for helpful suggestions regarding the experimental part of the present work. We gratefully acknowledge support for this research from grants provided by the National Science Foundation (CHE-8305808) and the Upjohn Co. We thank CNR of Italy for help through "Programma Strategico Dinamica Molecolare e Catalisi". S.A. and L.R. acknowledge help for this work from CNR (Italy) and CNRS (France) as part of a bilateral project.

Registry No. (*R*)-(+)-Limonene, 5989-27-5; (*S*)-(−)-limonene, 5989-54-8; (*S*)-(−)-perillyl alcohol, 100692-55-5; (*S*)-(−)-perillaldehyde, 23963-70-4; (*R*)-(+)-*p*-menth-1-ene, 1195-31-9; (*R*,*R*)-(+)-*p*-menth-7-en-9-ol, 13835-30-8.

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^{13}C NMR Identification of Intermediates Formed by 2-Methyl-2-propanol Adsorption in H-ZSM-5[†]

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Abstract: ^{13}C NMR spectroscopy has been used to characterize intermediates formed by the adsorption of 2-methyl-2-propanol, $(CH_3)_3{}^{13}COH$, on a H-ZSM-5 zeolite. Previous adsorption studies had shown that, upon exposure of H-ZSM-5 to this alcohol and subsequent evacuation at 295 K, an adsorption complex could be formed, which had a coverage of 1 alcohol molecule/Al atom in the zeolite and had carbenium-ion-like properties. In the present NMR studies, it is shown that the adsorbed species can best be described as a silyl ether, with the alkyl group covalently bonded to the zeolite framework oxygen. Furthermore, the adsorption and evacuation conditions used for preparing the samples are found to be very important since these silyl ether intermediates are highly reactive. The ^{13}C NMR spectrum obtained following adsorption shows two prominant features, one at 77 ppm from TMS, which is assigned to carbon that is bonded to the oxygen, and a second at 29 ppm, which is due to aliphatic carbons formed in secondary reactions. ^{13}C NMR spectra were taken of samples at 10 K and after heating to 373 K to verify these assignments, as well as search for additional features that could be masked by dynamics at room temperature. No spectral features were observed in the region expected for carbenium ions, even though the chemistry observed for the adsorption intermediate was consistent with this chemistry and similar to that observed following olefin adsorption on H-ZSM-5. This implies that the steady-state concentration of carbenium ions in H-ZSM-5 is low or that the lifetime of these species is short.

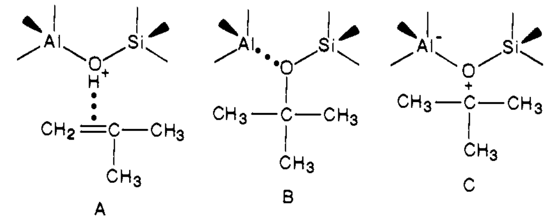
In recent studies of the acid sites in high-silica zeolites, it has been demonstrated that most of the simple alcohols form a well-defined adsorption complex in H-ZSM-5 with a stoichiometry of 1 molecule/Al site following adsorption and evacuation.[1-4] The reactivities of the different alcohols in this 1:1 adsorption complex appear to correlate with the relative stabilities of their respective carbenium ions, implying that proton transfer from the hydroxyls at the Al sites plays a major role in adsorption and reaction at these sites.[3] Furthermore, since the observed reactivity of the 1;1 adsorption complexes is found to be independent of SiO_2/Al_2O_3 ratios in the range from 38 to 520, it follows that H-ZSM-5 contains discrete sites associated with each Al atom, all having the same acid strength.[5]

The results for 2-methyl-2-propanol adsorption are particularly interesting because this molecule dehydrates at room temperature to form a bound intermediate with reaction properties that are very similar to those of a carbenium ion. The results, which suggest the presence of carbenium-ion-like intermediates, are the following:

(1) Following the adsorption and subsequent evacuation of 2-methyl-2-propanol, thermogravimetric analysis (TGA) shows that a coverage corresponding to approximately 1 molecule/Al site is retained on the zeolite.[3]

(2) Adsorption of the alcohol leads to the disappearance of the sharp zeolite hydroxyl stretch at 3605 cm^{-1} in the IR spectrum at a coverage of 1 molecule/Al site. Furthermore, the IR spectral features of the adsorbed species are significantly different from the unreacted alcohol.[4]

Chart I



(3) The adsorbed species undergoes rapid H/D exchange at 295 K when exposed to D_2O vapor, resulting in the formation of C-D bonds at the expense of C-H bonds.[4]

(4) No unreacted alcohol and only a small amount of water are observed in temperature-programmed desorption (TPD), and most of the desorbing product leaves the zeolite as octene and other olefin products.[3]

(5) The adsorbate complex will react with other gas-phase species. For example, exposure to ethanol at 295 K, followed by TPD, gives a complex product distribution that clearly implies some chemical reaction.[6]

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Although these results suggest the presence of a complex that has the stoichiometry and the chemistry of a carbenium ion, they give little direct information about the structure of this species. For example, all of the structures suggested in Chart I could explain our findings. These alternative structures are shown, along with the carbenium ion, for the *tert*-butyl intermediate, which would be formed from the dehydration of 2-methyl-2-propanol. In A and B, the carbenium ion is viewed as a metastable species, which may be formed by thermal activation from the hydrogen-bonded olefin or alkyl silyl ether ground state.[7,8]

In this paper, we present the results of a ^{13}C NMR study of 2-methyl-2-propanol adsorption in an attempt to identify the stable structure of the intermediate formed at the Al site. We will demonstrate that the dehydrated intermediate exhibits a chemical shift for the central carbon atom, which is characteristic of a covalently bonded, silyl ether type species similar to that shown in B. Using this new information, along with kinetic data obtained in previous studies,[1-4] we have calculated an approximate potential energy diagram of the reaction coordinate for 2-methyl-2-propanol dehydration on H-ZSM-5.

