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Reactions of Propene on Zeolite HY Catalyst Studied by in Situ Variable-Temperature Solid-State Nuclear Magnetic Resonance Spectroscopy

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Abstract: The oligomerization reactions of propene on zeolite catalyst HY have been studied in detail by in situ variable-temperature ^{13}C solid-state NMR with cross polarization (CP) and magic-angle spinning (MAS). Propene is shown to be highly mobile in the zeolite at temperatures far below the onset of chemical reactivity. Alkoxy species formed between protonated alkenes and zeolite framework oxygens are found to be important long-lived intermediates in the reactions. Simple secondary or tertiary carbocations either do not exist as free ions in the zeolite at low temperature or are so transient that they are not detected by NMR even at temperatures as low as 163 K. There is, however, evidence for long-lived alkyl-substituted cyclopentenyl carbocations, which are formed as free ions in the zeolite at room temperature. These carbocations do not form until all of the propene is consumed and hence do not play a significant role in the oligomerization reactions. A detailed reaction mechanism is proposed to account for all of the experimental observations. Novel experimental techniques are introduced which will be applicable to the study of many highly reactive catalyst/adsorbate systems.

The reactions of hydrocarbons on zeolite catalysts are, from an economic standpoint, among the most important reactions in all of chemistry. It is therefore ironic that so little direct information is available about the mechanisms of such reactions. As a result of numerous indirect experiments examining product distributions, catalyst acidity, isotopic label scrambling, and the roles of impurities and poisons, many of the reactions of hydrocarbons on acidic zeolite catalysts[1] have been rationalized in terms of carbocation[2] intermediates. It has been increasingly recognized, however, that there are some problems with the carbocation formalism. Solid acid catalysts often show selectivity patterns and sensitivities to pretreatment conditions that are difficult to interpret in terms of the carbocation hypothesis,[3] and some workers have postulated that carbocations actually represent one extreme of a spectrum of possible reaction mechanisms with concerted processes on the opposite extreme.[4] For example, Kramer and co-workers have postulated the existence of alkoxy intermediates in order to account for the activation energy for the isomerization of alkenes on the surface of amorphous silica–alumina.[3] With the development of techniques for the preparation and study of stable carbocation species in superacid solutions it became possible to directly study the structure and reactivity of carbocations in solution, but analogous studies of reactive intermediates on solid acid catalysts remained technically unfeasible until the development of high-resolution solid-state NMR methods such as cross polarization (CP) and magic-angle spinning (MAS).[5]

In a recent communication,[6] Zardkoohi and co-workers reported the observation of carbocations produced by the adsorption of propene-*2*-^{13}C on zeolite HY at room temperature. Since propene rapidly and completely oligomerizes on HY catalyst at room temperature, it was not possible in that study to observe any of the reactions in progress, and all of the conclusions of that study were based on interpretations of ^{13}C CP/MAS spectra of a mixture of products in the zeolite. In the present investigation, we have used a novel method for the study of highly reactive adsorbates on catalysts by in situ variable-temperature magic-angle spinning NMR[7] to probe, in considerable detail, the sequence of reaction steps that occurs subsequent to the adsorption of propene on HY. Although these studies do provide further evidence for the formation of long-lived carbocation species in the catalyst under some circumstances, the present results question the role of fully developed carbocations as long-lived intermediates in oligomerization reactions of propene on zeolite HY at room temperature. Instead, evidence for the role of alkoxy species as catalytic intermediates is presented. We also demonstrate, contrary to previous assumptions,[6] that the ^{13}C labels of propene do not scramble prior to reaction. Support for the proposed mechanisms is developed by spectroscopically following the fate of labels through the course of in situ experiments. We also show that propene is highly mobile in the zeolite at temperatures far below the onset of chemical reactivity.

A novel experimental technique described in this contribution will be applicable to the study of a number of highly reactive catalyst/adsorbate systems.

Experimental Section

Sample Preparation. Propene-*1*-^{13}C (99.3% ^{13}C) and propene-*2*-^{13}C (99.2% ^{13}C) were obtained from MSD Isotopes. Propene-*3*-^{13}C (99.2% ^{13}C) was supplied by Cambridge Isotopes. Natural-abundance propene (99.0%) was obtained from Matheson Gas Products. NaY zeolite (Strem) was exchanged five times with 1 M NH_4NO_3 (99.85%, Mallinckrodt) to obtain NH_4Y zeolite which was then converted to HY catalyst by a multistep activation procedure.[8] After 1 h at a final temperature of 673 K, the catalyst was evacuated to a final pressure of $<5 \times 10^{-5}$ Torr. Using trimethylphosphine as a probe molecule, Lunsford and co-workers have shown that zeolite HY calcined at 673 K does not contain Lewis acid sites,[9,10] although samples calcined at 773 K and above

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[1] See, for example: (a) Gates, B. C.; Kazer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw Hill: New York, 1979. (b) Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversion*; Academic Press: New York, 1981. (c) Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980.

