol (excess) at 25°C and evacuated up to 65°C for 4 h; (b) further evacuation up to 110°C for 3 h; (c) further evacuation up to 155°C for 2 h; (d) $H_3PW_{12}O_{40}$ (preevacuated at 350°C) exposed to n-propanol (excess) at 25°C and evacuated at 25°C for 3 h; (e) $H_3PW_{12}O_{40}$ (preevacuated at 350°C) exposed to i-propanol (excess) at 25°C and evacuated at 25°C for 3 h.

tion, i.e., relatively weak bands of the sorbate in the stretching region ($\approx$3000 cm^{-1}), with bands of moderate intensity in the deformation region (1600–1200 cm^{-1}), superimposed on a sloping background continuum, the intensity of which increased toward lower wavenumbers. In correspondence to the C_1 and C_2 alcohols, n-C_3H_7OH showed a broad, albeit relatively weaker, band at $\approx$1520 cm^{-1}, attributable to the COH asymmetric deformation in $C_3H_7OH_2^+$ whereas this band was absent in i-$C_3H_7OH_2^+$, unless shifted to $\approx$1480 cm^{-1}. Such a displacement is not altogether surprising as evidence for significant coupling has already been observed in $CH_3(CD_3)OH_2^+$ (26). Other major differences occur in the position of the CH_3 asymmetric

and symmetric deformations, lying at 1463 and 1388 cm^{-1}; and at 1448 and 1392, 1382 cm^{-1} for the linear- and branched-chain, respectively.

Upon evacuation at 50–60°C for several hours, the bands of the protonated alcohols completely disappeared and were replaced by the familiar deformation band envelope characteristic of the isopropyl, or isopropoxyl, grouping. The PAS spectrum obtained from the iso-alcohol is shown in Fig. 5a. Notwithstanding the development of bands at 1471, 1376, 1366, and 1330 cm^{-1}, the most remarkable change from the spectrum of the protonated alcohol was the development of the intense stretching vibration at 2969 cm^{-1} along with weaker bands at 2877 and 2905 cm^{-1}. The two former bands are assigned to the CH_3 asymmetric and symmetric modes, respectively, while the latter is ascribed tentatively to the C–H stretch (33). As the relative intensities and positions of the CH_3 stretching and bending vibrations observed here are more typical of systems free from H-bonding interactions, this may be taken as additional, albeit indirect, evidence for C–O bond cleavage in i-$C_3H_7OH_2^+$ and concomitant alkylation of the Keggin unit. Bands at 1460(s), 1375(s), and 1325(m) have been reported in $W(O-i-C_3H_7)_6$ (28). Upon evacuation up to 155°C (Figs. 5b,c), the CH_3 stretch was progressively diminished while the deformation bands remained almost unchanged in intensity, an extraordinary phenomenon which could not be explained simply by loss of C_3H_6 (already detectable above $\approx$60°C by GLC) as material balance indicated the retention of the greater portion ($\approx$60%, as C_3H_7) of the original sorbed component. As the CH_3 deformation bands showed progressive shifts to higher wavenumbers viz. 1471 → 1488, 1376 → 1383, 1366–1368 cm^{-1}, the possibility of increasing H-bonding interaction, most probably with adjacent O ions in nearest neighbour Keggin units, might explain the observed paradox. In support of this contention, there is a systematic increase in the splitting of the CH_3

symmetric deformation, characteristic of a narrowing C–C–C bond angle, and an ultimate splitting and overall shift of the W–O stretching vibrations to higher wavenumbers. The latter effect, characteristic of a shorter anion–anion separation (26) indicates shrinkage of the lattice parameter and implies closer approach of CH_3 and terminal or bridging O in the Keggin unit, thus facilitating potential H-bonding. More difficult to explain, however, is the absence of systematic broadening and shifts in the CH_3 stretch as its intensity decreases, the expected result of such an interaction. Similar treatment of the n-propyl system reproduced closely the spectral changes and product recovery data described above. Additional evidence that the marked temperature (bulk structure) sensitivity of the stretching vibrations exhibited here is general to sorbed alkyl groups of a certain chain length derives from less clear-cut observations made during the interaction of C_2H_4 with sorbed C_2H_5 at 100°C (see Fig. 2). The same spectra (34) exhibit a systematic, though less pronounced, increase in absorption (in the range 3000–2850 cm^{-1}) characteristic of the CH_3 and CH_2 stretch, followed by its marked attenuation upon further heating up to 150°C, despite little or no accompanying product desorption.