Experimental Section

The NMR experiments were performed with a home-built, solid-state, pulsed NMR spectrometer, which employs a heterodyned receiver (bandwidth of approximately 1 MHz between 5 and 150 MHz) and passive diode duplexing circuitry. All spectrometer functions were computer controlled with signal averaging performed in quadrature phase cycling at digitizing rates ranging from 200 ns to 100 ms per point. Complete specifications of the spectrometer and data analysis system have already been reported in detail elsewhere.[9]

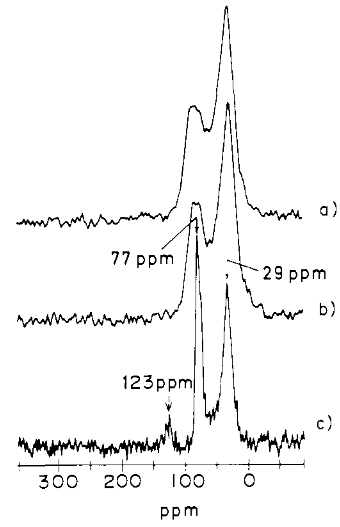

Figure 1. ^{13}C NMR spectra of the intermediate formed by the adsorption of $(CH_3)_3{}^{13}COH$ on H-ZSM-5 using conditions that gave a coverage of 1 molecule/Al. Spectra were taken under the following conditions: (a) at 200 K with 2048 scans, (b) after allowing the sample to warm to 295 K for approximately 1 h, and (c) with 1024 scans and magic angle spinning at 1.8 kHz.

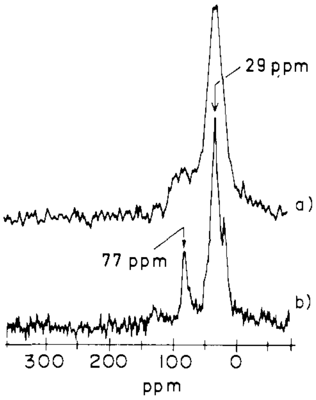

Figure 2. ^{13}C NMR spectra taken on the same sample used to obtain spectra Figure 1 after the sample had been heated to 373 K for 5 min in a sealed tube. Spectrum b was taken with magic angle spinning; spectrum a was taken without.

The ^{13}C NMR spectra were obtained with standard pulse-Fourier transform techniques in a 3.55-T magnetic field at a resonance frequency of 37.84 MHz. Two different, double-resonance probes were used in the experiments. The first, a magic angle spinning, variable-temperature (100–300 K) Doty probe, was used for most of the experiments.[29] The second, a static, cryogenic probe, was used to examine spectral changes down to 10 K.[30] To eliminate effects of receiver dead time, the standard $90°-\tau-180°$ Hahn spin-echo pulse sequence ($\tau \sim 100$ ms) was used in all experiments with proton decoupling. Cross polarization for signal enhancement was not very effective because of short ^{13}C $T_{1\rho}$ and T_1 and was not used. However, the combination of short T_1's and the use of isotopically enriched samples allowed us to achieve reasonable signal to noise ratios with signal averaging over relatively short time periods. All spectroscopic data reported in this paper are referenced to liquid TMS.

The 95% ^{13}C-enriched $(CH_3)_3{}^{13}COH$ used in all the NMR studies was prepared by MSD Isotopes, Inc. The ^{13}C distribution was checked by conventional liquid-phase ^{13}C NMR, which confirmed the enrichment at the hydroxyl carbon of the molecule (68.8 ppm in the Doty probe). Because of the reactive nature of the intermediates, it was vital to the interpretation of the results that preparation of the samples for the NMR studies be as nearly identical as possible with that used in previous TPD–TGA experiments. It is only under these conditions that we could stabilize a dehydrated complex at a coverage close to 1 molecule/Al.[3] The following procedure was therefore employed: Between 30 and 35 mg of zeolite was dispersed on each of four flat pans, which were then suspended in a glass tube attached to the high-vacuum system used in the previous TPD–TGA experiments. Following evacuation and heating to 700 K, the H-ZSM-5 samples were exposed to 10 Torr of $(CH_3)_3{}^{13}COH$ vapor at 295 K for 5 min followed by 1.5 h of evacuation to remove excess alcohol and water. The samples were then stored in dry ice (195

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K) to minimize secondary reactions such as oligomerization or C-scrambling. However, subsequent NMR characterization showed that, even with these precautions, secondary reactions could not be entirely eliminated. In the Doty probe, the sample transfer was accomplished in a glovebox under an inert atmosphere to the sapphire rotors with Macor O-ring end caps. For NMR experiments utilizing the cryogenic probe, the samples were sealed in a tube with a glass-to-metal seal, partially filled with He for heat transfer, and mounted in the configuration shown in Figure 1b of ref 30.