[2] The term carbenium ion is more explicit for trivalent carbons bearing a positive charge, because this nomenclature distinguishes carbenium ions from pentavalent carbonium ions. In this contribution, we use the more familiar term carbocation instead of carbenium ion to conform to common usage in the literature of heterogeneous catalysis.

[3] Kramer, G. M.; McVicker, G. B.; Ziemiak, J. J. *J. Catal.* **1985**, *92*, 355.

[4] See: Reference 1a, p 28.

[5] For reviews of the CP/MAS NMR technique, see: (a) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 210. (b) Maciel, G. E. *Science (Washington, D.C.)* **1984**, *226*, 282.

[6] Zardkoohi, M.; Haw, J. F.; Lunsford, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 5278.

[7] For reviews of the variable-temperature MAS NMR technique, see: (a) Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208. (b) Haw, J. F. *Anal. Chem.* **1988**, *60*, 559A.

[8] Zeolite HY was obtained from NH_4Y by: (a) first slowly heating the catalyst to 373 K over a 2-h period; (b) maintaining that temperature for 1 h; (c) slowly increasing the temperature in 100 K increments to a final temperature of 673 K with a 1-h wait after each step.

[9] Lunsford, J. H.; Rothwell, W. P.; Shen, W. *J. Am. Chem. Soc.* **1985**, *107*, 1540.

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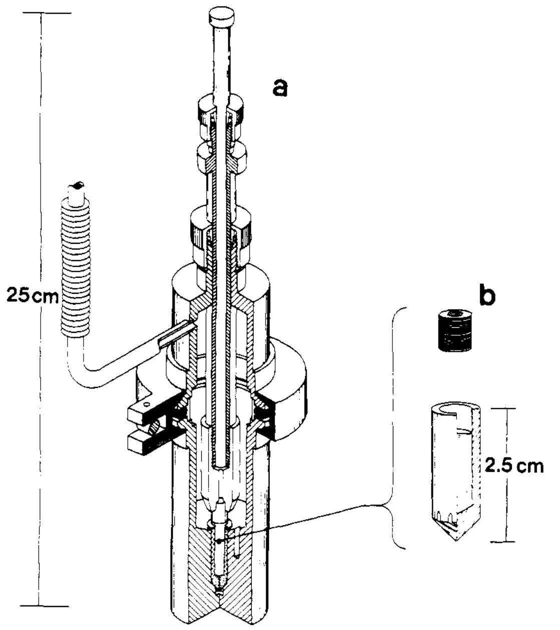

Figure 1. (a) Diagram of the CAVERN apparatus used for adsorbing propene onto HY catalyst at cryogenic temperatures and sealing the magic-angle spinning rotor. (b) Expanded view of the magic-angle spinning rotor and cap.

do possess Lewis sites. Similar conclusions were reported by Ward, who found that Lewis sites were virtually nonexistent in HY samples that were calcined at temperatures less than 523 K.[11]

For several of the experiments, a final temperature of 573 K was used to investigate the effect of lower calcination temperature. In all cases, activated catalyst was either used immediately after preparation or stored for at most a few days in a sealed tube kept in a glovebox filled with argon.

Several dozen samples were prepared for NMR study by a procedure similar to that described in ref 6. Approximately 0.15 g of zeolite HY was exposed to 35–45 Torr propene, and the loading (typically 0.4 mmol of propene) was measured with a mercury manometer. In carrying out these adsorptions, the catalyst was allowed to contact the gas for approximately 20 min at room temperature. In some cases, adsorptions were carried out at ice temperature and/or different loadings were used to investigate the effects of sample preparation conditions. MAS sample rotors were packed in a glovebox under argon or, in some cases, under 99.9995% nitrogen (M. G. Industries) with a water content of less than 1 ppm and an oxygen content of less than 2 ppm. No differences were observed between samples prepared under the different high-purity inert gases. Although the labeled propene samples were prepared by the vendors using techniques that should preclude contamination with water, we also investigated the use of cold trapping prior to adsorption as a sample cleanup step. As expected, no differences were observed in the NMR spectra.

With the exception of samples deliberately exposed to atmospheric moisture, all of the NMR spectra acquired in this study were obtained while spinning on dry nitrogen boil-off gas from a Dewar. All samples were packed in either a special type of MAS rotor designed for air- and moisture-sensitive compounds[12] or a variant of that design (vide infra).