Sustained catalysis of i-C_3H_7OH at 250 and 350°C resulted in the recovery of essentially only C_3 and C_4 hydrocarbon products. The C_3/C_4 ratio showed little temperature dependence, lying in the range 2 : 1–3 : 1. Progressive carbonization was evident from the darkening of the catalyst during this treatment.

b. C_4 alcohols. The room-temperature sorption of C_4 alcohols into $H_3PW_{12}O_{40}$ was markedly slower and less extensive than for the C1–C3 series. Uptakes of 0.34, 1.3, and 0.45/KU were obtained for normal-, iso-, and tert-butanols, respectively, after exposure for 10–16 h. From steric considerations, the ease of sorption into the bulk would be expected to be normal-, iso-, tert-. The somewhat anomalous position of the

normal alcohol may perhaps be explained by the limited vapor pressure ($\approx$0.5 cm) utilized in the experiment (the saturated vapor pressures for the alcohols at 25°C from tables (35) are 0.77 cm (n), 1.3 cm (i), and 3.6 cm (t)).

After evacuation at 25°C, the "irreversible" component amounted to $\approx$0.70/KU for i-C_4H_9OH, and $\approx$0.30/KU for n- and t-C_4H_9OH. The PAS spectra of $H_3PW_{12}O_{40}$ exposed to n-C_4H_9OH and t-C_4H_9OH at 25°C showed only very weak new bands in the region $\approx$1470, and 1340 cm^{-1}, respectively, with little or no enhancement on heating up to 150°C in an alcohol atmosphere. However, dehydration activity was readily detected above $\approx$60°C, as monitored volumetrically (with selective trapping). Conversions of typically $\approx$12% ($\approx$0.2 molecules/KU) to ΣC_4 hydrocarbons in 1 h at 150°C were measured with negligible ether formation. Thus, the steady-state concentrations of sorbed intermediate(s) in the dehydration of n- and t-C_4H_9OH were insufficient for adequate characterization by PAS. It may be speculated, in this regard, that the dehydration of n- and t-C_4H_9OH is restricted to the uppermost surface layers(s) of the catalyst. For i-C_4H_9OH, on the other hand, bands were readily observed for the "irreversibly sorbed" component at 25°C (see Fig. 6a). The stretching and bending vibrations of the isobutyl grouping, appearing at $\approx$3000 cm^{-1} and in the region 1500–1300 cm^{-1} respectively, resemble those of the isopropyl moiety. Peaks of the familiar deformation band enveloped appear at 1468, 1387, 1370, and 1333^{-1} while the weak shoulder at $\approx$1505 cm^{-1} may correspond to the COH asymmetric deformation in i-$C_4H_9OH_2^+$. Assuming the latter assignment is correct (there being no other feature in this region characteristic of the protonated alcohol), its relative intensity signifies that extensive C–O bond cleavage has already occurred at room temperature. This inference is supported by the sharpness and higher intensity of the stretching (relative to the
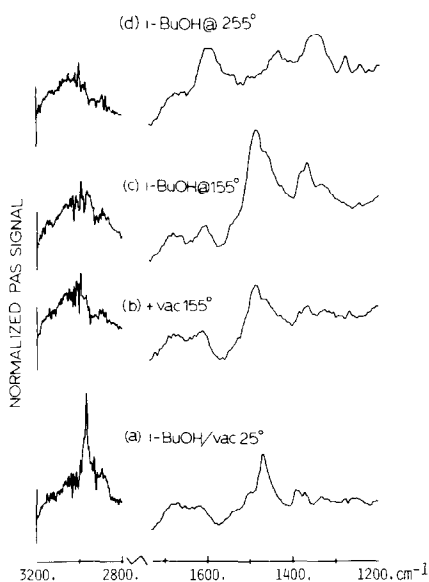
FIG. 6. (a) $H_3PW_{12}O_{40}$ (preevacuated at 350°C) exposed to isobutanol (excess) at 25°C and evacuated at 25°C for 3 h; (b) further evacuation up to 155°C for 1 h; (c) further heating in excess isobutanol ($P \approx 11$ Torr) at 155°C for 5 h; (d) as (c) at 255°C for 2 h.