To illustrate the importance of sample preparation, we have also obtained results using a more conventional procedure. Here, samples were prepared from 150 mg of loosely packed zeolite in a 1-cm-o.d. Pyrex tube. The samples were exposed to the vapor pressure of the alcohol for 30 min at 295 K, evacuated for 20 h to remove excess alcohol and water, and sealed off from the vacuum line with a gas torch. Later characterization demonstrated that the weight change in TGA on these samples corresponded to approximately 2.5 molecules/Al site. Furthermore, TPD indicated that all of these molecules had reacted to form large hydrocarbon species. The products observed in these samples are apparently the result of secondary reactions, which are enhanced by the presence of excess alcohol and the length of time for exposure of the sample to the alcohol at 295 K. Samples prepared in this way will be referred to as high-coverage samples to distinguish them from samples with a coverage close to that of 1 molecule/Al.

The zeolite samples were obtained as an NH_4-ZSM-5 powder from the Mobil Oil Corp. Electron microscopy indicated that the zeolite particles were uniformly between 0.4 and 0.5 μm in diameter. X-ray diffraction of these samples agreed with the published data for ZSM-5.[10] We checked the silica-alumina ratio by measuring the desorption of NH_3 from NH_4-ZSM-5 and obtained a ratio of 72, in good agreement with the value of 70 reported to us by Mobil. All experiments reported in this paper were performed on H-ZSM-5 prepared by heating NH_4-ZSM-5 to 700 K in vacuo.

Results

Figures 1 and 2 show the ^{13}C NMR spectra of a sample prepared on flat pans in high vacuum. The adsorbate coverage on this sample is close to 1 molecule/Al, and TPD and TGA indicate that dehydration and subsequent water desorption have occurred under these conditions.[3] Figure 1 shows spectra at 200 and 295 K immediately after removal from the dry ice. Two broad features are evident in the vicinity of 80 and 30 ppm, respectively, relative to TMS. The MAS spectrum shows the relative intensities of these two broad features to be in a ratio of 2;3. Different sample preparations give different (and usually smaller) ratios, with the value in Figure 1 representing an upper limit for the relative intensity of the 80 ppm band by the general methods of this study. Since the initial alcohol was labeled only at the hydroxyl carbon, the presence of a band in the range found for aliphatic carbon atoms ($\sim$30 ppm) indicates that some additional reaction has occurred, which changes the labeled carbon atom from a hydroxyl to an aliphatic-type environment. As will be discussed in more detail later, this feature is probably due to oligomerization of the intermediate and indicates the difficulty of exclusively forming an adsorbed, 1:1 complex.

It should be noted that no resolvable spectral feature could be separated from the noise in the region expected for carbenium ions (330 ppm)[13] at any temperature below 300 K, even after extensive signal averaging. Further, the absence of significant line shifts in the spectrum of this sample with temperature would tend to eliminate the possibility that an activated exchange process is important below 300 K between different species in equilibrium in the time scale of 10^{-5} s or less ($\sim$100 ppm).[27,28] Finally, the additional small feature observed in the MAS spectrum at 123 ppm appears in the region of a carbon-carbon double bond,

While no changes were observed in spectra obtained on the sample in Figure 1 for reasonable time scales (less than several hours) at temperatures less than 295 K, heating the sample to higher temperatures had a dramatic effect, as shown in Figure 2. In Figure 2, the same sample used to obtain the spectra in Figure 1 was transferred to a sealed Pyrex tube and heated to 373 K for 5 min before returning it to the sapphire rotor of the Doty probe maintained at 295 K. Under these conditions, no desorption could take place and the spectral changes are entirely due to chemical changes of the adsorbate within the zeolite framework. The substantial decrease in intensity of the feature at 80 ppm indicates that fewer ^{13}C atoms are now attached to the oxygen atoms. Conversely, the region near 30 ppm has grown more complex and intense. The multiplicity of lines in this region suggests aliphatic carbon atoms in a variety of different environments,[15] as expected following oligomerization. The continued absence of significant intensity in the region of carbon-carbon double bonds (>100 ppm) indicates that most of the oligomers are still attached through what will be shown later as alkyl silyl ether type linkages.

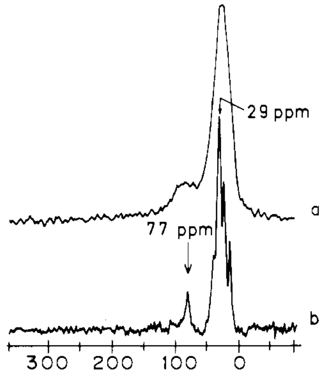

Figure 3. ^{13}C NMR spectra of the intermediates formed from $(CH_3)_3{}^{13}COH$ adsorption on H-ZSM-5 with a larger sample size and longer exposures. The coverage of alcohol on this sample as determined from TGA corresponded to approximately 2.5 molecules/Al atom. Spectrum b was taken with magic angle spinning; spectrum a was taken without. The five peak maxima in the aliphatic region occur at 13, 23, 28, 32, and 38 ppm.

The highly reactive nature of the dehydrated alcohol inside the zeolite can lead to large differences in the spectra depending on the extent of secondary reactions. Sample preparation is therefore very important in understanding the appearance or disappearance of specific spectral features. An example of how important these secondary reactions can be is shown in Figure 3, which shows spectra obtained on a sample prepared by less rigorous evacuation procedures, as described in the Experimental Section. These conditions lead to higher coverages, 2.5 molecules/Al site in this case. The presence of the large excess of alcohol at 295 K leads to spectral features, with regard to both frequency and relative intensity, very similar to that observed after heating the low-coverage sample shown in Figure 2. This NMR spectrum can therefore be interpreted in the same manner, with the exception that the products of secondary reactions now completely dominate the spectrum of the intermediate.