A second method of sample preparation involves novel apparatus and techniques and hence requires a detailed discussion. We have previously established that the adsorption of propene on HY at room temperature resulted in extensively oligomerized products. Indeed, no unreacted propene was observed in ref 6. In order to use MAS NMR to study the chemistry of propene on HY, it is necessary to prepare the sample at cryogenic temperatures and seal it in an MAS rotor in such a fashion as to preclude warming or exposure to atmosphere. These are technically demanding requirements, but they can be met by using the device depicted in Figure 1, which we call the cryogenic adsorption vessel enabling rotor nestling (CAVERN). It was constructed from two large stainless steel parts: the housing (upper part) and base (lower part), which are joined by an MDC Kwik-Flange hinged clamp assembly. The vacuum integrity of this joint is maintained with an O-ring. We found that the Viton O-ring supplied with the clamp assembly tended to leak at reduced temperatures, so we replaced it with an Eypel-F (Ethyl Corp.) polyphosphazene O-ring. A stainless steel feedthrough mounted in a Cajon Ultra-Torr fitting welded to the top of the housing is used to push (nestle) the rotor cap into place following adsorption.

The rotor design used with the CAVERN apparatus (inset of Figure 1) is a variant of another novel design which we recently reported.[12] The rotor and cap are machined from Kel-F. A series of grooves on the outside of the cap provides the equivalent of 12 O-rings after the cap is pushed into the rotor. This rotor design provides a highly effective method of sealing the sample at cryogenic temperatures and is, in our experience, more reliable than sealed glass ampules, which require flame sealing or epoxy plugs and, in any event, are often difficult to spin.

In a typical low-temperature adsorption experiment, 0.2 g of freshly activated catalyst is loaded into the rotor which is then placed in the base of the CAVERN. The rotor cap is press fit into the feedthrough of the housing, and then the CAVERN is assembled and sealed. All of the above operations are performed in a glovebox under argon. The CAVERN is removed from the glovebox and connected to the vacuum line via a $^1/_4$-in.-diameter flexible stainless steel glass-end tube which is terminated with a glass stopcock and joint (not shown). The CAVERN is then evacuated to 10^{-5} Torr and cooled to approximately 170 K by raising a bath (typically liquid nitrogen or liquid nitrogen–pentane slush) over the base. A thermistor mounted in the base and adjacent to the rotor facilitates temperature regulation. Propene is then adsorbed onto the catalyst in much the same fashion as described above for samples prepared at room temperature. Once adsorption is judged to be complete, the rotor is sealed by pushing down on the feedthrough. The CAVERN is then removed from the vacuum line and opened to reveal a sealed rotor at cryogenic temperature. The sample can either be studied immediately after preparation or be stored at 77 K for an indefinite period. In either case, the rotor is transferred without warming to a CP/MAS NMR probe precooled to approximately 173 K. The above procedure presents the spectroscopist with an unreacted sample of propene adsorbed on HY catalyst prepared under conditions that exclude atmosphere. We have not seen any evidence that propene reacts with the walls of the CAVERN prior to adsorption on the catalyst.

NMR Spectroscopy. All variable-temperature ^{13}C solid-state NMR experiments were performed at 25.02 MHz on a Chemagnetics M-100S spectrometer by using a CP/MAS probe and variable-temperature procedures which we have previously described.[13] Most of the room-temperature NMR experiments were also performed on this instrument. In addition, a Bruker MSL-300 spectrometer equipped with a Chemagnetics CP/MAS probe was used to obtain room-temperature ^{13}C MAS spectra at 75.47 MHz for several samples.

Results and Discussion

The effectiveness of the CAVERN apparatus was tested by adsorbing natural-abundance propene at 201 K and transferring the sealed rotor to a CP/MAS NMR probe which had been precooled to 173 K. The ^{13}C MAS spectrum of this sample at 203 K (Figure 2a) shows three peaks at the chemical shifts expected for unreacted propene.

The extent to which propene reacts on the catalyst when adsorption takes place at room temperature can be appreciated in Figure 2b–d, which show 25.02-MHz ^{13}C CP/MAS spectra of samples prepared by room-temperature adsorption of propene-*1*-^{13}C (Figure 2b), propene-*2*-^{13}C (Figure 2c), or propene-*3*-^{13}C (Figure 2d) on zeolite HY. The intense resonances in Figure 2b–d, which show hints of fine structure, are consistent with the aliphatic carbons of branched alkanes and alkenes. It is clear from Figure 2 that propene is completely consumed by oligomerization reactions on HY at room temperature, as was previously reported. In ref 6 it was assumed that the ^{13}C label on propene would scramble through a protonated cyclopropane intermediate[14] prior to oligomerization. The ^{13}C CP/MAS spectra of the three isotopomers (Figure 2b–d) are unique, however, implying ^{13}C-label retention. Further evidence for label retention will be presented later in this contribution.