deformation) vibrations, suggesting the formation of the sorbed alkyl species (see section 2a). Indeed, upon evacuation at 155°C, the spectral changes (Fig. 6b) paralleled those observed in the isopropyl system. The stretching vibrations were almost eliminated whereas the deformation band envelope was slightly shifted but remained essentially intact, the CH_3 asymmetric mode at ≈ 1468 cm^{-1} showing the greatest shift to ≈ 1485 cm^{-1}. Heating at 150°C in alcohol atmosphere (Fig. 6c) resulted in intensification of the deformation bands, but the stretching bands remained essentially absent. Thus, at this stage, the spectrum resembled closely those obtained by similar treatment of C_2H_5OH (Fig. 1d) and i-C_3H_7OH (Fig. 5c). Upon evacuation up to 255°C (Fig. 6d), the bands at 1485, 1380, 1368, and 1333 cm^{-1} were replaced by new bands at ≈ 1350 and 1280 cm^{-1} (characteristic of tert-butyl), a band at 1435 cm^{-1}, and a flat background continuum suggestive of carbonization. GLC analysis of the desorbate at 150°C showed that it comprised es-

sentially C_4 hydrocarbons ($\approx 50\%$ olefins), with a trace of C_3 while evacuation up to 255°C yielded essentially i-C_4H_{10} with some C_3H_8. Sustained catalysis at 250°C in alcohol atmosphere resulted in further development of the bands at 1350 and 1280 cm^{-1}, and no significant change was observed in the product distribution.

3. Methanol

Sorption of excess CH_3OH on $H_3PW_{12}O_{40}$ (preevacuated at 350°C) at 25°C, followed by evacuation up to 150°C for 1 h reproduced the spectrum reported earlier (26), as expected. The methoxyl bands at 1453 and 1435 cm^{-1}, resulting from bulk methylation, are clearly seen in Fig. 7a. Evacuation at 150°C for a further 2 h produced no change in the spectrum and no additional recovery of dimethyl ether (DME) or H_2O. However, after 1 h at 200°C (Fig. 7b) bands at ≈ 1490, 1387, 1366, and 1331 cm^{-1}, characteristic of iso-butyl (and/or isopropyl) developed at the expense of the CH_3 bands. Evacuation for a further 4 h at 200°C (Fig. 7c) resulted in almost complete removal of CH_3, albeit with no appar-
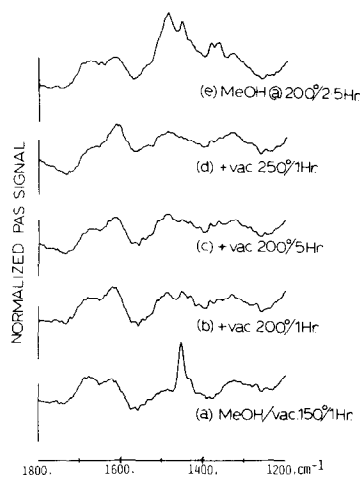

FIG. 7. (a) $H_3PW_{12}O_{40}$ (preevacuated at 350°C) exposed to methanol (excess) at 25°C and evacuated up to 150°C for 1 h; (b) further evacuation up to 200°C for 1 h; (c) evacuation at 200°C for a further 4 h; (d) further evacuation up to 250°C for 1 h; (e) $H_3PW_{12}O_{40}$ (preevacuated at 350°C) heated in excess methanol ($P \approx 80$ Torr) at 200°C for 2.5 h.