While the present results cannot provide a detailed description of the spin Hamiltonian for this complex system (mainly because of the complexity of the chemistry and the difficulty in controlling the species formed during preparation), they can be used to provide some useful insight to the nature of the reactive species attached to the zeolite framework, which is initially formed by dehydration of the alcohol at the Al site, as well as to the secondary products formed by reaction of this intermediate. When the spectra from Figure 1 are used, since these correspond to the sample with the optimum fraction of ^{13}C atoms attached to the zeolite framework, and when the constraints that the relative intensities of the two broad features be in the ratio of 2:3, independent of temperature and whether or not MAS was employed are fixed, the broad overlapping features at 295 and 200 K can be deconvoluted, as shown in Figures 4 and 5. The stick spectra at the bottom of both figures correspond to the positions (77 and 29 ppm) and relative intensity (2 and 3, respectively) of the deconvoluted powder patterns, assuming all anisotropies and line broadening have been removed. A reasonable, although not perfect, fit to the data can be obtained if the feature near 30 ppm is approximated by a temperature-independent Lorentzian and if the feature near 80 ppm is represented by an axially or nearly axially symmetric chemical shift tensor in which a Lorentzian broadening function is convoluted into the theoretical powder line shape. Further, with decreasing temperature, it must be assumed that a "rigid" tensor

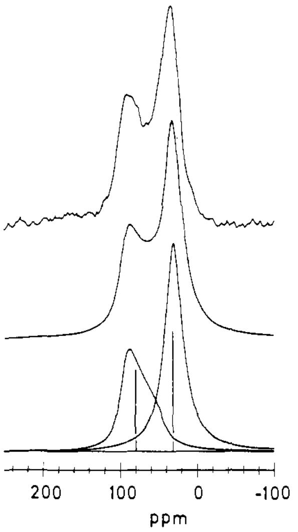

Figure 4. Simulation of the static ^{13}C NMR spectrum obtained at low coverages at 200 K. The top spectrum is the same as Figure 1a. For the band near 30 ppm, a Lorentzian line shape was assumed with a frequency of 29 ppm and a width of 27 ppm. The band near 80 ppm was modeled as an axially symmetric powder pattern with $\sigma_\parallel$ = 93 ppm and $\sigma_\perp$ = 44 ppm, with Lorentzian line broadening of 21 ppm. The areas of the bands at 80 and 30 ppm are in a ratio of 2:3.

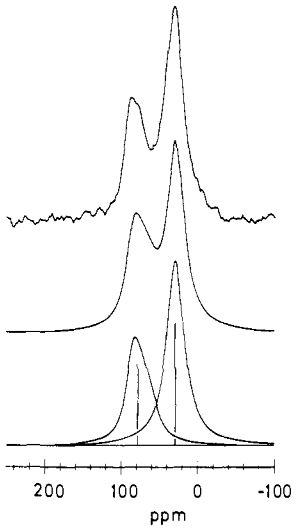

Figure 5. Simulation of the static ^{13}C NMR spectrum obtained at low coverages at 295 K. The top spectrum is the same as Figure 1b. For the band near 30 ppm, a Lorentzian line shape was assumed with a frequency of 29 ppm and a width of 27 ppm. The band near 80 ppm was modeled as an axially symmetric powder pattern with $\sigma_\parallel$ = 87 ppm and $\sigma_\perp$ = 55 ppm, with Lorentzian line broadening of 21 ppm. The areas of the bands at 80 and 30 ppm are in a ratio of 2:3.

grows out of the spectrum due to a slowing of the motion of the adsorbed dehydrated alcohol. This effect has been observed for primary and secondary alcohols adsorbed on H-ZSM-5[6] and is shown for the unreacted, near 1:1 complex for isotopically labeled 2-propanol ($(CH_3)_2{}^{13}CHOH$) in Figure 6. The rigid tensor for adsorbed 2-propanol appears at approximately 130 K; but, for the dehydrated intermediate formed from 2-methyl-2-propanol, it probably occurs at or slightly below 200 K.

The parameters of the powder-averaged, axially symmetric tensors at 295 and 200 K are $\sigma_\parallel$ = 87 and 93 ppm, respectively, and $\sigma_\perp$ = 55 and 44 ppm, respectively, with $\bar{\sigma}$ = 77 ppm in both cases. This isotropic shift, $\bar{\sigma}$, is in good agreement with chemical shifts observed in silyl ethers (or alkoxy silanes if the oxygen atom is viewed as part of the hydrocarbon ligand) model compounds. For example, the isotropic chemical shifts of the *tert*-butoxyl group in bis[(2-ethylhexyl)oxy]di-*tert*-butoxysilane are 72.6 and 31.5 ppm for the central and methyl carbons, respectively.[11] The additional shift of the C–O carbon to lower ppm in the zeolite

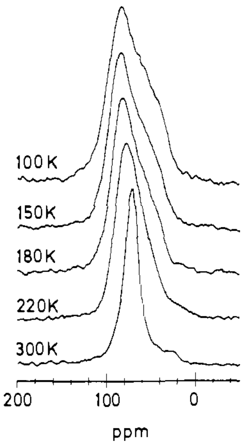

Figure 6. Static ^{13}C NMR spectra of labeled 2-propanol, $(CH_3)_2{}^{13}COH$, adsorbed on H–ZSM-5 at a coverage near 1 molecule/Al atom. The spectra show the evolution of the axially symmetric powder pattern at low temperatures.