The spectrum of propene-*2*-^{13}C adsorbed at room temperature (Figure 2c) is essentially identical with that reported in ref 6.

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(10) Lunsford, J. H.; Tutunjian, P. N.; Chu, P.-j.; Yeh, E. B.; Zalewski, D. J. *J. Phys. Chem.*, in press.

(11) Ward, T. R. *J. Catal.* **1967**, *9*, 225.

(12) Haw, J. F.; Speed, J. A. *J. Magn. Reson.* **1988**, *78*, 344.

(13) Haw, J. F.; Campbell, G. C.; Crosby, R. C. *Anal. Chem.* **1986**, *58*, 3172.

(14) Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *J. Am. Chem. Soc.* **1973**, *6*, 53.

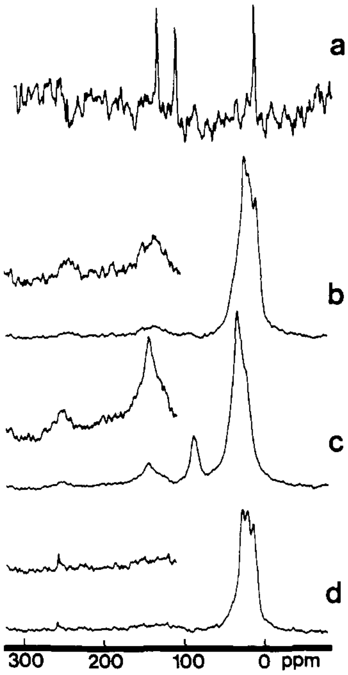

Figure 2. (a) ^{13}C MAS NMR spectrum of natural-abundance propene adsorbed on HY catalyst at 188 K with the CAVERN apparatus. The spectrum was obtained at 193 K and is the result of 1000 transients. (b) ^{13}C CP/MAS spectrum of propene-*1*-^{13}C adsorbed on HY catalyst at room temperature. (c) ^{13}C CP/MAS spectrum of propene-*2*-^{13}C adsorbed on HY catalyst at room temperature. (d) ^{13}C CP/MAS spectrum of propene-*3*-^{13}C adsorbed on HY catalyst at room temperature. The latter three spectra were obtained at 298 K, and each is the result of 3000 transients.

Several low-intensity signals at 250, 143, and 87 ppm in Figure 2c are sensitive to sample preparation conditions and, as we will show, are highly significant with regard to the chemistry of propene catalyzed by zeolite HY. The assignments of these resonances will prove critical to the differentiation of possible mechanisms for the reactions of olefins on acidic zeolites and will, therefore, receive considerable attention later in this contribution. The relative intensities of resonances in solid-state NMR spectra depend on the manner by which transverse magnetization is generated and the relevant relaxation rates. Cross polarization spectra emphasize relatively immobile constituents, while Bloch decay (i.e., single-pulse excitation) spectra emphasize constituents with short ^{13}C spin–lattice relaxation times (T_1). ^{13}C T_1s were measured at room temperature for a sample of propene-*2*-^{13}C adsorbed on an HY sample activated at 573 K. This sample contained some unreacted propene as well as oligomeric products and the 87-ppm resonance. Both unreacted propene and the signals in the aliphatic region of the spectrum had ^{13}C T_1s of approximately 80 ms, whereas the 87-ppm resonance was found to have a T_1 of 2–3 s. The former value is consistent with mobile adsorbates on catalysts, but the latter value is suggestive of a rigid species. Bloch decay spectra obtained with pulse delays of several seconds will, therefore, be reasonably quantitative while the cross polarization spectra will significantly underestimate the unreacted propene and the mobile oligomers. In a separate Bloch decay experiment on a more sensitive high-field instrument, the integrated intensity of the 87-ppm resonance was found to be approximately 2% that of the other signals in the spectrum, indicating that the functionality corresponding to this resonance is actually present in small concentrations. It is emphasized in the cross polarization spectra as a result of its low mobility (vide infra). In a separate measurement, the peaks in this spectrum were found to have ^{13}C $T_{1\rho}$ values of 5–10 ms.

The CAVERN apparatus makes possible in situ MAS NMR experiments of highly reactive catalyst/adsorbate systems. By following the course of reactions in situ, it is possible to get far more mechanistic information than is available by examination of the system after all reactions have gone to completion. Propene-*2*-^{13}C was adsorbed on HY at a temperature of 203 K with the CAVERN apparatus, and the sealed rotor was transferred to the CP/MAS probe, which had been precooled to 203 K. The rotor was induced to spin at approximately 3 kHz, the temperature was raised stepwise in 10 K increments, and ^{13}C spectra were acquired following equilibration at each temperature.[15] Representative spectra are shown in Figure 3. Both cross polarization (2-ms contact time, 1-s pulse delay) and Bloch decay (90° ^{13}C pulse, 2-s pulse delay) spectra were collected at each temperature. The spectra in Figure 3 do not show peaks due to propene-*1*-^{13}C or propene-*3*-^{13}C at any temperature, a result that further confirms ^{13}C-labeled retention in the reactions of propene on HY at low temperatures.