ent intensification of the bands of the iso species, and revealed a broad absorption at ≈ 1340 cm^{-1}. Some H$_2$O and a small amount of DME were desorbed at this temperature. After 1 h at 250°C (Fig. 7d), the band at 1340 cm^{-1} and a weaker feature at ≈ 1280 cm^{-1}, both characteristic of tert-butyl, became more prominent at the expense of the iso species, and a background continuum developed indicative of carbonization. No DME or hydrocarbons were recovered at this temperature. Thus, heating the sorbed CH$_3$ intermediate *in vacuo* evidently causes a transformation similar to that observed in the case of the C$_2$H$_5$ species, although its initiation appears to require a somewhat higher temperature (see section 1). Heating in excess CH$_3$OH at 200°C for 2.5 h resulted in a spectrum (Fig. 7e) dominated by the "iso-species" band envelope and a weaker band of sorbed CH$_3$ at 1453 cm^{-1}. Equivalent treatment at 250 and 300°C produced spectra resembling that obtained by heating *in vacuo* up to 250°C (Fig. 7d); i.e., the major features were characteristic of sorbed tert-butyl. The conversion at 200°C was rather low and only DME, C$_3$H$_8$, and i-C$_4$H$_{10}$ could be reliably detected. At 250 and 300°C, the product distributions were similar, viz. C$_3$H$_8$ > DME > *n*-C$_4$H$_{10}$ $\approx$ C$_2$H$_6$ > i-C$_4$H$_{10}$ > C$_2$H$_4$.

In view of the general correspondence in thermally induced behavior of the sorbed alkyl species from both C$_2$H$_5$OH and CH$_3$OH, and the foregoing evidence that C$_2$H$_4$ may be at least initially responsible for chain growth in the former case (see section 1), it was of interest to examine the interaction of C$_2$H$_4$ with the sorbed methyl intermediate. As a preliminary step, a reference spectrum (Fig. 8a) was generated by exposing the acid to excess CH$_3$OH at 25°C, followed by heating at 175°C *in vacuo* for 3 h. The degree of transformation to the isobutyl (or isopropyl) species appeared somewhat less than that observed from *in vacuo* treatment at 200°C for 1 h (Fig. 7b). However when, in a separate experiment, the sorbed methyl intermediate was created
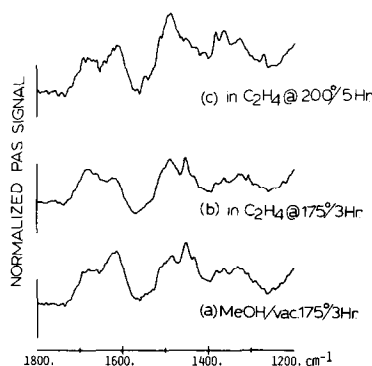

FIG. 8. H$_3$PW$_{12}$O$_{40}$ (preevacuated at 350°C) exposed to methanol (excess) at 25°C and evacuated up to 175°C for 3 h; (b) H$_3$PW$_{12}$O$_{40}$ (preevacuated at 350°C) exposed to methanol (excess) at 25°C, evacuated up to 150°C for 3.5 h, then heated in excess C$_2$H$_4$ ($P \approx 45$ Torr) up to 175°C for 3 h; (c) further heating in excess C$_2$H$_4$ up to 200°C for 5 h.
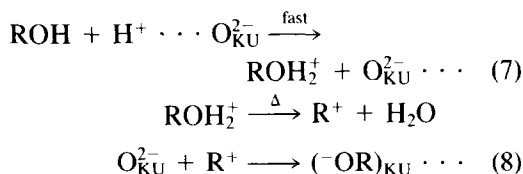
by evacuation at 150°C and the sample subsequently heated in excess C$_2$H$_4$ at 175°C for 3 h, the conversion (Fig. 8b) was evidently greater. Furthermore, after heating in C$_2$H$_4$ at 200°C for 5 h (Fig. 8c), the bands characteristic of methyl were essentially removed and the iso species band envelope showed greater development compared to that obtained after the same treatment *in vacuo* (Fig. 7c). Thus, the presence of C$_2$H$_4$ caused a systematic enhancement of chain growth under otherwise equivalent conditions. An overall uptake of ≈ 0.2 C$_2$H$_4$/KU was measured at this stage, consistent with the spectral evidence for its interaction with the solid. Exposure of the preevacuated acid to C$_2$H$_4$ alone under the above conditions produced no measurable uptake and no new bands in the PAS spectrum.