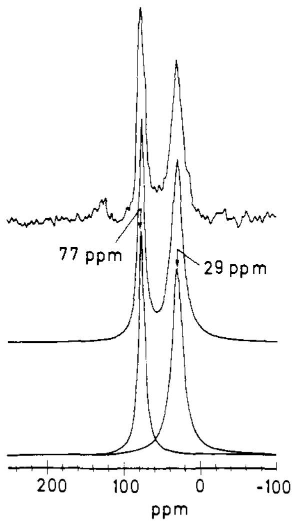

Figure 7. Simulation of MAS ^{13}C NMR spectrum from Figure 1c. A Lorentzian line shape was assumed for both peaks, with frequencies at 77 and 29 ppm and peak widths of 10 and 17 ppm, respectively. The areas of the bands are in a ratio of 2:3.

complex compared to this model compound may be the result of the electron donation to Al. For example, the shift of the central carbon in a *tert*-butoxyl group bound to the more electropositive element, Ti, is 79.7 ppm in $Ti(t\text{-}BuO)_4$.[12] Alternatively, one could view interactions of the Al atom with the silyl ether as giving oxonium ion character to the intermediate. A shift of 19 ppm is observed for the hydroxylic carbon in ethanol when the oxonium ion is formed in FSO_3H-SbF_5/SO_2 solutions at −70 °C.[31] Therefore, we conclude that the NMR characteristics of the dehydrated intermediates are consistent with structure B of Chart I.

It is difficult at present to make an analogous argument for the anisotropies for a silyl ether or oxonium type intermediate bound to the zeolite structure as was used above for the isotropic shift mainly because of a lack of data on model compounds. However, from the examination of reported anisotropies for a variety of compounds with CO-type linkages,[32] the parameters we have used for the carbon bound to the oxygen appear reasonable. A Lorentzian line shape was used for the alkyl carbons (30 ppm) because this peak is made up of carbon atoms with different isotropic shifts.[15] Also, if chemical shift anisotropy is

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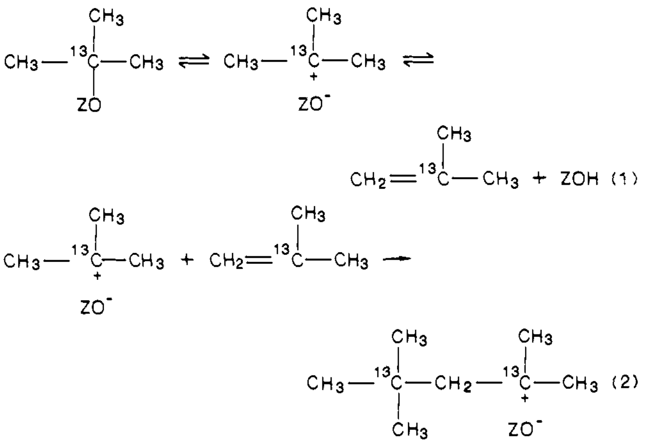
Scheme I



not averaged in these carbons by motion, then one would expect a more symmetric and smaller anisotropy powder pattern ($\sigma_{11} \neq \sigma_{22}$), by analogy with the chemical shift anisotropy of other alkyl carbons.[32] The residual line widths of the deconvoluted MAS spectrum, shown in Figure 7, may be due to the range of different products formed in oligomerization of the intermediates and/or inhomogeneities at the Al sites.

Many of the spectral features observed in our study are related to the secondary chemistry of the intermediate, the initial steps of which can be explained by the reactions shown in Scheme I. The presence of a small concentration of olefins in the zeolite has been verified in the NMR studies by the signal at 123 ppm. Other evidence that an equilibrium exists between the adsorbed intermediate and the olefin comes from infrared spectroscopy and TPD measurements.[3,4] In IR experiments, rapid H/D exchange was observed for adsorbed 2-methyl-2-propanol upon exposure to D_2O vapor at 295 K. A logical mechanism for this isotopic scrambling would involve rapid and reversible reaction as shown in (1) of Scheme I, followed by H/D exchange of ZOH with D_2O.[4] In TPD studies of 2-methyl-2-propanol on H-ZSM-5, we observed gas-phase butene desorbing from the sample during the evacuation stage of complex formation when the SiO_2/Al_2O_3 ratio was large enough to limit the second-order chemistry like that shown in Scheme I.[5]

The oligomerization chemistry represented in Scheme I cannot, however, account for the complexity of the MAS spectra of the larger oligomers in the 10–40 ppm range. The spectra in this region for both Figures 2 and 3 exhibit several well-resolved features, including a band at 13.0 ppm, which implies that the labeled carbon has found its way into methyl or methylene groups that are well isolated from the oxygen or silicon atoms.[15] Even extending the reactions in Scheme I to larger oligomers restricts all aliphatic ^{13}C atoms to quaternary positions, while the observed reorganization of the carbon skeleton clearly required C–C bond breaking. This is additional evidence for carbenium ion intermediates, even though they are not spectroscopically observable in the present study. It is well-known that carbenium ions readily rearrange in solution via 1,2 or 1,3 hydride or alkyl shifts.[16] The interesting aspect of such rearrangements in the present case is that it occurs at room temperature, even though both the monomeric carbenium ion and the oligomeric intermediates involved in Scheme I are tertiary cations.