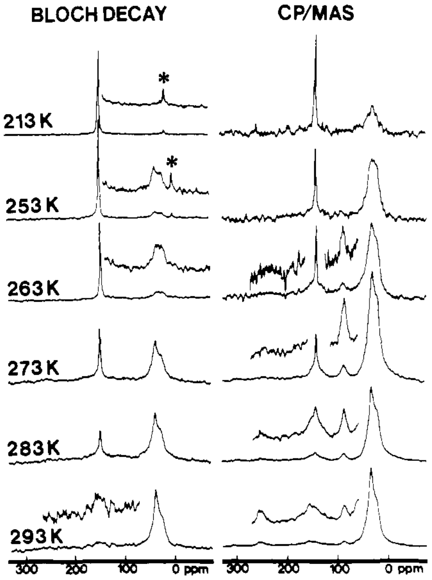

Figure 3. ^{13}C MAS NMR spectra showing propene-*2*-^{13}C reacting on HY catalyst as the temperature was raised from 213 K to ambient. The sample was prepared with the CAVERN apparatus. Each Bloch decay spectrum is the result of 36–144 transients, and each CP spectrum is derived from 400 (lower temperatures) to 3000 (higher temperatures) transients (conditions are described in the text). * denotes spinning sidebands.

Very little of the propene had reacted by the time the sample temperature was raised to 213 K (Figure 3). The Bloch decay spectrum at that temperature shows a single resonance at 139 ppm, while the cross polarization spectrum shows a trace of oligomer and a weak signal due to (mobile) propene-*2*-^{13}C. Equilibrating the temperature at 253 K resulted in a significant increase in oligomer. Since the Bloch decay spectrum is relatively quantitative, we can estimate that a 29% conversion of propene has been reached at this point in the experiment.

After the temperature was raised to 263 K, a Bloch decay spectrum (Figure 3) indicated that approximately 34% of the propene had reacted. The signal-to-noise of the cross polarization spectrum at this temperature is fairly good due to the progress of reaction, and two additional signals can be observed at 87 and ca. 140 ppm. These spectral features greatly increased in intensity after the temperature was raised to 273 K and approximately 70% of the propene was consumed. Both signals are present in the spectrum of propene-*2*-^{13}C adsorbed at room temperature (Figure 2c). In ref 6, the resonance near 87 ppm was assigned to carbons adjacent to a carbocation center. This assignment is perhaps plausible for carbons adjacent to a nonequilibrating ion, which from the superacid solution work of Olah and co-workers are known to have chemical shifts between 42 and 70 ppm.[16] Carbons adjacent to equilibrating carbocations have much lower chemical

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[15] Taking the beginning of acquisition of the 213 K spectra as zero time, the following temperature–time course was used: 253 K, 100 min; 263 K, 113 min; 273 K, 175 min; 283 K, 225 min; 293 K, 380 min.

[16] Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026.