DISCUSSION

A. Dehydration of Alcohols

The authors have recently elucidated the mechanism of dehydration of CH$_3$OH over H$_3$PW$_{12}$O$_{40}$ using PAS-FTIR (26), and the results of the present study have shown that dehydration of higher alcohols proceeds via the same initial route, i.e., protonation at the alcoholic O, followed by C–

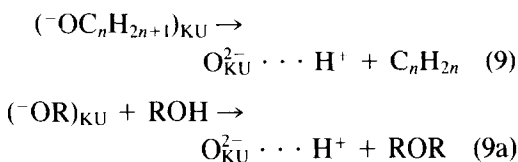O bond cleavage, expulsion of H_2O and alkylation of the Keggin unit, as formally represented below:

$$ROH + H^+ \cdots O_{KU}^{2-} \xrightarrow{\text{fast}}$$
$$ROH_2^+ + O_{KU}^{2-} \cdots \quad (7)$$
$$ROH_2^+ \xrightarrow{\Delta} R^+ + H_2O$$
$$O_{KU}^{2-} + R^+ \longrightarrow (^-OR)_{KU} \cdots \quad (8)$$

where $R = C_nH_{2n+1}$.

The degree of protonation of the alcohol under equilibrium conditions will be governed by the pK_a of ROH_2^+ relative to that of the preevacuated acid, which has already been reported to be as high as -8.2 (4) though more recent studies have indicated a range of values from $pK_a = -3.0$ to -8.2 (26). As simple aliphatic alcohols are generally reported to have pK_a's in the range -2 to -4 (37), protonation of the sorbed alcohol should be extensive, if not complete, up to the stoichiometric loading, i.e., 1 ROH/H^+, as observed for CH_3OH (26). The general trend of a decreasing "irreversible-uptake" of the alcohols (taken to represent $[ROH_2^+]$) with increasing carbon number is considered to arise essentially from steric control of alcohol diffusion into the bulk, as reflected in a similar trend in total uptake.

The spectral evidence indicates a difference in the rate of step (8) for the alcohols, i.e., C–O bond cleavage and alkylation of the Keggin unit, in the order: i-C_4H_9OH > i-C_3H_7OH $\approx$ n-C_3H_7OH > C_2H_5OH > CH_3OH, which follows closely the order of decreasing stability of the corresponding alkyl carbenium ion (38). Indeed, Olah et al. (39) have reported very similar results for alcohols in strong acid solution, using NMR to monitor the decrease in intensity of the $^+OH_2$ multiplet with increase in temperature. They found that the threshold temperatures for the onset of cleavage were ≈ 40 and $60°C$ for $C_2H_5OH_2^+$ and $CH_3OH_2^+$, respectively, i.e., remarkably similar to those observed over $H_3PW_{12}O_{40}$, implying that the anion structure in the solid may play a less active role in this process than was previously suspected (26). The only inconsis-

tency in this correlation is the anomalous position of i-$C_3H_7OH_2^+$, which should be less stable than the C_4 analog, as observed in solution (39). The reason for this is unclear although it must be admitted that the interpretation of the IR data is less certain in this case (see section 2a).