While the presence of labeled carbon in aliphatic positions in Figure 1 appears to be due predominantly to formation of oligomers, it is interesting to consider the possibility that some of the labeled, aliphatic carbons could be due to scrambling of a monomeric adsorbate. While the rate is slow below 350 K,[16] scrambling of *tert*-butyl carbenium ions has been observed in solution phase and there is evidence that carbenium ions formed in the solid-state may have lower energy barriers for rearrangements than for those formed in solution.[17] However, if the monomeric adsorbed intermediates were able to undergo rapid scrambling, a 1:3 ratio would have been expected for the intensities of the two peaks in the NMR spectrum shown in Figure 1 rather than the approximately 2:3 ratio observed experimentally. In a recent study of *sec*-butyl carbenium ions in solid acids, significant variations in the ^{13}C NMR spectrum were observed as a function of temperature as a result of rapid exchange dynamics.[17] As previously indicated, no changes other than a progressive line broadening have been observed down to 10 K in our studies.

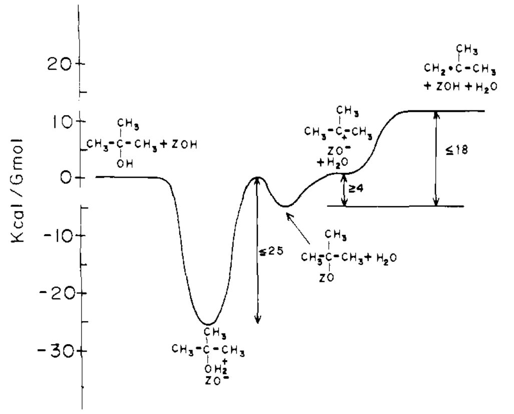


Figure 8. Plot of the chemical reaction profile for the dehydration of 2-methyl-2-propanol on H–ZSM-5 in the form of a potential energy diagram. Estimates of the various energies are discussed in the text.

Discussion

From our previous work with 2-methyl-2-propanol on H–ZSM-5, we were able to show that carbenium-ion-like intermediates could be formed at 300 K. The ^{13}C NMR spectra presented in this paper indicate that the stable structure of these intermediates is best described as that of an alkyl silyl ether or alkoxide covalently bound to the zeolite lattice. Two important questions remain: (1) Can these results be generalized to include different adsorbates and zeolites? (2) How does one rationalize the observed carbenium ion chemistry via a silyl ether intermediate? We will address each of these questions separately.

In retrospect, the fact that the carbenium-ion-like intermediate is covalently bonded to the zeolite framework should not be particularly surprising. It is well-known that protons present at the Al site in dehydrated H–ZSM-5 show a sharp ν(O–H) stretching peak in the infrared spectrum and are usually considered to be covalently bonded as silanol groups to the zeolite framework.[18] Furthermore, in order to form long-lived carbenium ions in solution phase, the solvent must be nonnucleophilic and have a high dielectric constant. The high dielectric constant is important in order to facilitate separating oppositely charged species.[19] For example, a typical super acid capable of forming carbenium ions from alcohols consists of a mixture of HSO_3F, a strong Brøsted acid with a dielectric constant of 130,[20] and SbF_5, a strong Lewis acid that contributes to the nonnucleophilic nature of the acid mixture. While recent reaction experiments suggest that zeolites can be relatively nonnucleophilic,[21] zeolites probably do not possess a high dielectric constant. Furthermore, once the alcohol has dehydrated, the zeolite bears a negative charge. Oxyanions are extremely nucleophilic; so, the charge would have to be efficiently delocalized over the framework to prevent bonding to the hydrocarbon intermediate after the loss of water.

It is interesting to compare our NMR results to other studies of intermediates formed by olefin adsorption on zeolites. Since we can evacuate the water formed from the dehydration reaction of 2-methyl-2-propanol (Figure 8) at 295 K, the intermediates that we have characterized are almost certainly the same as that formed by adsorption of methylpropene on H–ZSM-5. This statement is supported by the observation that the alcohol-derived intermediate oligomerizes further when the sample is heated. Van den Berg et al.[22] have reported the ^{13}C spectra of small olefins adsorbed on H–ZSM-5, which indicate only the presence of aliphatic carbon atoms. No bands were observed at frequencies that could be associated with either olefinic species, carbenium ions, or carbons bound to oxygen. Since termination of olefin oligomerization must result in the formation of one of these per hydrocarbon chain, it must be concluded that very large chains are formed in the zeolite cavities exposed to simple olefins. Further, if the assignment by these workers of CH, CH_2, and CH_3 groups on the basis of chemical shifts is correct, then the chains in the zeolite are linear on the basis of relative intensities of peaks in the spectrum.

There are, however, two important assumptions in their analysis that are subject to question. One is the assignment of CH, CH_2, and CH_3 species to specific regions of the ^{13}C NMR spectrum between 10 and 30 ppm when, in fact, they are strongly overlapping depending on the environment, even in simple alkanes.[15] The second is the use of peak intensities in the spectrum to determine the concentrations of local structure since this may be in error when using cross-polarization techniques. Regarding the intensities of the peaks in the aliphatic region, it is interesting to note that the ^{13}C NMR spectrum following exposure to several different olefins is very similar to that following 2-methyl-2-propanol adsorption. This similarity would suggest there is one preferred hydrocarbon skeleton formed in the zeolite cavities from all molecules studied, which implies facile skeletal reorganization of the intermediates.

In a more recent ^{13}C NMR study of propene adsorption on H–Y,[23] identifiable, albeit weak, spectral features were observed in the region expected for carbenium ions. However, the most prominent feature observed in that study, besides the intense peaks associated with aliphatic carbons of oligomer chains, was a peak at approximately 70 ppm from TMS. This peak was assigned by the authors to the carbon atom next to a carbenium ion center; however, such carbon atoms normally exhibit frequencies that are shifted between 15 and 30 ppm from normal aliphatic carbon atoms. They would therefore be expected to appear between 45 and 60 ppm from TMS.[24,25] While the presence of the zeolite environment makes this assignment plausible, our observation of a strong feature close to this frequency on adsorption of 2-methyl-2-propanol, which we have argued is due to a silyl ether species, suggests that the peak observed with propene adsorption on H–Y could also be due to a silyl ether species.