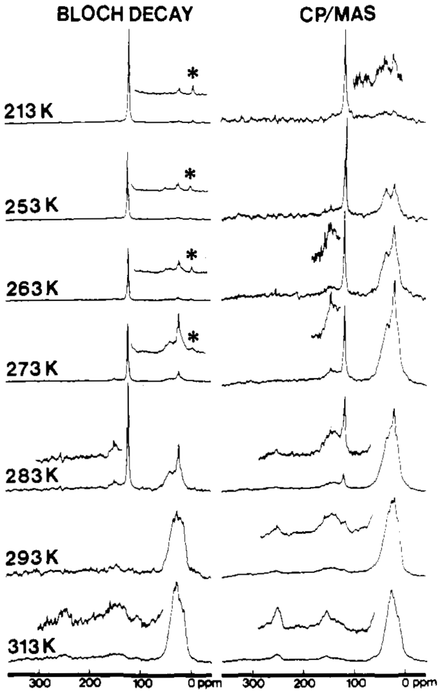


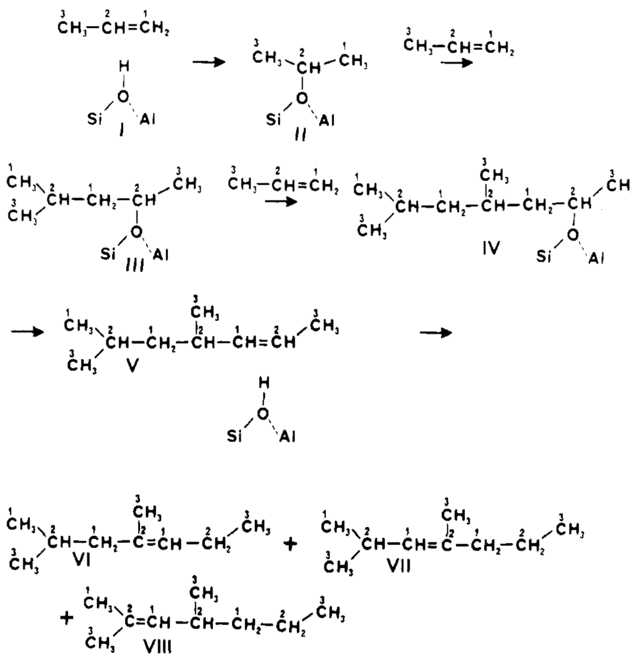
Figure 4. ^{13}C MAS NMR spectra showing propene-*1*-^{13}C reacting on HY catalyst as the temperature was raised from 213 to 313 K. The sample was prepared with the CAVERN apparatus, and the conditions were identical with those for Figure 3. * denotes spinning sidebands.

shifts (21–48 ppm). But the ^{13}C CP/MAS spectrum at 273 K does not show the resonance at 250 ppm, which in ref 6 was assigned to the trivalent carbon of a nonequilibrating ion. The assignment of the 87-ppm resonance to carbons adjacent to carbocation centers should, therefore, be abandoned. Surveying standard references[17] on ^{13}C chemical shifts provides two possible assignments for the resonance at 87 ppm: (1) The chemical shift is possibly consistent with nonterminal alkyne carbons, but this assignment is chemically implausible and can, in any event, be ruled out on the basis of other spectroscopic evidence (vide infra). (2) The chemical shift is suggestive of the oxygen-substituted carbon in alcohols, ethers, and other alkoxy species (e.g., alkyl silyl ethers). We will show that the 87-ppm resonance is due to an alkoxy species formed from protonated olefins and the framework of the zeolite. The broad peak at 143 ppm (which underlies the sharp signal due to unreacted propene) is assigned to olefinic carbons of oligomeric species in the zeolite.

Referring again to Figure 3, one notes that all of the propene was consumed by the time the temperature was equilibrated at 293 K. The CP spectrum at this temperature is essentially identical with that obtained for the adsorption of propene-*2*-^{13}C at room temperature (Figure 2c). The peak at 250 ppm in these spectra is assigned to a carbocation; the probable identity of this ion, as well as its catalytic significance, will be discussed in a later section.

The reactions of propene-*1*-^{13}C on HY catalyst were also studied by using the CAVERN apparatus and variable-temperature ^{13}C MAS NMR. Great care was taken to use the same time–temperature profile[15] for the two CAVERN experiments. The results of this experiment are shown in Figure 4. No evidence of ^{13}C-label scrambling to yield other isotopomers of propene was observed in the CAVERN experiment with propene-*1*-^{13}C. Overall, the results for propene-*1*-^{13}C are similar to those for propene-*2*-^{13}C; as the temperature is raised, propene is consumed and oligomers are formed. There are, however, two obvious and mechanistically significant differences between the spectra in Figures 3 and 4: (1) The peak at 87 ppm that is observed in the CAVERN experiment with propene-*2*-^{13}C (Figure 3) is not observed with propene-*1*-^{13}C. (2) The aliphatic carbon resonance envelope has different features and extends to higher field for the sample prepared from propene-*1*-^{13}C, suggesting that the formation of methyl groups is one of the fates of C-1 of propene.

Scheme I



From the results of the in situ MAS NMR experiments it is possible to propose a detailed mechanism for the oligomerization reactions of propene on zeolite HY (Scheme I).

The numbering scheme (1–3) used for the structures in Scheme I predicts the locations of ^{13}C labels derived from propene-*1*-^{13}C, propene-*2*-^{13}C, and propene-*3*-^{13}C, respectively. Propene reacts with an acid site (I) in the zeolite to yield an isopropoxy species (II).[18] The intrazeolitic propene concentration is so high at this stage of the reaction (and/or II is so reactive) that Markownikoff addition of the isopropyl group to a second propene molecule rapidly occurs to yield a six-carbon alkoxy species (III). The observation in these experiments that the C-1 and C-3 labels of propene are not scrambled indicates that reaction of II with a second propene molecule to yield III is a much faster process under these conditions than cleavage of II to reform propene.