For alcohols with $C \geq 2$, the dehydration cycle may be completed via two parallel reactions, i.e., olefin (step (9)) or ether (step (9a)) production:

$$(^-OC_nH_{2n+1})_{KU} \rightarrow$$
$$O_{KU}^{2-} \cdots H^+ + C_nH_{2n} \quad (9)$$
$$(^-OR)_{KU} + ROH \rightarrow$$
$$O_{KU}^{2-} \cdots H^+ + ROR \quad (9a)$$

However, in practice, olefin formation already predominates at C2, and is the exclusive reaction at C3. Leaving aside the possibility of thermodynamic control, which would be expected to favor olefin formation from entropy considerations, there is almost certainly progressive kinetic control disfavoring ether formation via steric restrictions on the diffusion of the second alcohol molecule into the bulk against the counterflow of the larger olefin.

B. Chain Growth, Rearrangement, and Conversion to Hydrocarbons

1. Ethanol. The results of the present study of C_2H_5OH conversion over $H_3PW_{12}O_{40}$ have clearly revealed that dehydration precedes, and ultimately facilitates, chain growth. The ethyl cation, essentially fully formed at $\approx 100°C$, is stabilized in varying degree by partial bond formation with neighboring O ions in the Keggin unit. On heating to $\approx 150°C$, the less-stable species yield C_2H_4 which is then free to diffuse through the bulk and react with residual sorbed ethyl to form n-butyl, which rapidly rearranges to the isobutyl form at this temperature. The low quantity of C_4 hydrocarbons recovered at this stage suggests that the isobutyl species thus created is more thermally stable than certain corresponding species derived directly from isobutanol,

i.e., those responsible for a significant rate of C$_4$ hydrocarbon production (including a substantial proportion of olefins) at the same temperature. As the most facile decomposition process is deprotonation and olefin desorption, this result implies that the principal factor controlling the stability of the sorbed alkyl intermediate is the basicity of the O atom with which it is associated, i.e., the propensity of O to accept a proton. Recent theoretical calculations (40) indicate that the bridging O atoms in the peripheral WO$_6$ octahedra of the Keggin unit are less basic than the isolated terminal O atoms and, thus, would be expected to exert a greater stabilizing influence. Consistent with the above line of reasoning, most of the isobutyl species detected by PAS remain stable up to 200°C, a temperature above which cracking, hydrogen transfer, and carbonization become predominant. Despite these complicating side-reactions, however, evidence can be seen for further rearrangement to the tert-butyl form above 200°C, consistent with the proposed carbenium-ion character of the iso species (as required by charge balance in the dehydration step and as manifested in its reaction with NH$_3$). Some measure of the stabilizing influence of the anionic environment in the bulk of the catalyst may be realized by comparing the threshold temperatures for rearrangement of the sorbed n-butyl cation to the iso-($\sim$100°C) and tert-($\sim$200°C) forms with the corresponding values (typically <0°C) in strong acid solution (38, 39).

2. Methanol. The spectral changes observed when the sorbed methyl intermediate is heated above 150°C *in vacuo* show a remarkable similarity to those of the sorbed ethyl species, suggesting the operation of a common mechanism. Indeed, the enhancement in the rate of chain growth on exposure to C$_2$H$_4$, under otherwise equivalent conditions, reveals that the formation of this olefin may be of prime importance in the conversion of methanol to hydrocarbons, as proposed earlier by several workers (15, 16, 21), and consistent with the re-