The observation of carbenium ions following propene adsorption on H–Y, but not following alcohol adsorption on H-ZSM-5, must be due to differences either in the type of zeolite used or the sample preparation conditions. Regarding sample preparation, it is very clear that substantial oligomerization occurred upon the adsorption of propene in H–Y. Therefore, the carbenium ions that were observed were probably part of a very complex molecule and not simple monomeric secondary or tertiary ions. The presence of surrounding oligomer may also affect both the kinetic and thermodynamic stabilities of the intermediates. Regarding the zeolite, H–Y zeolites with SiO_2/Al_2O_3 ratios of 2.5 and 4.0 may be better able to support carbocations than an H-ZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 70 due to differences in the dielectric constant or nucleophilicity. Finally, the cavities in a Y zeolite are much larger than in a ZSM-5 zeolite. This may enable a planar carbenium ion to form more easily in the Y zeolite and change the relative stabilities of the silyl ether with a tetrahedral carbon and the carbenium ion. Obviously, further work is needed to resolve some of these issues.

Although our ^{13}C NMR spectra strongly support the formation of a silyl ether intermediate, probably complexed to an Al atom, it is very clear that we are observing carbenium-ion-like chemistry following adsorption of 2-methyl-2-propanol on H-ZSM-5. To better understand the behavior of this intermediate, it is useful to examine the chemical reaction profile in the form of a potential energy diagram. The accumulated data from our TPD-TGA,[3,5] IR,[4] and ^{13}C NMR studies suggest a potential energy surface like that shown in Figure 8. Using the free alcohol and zeolite on the left side of the reaction coordinate as a reference, we place the noninteracting olefin and water products on the far right side of the diagram at +12 kcal/g·mol based on the standard heat of reaction of 2-methyl-2-propanol to isobutene and water. The reaction is assumed to proceed by transfer of a proton from the zeolite to the alcohol to form an oxonium ion, which in turn dehydrates to form the silyl ether intermediate. Direct spectroscopic evidence for oxonium-ion-like species as the first-formed intermediates in alcohol adsorption has been presented elsewhere.[4,6] Between the silyl ether intermediate and both the oxonium ion and the olefin product, carbenium ion intermediates are implied. Since they were not observed in any of our experiments, the carbenium ions may not be true intermediates and may only exist as saddle points in the potential energy diagram. Finally, the reaction of the oxonium ion to form the alkoxide and water is irreversible in our experiments because of the evacuation of water after chemisorption. Admittedly, this representation of the reaction is qualitative until more detailed calorimetric or kinetic data have been acquired. However, reaction products as well as order of magnitude reaction rates are well described by this picture.

Various means can be used to estimate the energies of each species on the reaction coordinate. In an earlier paper, we estimated the energy associated with forming an oxonium ion on H-ZSM-5 from 2-methyl-2-propanol to be −25 kcal/g·mol. This was based on a comparison of proton affinities for methanol and 2-methyl-2-propanol and the measured heat of adsorption for methanol.[3] We know that the decomposition reaction occurs readily at 295 K from the fact that the water formed can be evacuated at room temperature[3] and from IR measurements.[4] From these observations, we estimate that a lower limit for the rate constant is 10^{-2} s^{-1}. Using a reasonable value for the preexponential factor of 10^{16} s^{-1},[26] we calculate that the energy difference between the oxonium ion and the transition state for dehydration is less than 25 kcal/g·mol. This places the silyl ether (the reaction product) and the hydrated carbenium ion (the presumed intermediate for dehydration) at ≤ 0 kcal/g·mol relative to the isolated alcohol. We may also obtain an indication of the stability of the silyl ether from the observation that isotopic exchange occurs very rapidly between D_2O and the intermediate.[4] (Complete deuteration of the intermediate occurred following 30-s exposure to 10 Torr of D_2O at 295 K.) Assuming that this intermediate must decompose completely to the olefin and a proton for exchange to occur and that the presence of excess D_2O does not appreciably affect the relative energies of the intermediate or products (a questionable assumption), a lower limit of approximately 1 s^{-1} for the rate constant for the ether-to-olefin reaction is obtained. Again assuming a "normal" preexponential factor, we calculate that the energy difference between the ether and the olefin cannot be greater than 18 kcal/g·mol. Since the olefin lies +12 kcal/g·mol above the starting alcohol, this places the silyl ether at ≥ -6 kcal/g·mol relative to the alcohol. Combining this result with that obtained from the dehydration of the oxonium ion places the silyl ether between −6 and 0 kcal/g·mol relative to the isolated alcohol.

Finally, the energy difference between the carbenium ion and the silyl ether can be estimated by assuming that equilibrium exists between these species. Since no peak corresponding to the carbenium ion was ever observed in our ^{13}C NMR spectra nor any evidence of rapid exchange between the silyl ether and the carbenium ion which would cause shifts in the peak position with temperature,[27,28] one can only assume that its concentration is very small. Using an upper limit of 1% for our ability to detect a carbenium ion and assuming that the entropy of reaction is negligible, we calculate that the enthalpy difference between the silyl ether and the carbenium ion is a minimum of 4 kcal/g·mol.