Referring again to Scheme I, species III reacts with another propene molecule to yield the nine-carbon species IV. The oligomers obtained by room temperature are almost certainly larger than those indicated in Scheme I, but for simplicity Scheme I only considers the chemistry of dimers and trimers. Cleavage of IV yields the disubstituted olefin V and reforms the acidic site I. V is assumed to isomerize in the acidic environment of the zeolite to thermodynamically more stable olefins such as VI–VIII. The most remarkable feature of Scheme I is the proposal that alkoxy species bound to the zeolite framework are long-lived intermediates in the oligomerization reactions of propene on zeolite HY. Since all of the evidence for this proposal is based on the assignment of the 87-ppm resonance, dozens of adsorptions were carried out under various conditions and a number of NMR experiments were performed to substantiate this assignment. The results of these efforts are summarized in the following paragraphs.

1. The relative intensity of the 87-ppm resonance does not correlate with that of the 250-ppm peak in either cross polarization or Bloch decay spectra when samples are prepared with different calcination temperatures, adsorption temperatures, or sample

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(17) (a) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy, second ed.*; Wiley: New York, 1980. (b) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden: Philadelphia, PA, 1978.

(18) Gorte and co-workers have postulated the existence of analogous intermediates formed from 2-methyl-2-propanol in HZSM-5: Aronson, M. T.; Gorte, R. J.; Farneth, W. E.; White, D. *J. Am. Chem. Soc.*, in press.

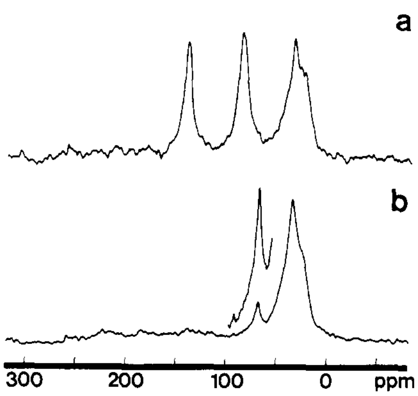

Figure 5. ^{13}C CP/MAS spectra of propene-*2*-^{13}C adsorbed at room temperature on zeolite HY activated at 573 K: (a) shortly after adsorption; (b) after further reaction at room temperature followed by several minutes of exposure to atmospheric moisture. Each spectrum is the result of 3000 scans.

loadings. For example, samples calcined at 573 K prior to adsorption of propene-*2*-^{13}C at room temperature show a large 87-ppm peak in the CP/MAS spectrum but no 250-ppm resonance (Figure 5a).

2. Intentional exposure of samples to atmospheric moisture resulted in the rapid loss of the 87-ppm signal accompanied by the formation of a new resonance at a chemical shift of 67 ppm. This latter chemical shift is consistent with that of the oxygen-substituted carbon of secondary ethers or alcohols with structures modeled by 2-pentanol (68 ppm) or 4-methyl-2-pentanol (66 ppm). It is not consistent with primary or tertiary alcohols or secondary alcohols with the hydroxyl group in other than the 2-position (e.g., 3-pentanol, 75 ppm). The 67-ppm resonance survives interrupted decoupling at room temperature. The results of these experiments are consistent with the hydrolysis of the proposed intermediates to alcohols.

3. Relaxation data for the 87-ppm resonance indicate a protonated carbon which is immobilized. This peak is the only one in samples prepared from any of the isotopomers that does not survive 50 μs of interrupted decoupling[19] at room temperature, indicating that it is due to an immobile methine or methylene carbon.

4. The 87-ppm signal is only observed for samples prepared from propene-*2*-^{13}C and never with the other two isotopomers, as predicted by the mechanism in Scheme I. If the 87-ppm peak were associated with a long-lived carbocation or formed through a mechanism involving a long-lived free carbocation, extensive label scrambling would be expected to occur as was assumed in ref 6.

5. The chemical shift of 87 ppm is 10–20 ppm downfield of alkyl silyl ether model compounds. This rather large shift is rationalized in one (or both) of two ways. (a) The resonance could be shifted downfield due to an interaction with the adjacent framework aluminum. Indeed, the chemical shift of the oxygen-substituted carbon of diisopropyl ether was observed to shift downfield 6 ppm when complexed with triethylaluminum in deuterochloroform solution. (b) The downfield shift might also reflect a small partial positive charge on the carbon, consistent with the "incipient carbocation" nature of the proposed intermediate.

Other features of Scheme I are also supported by the spectra in Figures 2–4. For example, the chemical shifts observed for the sample prepared from propene-*3*-^{13}C (Figure 2d) are consistent with methyl carbons. This assignment was checked by performing interrupted decoupling experiments at reduced temperatures (to minimize the complications of molecular motion) for samples prepared from each of the isotopomers adsorbed at room temperature. These spectra (Figure 6) show that although most of the aliphatic signals are attenuated by interrupted decoupling at 163 K for the 2-isotopomer and that some are attenuated for the 1-isotopomer, none are affected for the sample prepared from the 3-isotopomer.