duced induction period observed by Ono and Mori (9) when CH$_3$OH is converted in the presence of C$_2$H$_4$ over ZSM-5 zeolite. However, the initial stage of chain growth must clearly be different for the two alcohols as the formation of C$_2$H$_4$ from sorbed methyl is not a facile one-step process. Indeed, the spectral data show that C–C bond formation from *in vacuo* heating of sorbed methyl requires a somewhat higher temperature. Various mechanisms are conceivable but the two which are most consistent with the observable facts are the onium ylide mechanism, as recently propounded by Van den Berg *et al.* (17a), Olah *et al.* (17b,c), and Mole (18), and the carbene mechanism (15, 20). The former postulates the formation of the trimethyl oxonium ion, (CH$_3$)$_3$ O$^+$, via reaction of DME with CH$_3^+$, which subsequently undergoes deprotonation to the methylenedimethyloxonium ylide, (CH$_3$)$_2$O$^+$CH$_2^-$. This reacts with a second CH$_3^+$ (derived from DME) to form the dimethylethyl oxonium ion. Proton abstraction then yields C$_2$H$_4$ (which promotes further chain growth) and regenerates DME. The latter mechanism claims that the methylene diradical, :CH$_2$, is generated either from CH$_3$OH by a concerted process involving acidic and basic sites (15, 20), or from a surface methoxyl intermediate via proton abstraction by lattice O (25). The :CH$_2$ species is then responsible for chain growth, either directly or by intermediate olefin formation. In favor of the former model, DME was desorbed, albeit in small amount, during heating *in vacuo* in the temperature range in which chain growth was observed (150–200°C), and its reaction with sorbed CH$_3$ and deprotonation may be readily envisaged. However, the reaction of surface-bound methylenedimethyl oxonium ylide with a second sorbed CH$_3^+$ would appear unlikely on statistical grounds. In addition, no IR spectral features could be seen to verify the existence of such intermediates. The carbene model is appealing from the point of view of mechanistic simplicity, insofar as proton abstrac-

tion from the sorbed CH_3^+ can be considered as the analogous process to that seen in sorbed $C_2H_5^+$. Unfortunately, the creation of such a highly energetic intermediate as $:CH_2$ under conditions of only slightly increased severity is difficult to accept. However, recent theoretical calculation (41) provides some support for this model, in showing that methylene may be extensively stabilized by the charged environment within the framework of the ZSM-5 zeolite. Furthermore, this model also accommodates the fact that DME gives a very similar product distribution to CH_3OH (4). Evidence has already been reported for the existence of strongly bound DME, probably in protonated form, during CH_3OH dehydration over $H_3PW_{12}O_{40}$ (26). By analogy with $CH_3OH_2^+$ protonated DME may be thermally dissociated into CH_3^+ and CH_3OH. Thus, methylation of the Keggin unit is common to both routes, while DME yields CH_3OH (instead of H_2O), which may then be protonated to yield a second CH_3^+ ion as previously described. Tentative evidence for this process exists insofar as H_2O formation, along with methylation, has been detected by PAS (42). Notwithstanding the foregoing observations, the onium ylide route appears a perfectly acceptable alternative under "genuine" conversion conditions, i.e., in which a continuous supply of reactant, and hence also CH_3^+, is assured.

The product distribution(s) in the sustained catalysis experiments are significantly different from those obtained earlier in pulse-reactor studies (4). However, this is to be expected in view of the exceedingly high contact times used in the static experiments reported here, and provides some indication of the tendency of any olefin products to undergo secondary reactions such as H-transfer, cracking, and carbonization during extended contact with the catalyst.

In summary, this work has elucidated the role of Brønsted acidity in the overall process of alcohol conversion to hydrocarbons over $H_3PW_{12}O_{40}$ and, by virtue of the detec-

tion and characterization of sorbed intermediates using PAS-FTIR, gives firm foundation to the inference from product distributions etc., for carbonium-ion involvement in the mechanism (4, 15, 16). Ethylene has been shown to play an important role in chain growth in the lower alcohols, although the involvement of higher olefins is also likely but has not been investigated here.

The implication for catalyst development is that the activity and selectivity may be promoted by judicious control of the acid-strength distribution; i.e., weaker acid sites facilitate olefin formation, while stronger acid sites provide the source of more stable alkyl intermediates for subsequent reaction with olefin(s), i.e., chain growth. Carbonization, and resultant catalyst deactivation, may perhaps be controlled by limiting the number of very strong acid sites by ion exchange or selective poisoning.

ACKNOWLEDGMENT

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