The resulting energy diagram in Figure 8 is useful for describing the chemistry that occurs on H-ZSM-5 with 2-methyl-2-propanol. Regardless of whether one examines the process from the alcohol or olefin side of the diagram, the positions of each of the intermediates are consistent with all of the individual reaction steps. Furthermore, Figure 8 can be used to rationalize how the process may be affected by changes in reactant structure or reaction conditions. For example, the relative energies of the alcohol, oxonium ion, silyl ether, and olefin should be much less sensitive to the structure of the alkyl group than the energy of the carbenium ion. Therefore, changes in rates and product distribution with alcohol structure should still be dominated by carbenium ion stabilities, even though they may not be directly observable.[3] If the carbenium ion energy is increased even modestly, it will become kinetically difficult to dehydrate the oxonium ion to the ether at ambient temperature. However, the silyl ether intermediates (for example, a 2-propyl silyl ether from propene) may still be reached from the olefin side since this chemistry is more exothermic. Therefore, for the primary and secondary alcohols, the oligomerization chemistry characteristic of the olefins is not observed in our experiments.[3,4] In general, this type of diagram provides a useful framework for describing the link between alcohol reactants and complex hydrocarbon products via spectroscopically detectable reaction intermediates over H–ZSM-5.

Summary

The ^{13}C NMR spectrum of the intermediate formed from the adsorption and subsequent dehydration of 2-methyl-2-propanol on H–ZSM-5 at 295 K shows that the intermediates can best be described as silyl ethers in which an alkyl group is covalently bound to the zeolite lattice. No peaks were observed in ^{13}C NMR spectra that could be attributed to carbenium ions, although all of the results are consistent with the formation of an equilibrium between a silyl ether and a carbenium ion. This silyl ether intermediate undergoes the same oligomerization chemistry found with simple olefins in H–ZSM-5, implying that it is also important in olefin reactions on H–ZSM-5.

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Registry No. 2-Methyl-2-propanol, 75-65-0.

Steric Effects and Threshold Rotational Mechanisms in 1-Substituted 2,2-Dimesitylethenols[1]

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Abstract: The static and dynamic stereochemistry of 1-alkyl- (and 1-H) 2,2-dimesitylethenols ($Mes_2C{=}C(OR_2)R_1$) is studied and analyzed. The low-temperature ^1H NMR data for the enols are in agreement with a propeller conformation in solution. A ^1H dynamic NMR study shows that **1** ($R_1 = R_2 = H$) behaves differently from the other enols: enol **1** shows *two* different processes for the exchange of groups at each mesityl ring ($\Delta G^{\ddagger}_{c}$ = 10.4 and 14.2 kcal mol^{-1}). The 1-alkyl-substituted enols **2**–**5** (R_1 = Me, Et, *i*-Pr, *t*-Bu; R_2 = H) display a single measurable barrier, which decreases with the increase of the bulk of the R_1 substituent. Substitution of the enolic hydrogen of **1** by an isopropyl group affords the enol ether **6** (R_1 = H; R_2 = *i*-Pr). From comparison of the enantiomerization barrier and the mesityl rotational barrier in either **4** or **6** it is concluded that the threshold rotational mechanism is the one-ring flip for **1** and **6** and the two-ring flip for **2**–**5**. These conclusions are strengthened by molecular mechanics calculations on **1** and **2** that satisfactorily reproduce their experimental rotational barriers. The rotational barriers for the two-ring process of **1**–**5** are linearly correlated with Taft's E_s values, with ϕ_2 (the torsional angle of the ring cis to R_1), and with α_4 (the $C{=}C{-}R_1$ bond angle). The two latter relationships with the structural parameters represent dynamics–structure correlations, and from that with ϕ_2 a crude estimate of this ϕ_2 torsional angle in the transition state of the two-ring flip process is obtained.

Triarylvinyl systems $Ar'ArC{=}C(Y)Ar''$ (Y = OH, H, Cl, OAc, OR) exist in a propeller conformation where the aryl groups (the propeller "blades" radiating from the double bond) are all twisted in the same sense.[2-4] When all the rings are identical and have local C_2 axis, these systems exist solely in two enantiomeric forms (assuming an effective conical symmetry of the Y substituent). These enantiomeric forms can be viewed as differing in helicity, i.e., in the sense of twist of the rings.[5]

The "vinyl propellers" display correlated rotation of the aryl rings, which can be conveniently analyzed in terms of "flip" mechanisms. In these mechanisms[6] (all involving helicity reversal) the ring which "flips" passes through a plane perpendicular to the ideal double bond plane, while the remaining rings rotate concurrently, disrotatorily, in the opposite direction and pass through the double bond plane. Depending on the number of flipping rings the different flip mechanisms are designated zero-, one-, two-, or three-ring flip.[7] In contrast with molecular propellers of the type Ar_3Z and Ar_3CX (Z = C, B, or N; X = H, Me, or halogen) for which the rotational mechanism of lowest activation energy (threshold mechanism) is the two-ring flip,[8] the trimesitylvinyl propellers $Mes_2C{=}C(Y)Mes$ (Mes = 2,4,6-$Me_3C_6H_2$) display a substituent-dependent threshold mechanism. When the double bond substituent Y is hydrogen, the threshold mechanism is the [α,β]-two-ring flip[4] (in which the α ring and the β ring trans to the Y substituent "flip") whereas for bulkier substituents (Y = OH, Cl, OAc, OPr-*i*) the threshold mechanism is the three-ring flip.[2] The difference in the threshold mechanism was ascribed

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