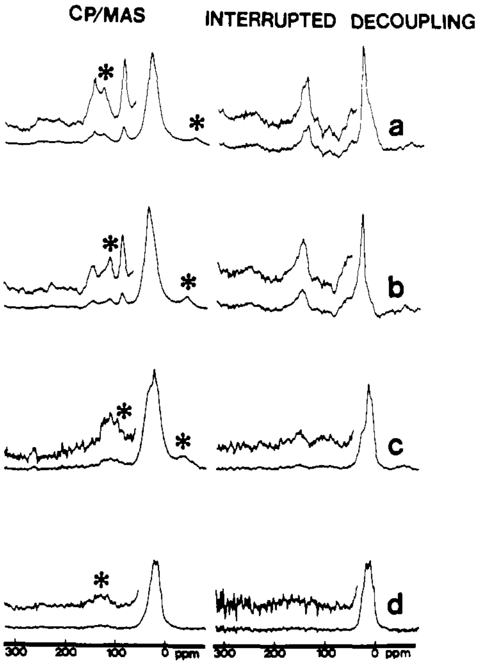

Figure 6. Low-temperature ^{13}C CP/MAS spectra of propene on HY obtained with and without interrupted decoupling (50 μs): (a) Propene-*2*-^{13}C at 203 K. (b) Propene-*2*-^{13}C at 163 K. (c) Propene-*1*-^{13}C at 163 K. (d) Propene-*3*-^{13}C at 163 K. All samples were prepared by room-temperature adsorption, and each spectrum is the result of 1000 acquisitions. * denotes spinning sidebands.

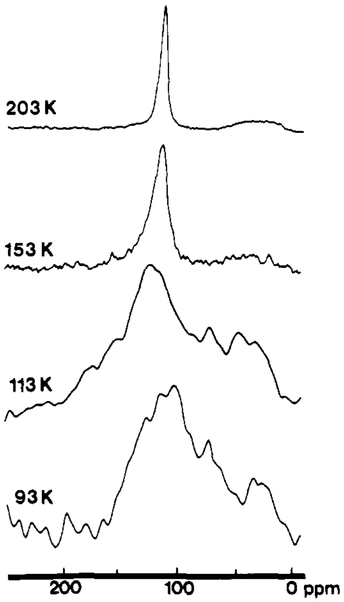

Figure 7. Stationary (nonspinning) ^{13}C CP spectra of propene-*1*-^{13}C adsorbed on HY catalyst at 198 K with the CAVERN apparatus.

The proposed mechanism requires that propene molecules be sufficiently mobile in the zeolite at low temperatures that they readily diffuse to relatively immobile alkoxy intermediates and participate in oligomerization reactions. The following experiment was performed to demonstrate that propene is highly mobile at low temperatures. With the CAVERN apparatus and a "rotor" bereft of spinning flutes, propene-*1*-^{13}C was adsorbed onto HY zeolite at 198 K. The sealed sample was transferred to a precooled probe, and nonspinning ^{13}C spectra were obtained between 203 and 93 K. The resulting spectra (Figure 7) reveal that the C-1 resonance of propene is less than 16-ppm wide until the sample is cooled below 153 K, at which point it begins to broaden. Since

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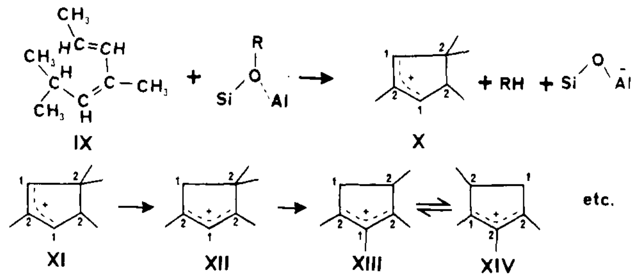
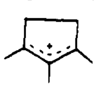
Scheme II



propene's melting point is 88 K, this broadening suggests that propene is inside the zeolite rather than condensed as an isotropic liquid on the exterior of the particles. Typical olefinic carbons in rigid solids have ^{13}C chemical shift anisotropy powder patterns that are approximately 200-ppm wide.[20] Our results indicate that propene is highly mobile in zeolite HY at temperatures well below that required for the onset of chemical reactivity.

We now discuss the assignment of the peak at 250 ppm, which we frequently see in ^{13}C CP/MAS spectra of propene-*2*-^{13}C or propene-*1*-^{13}C on HY at room temperature. In ref 6, this feature was assigned to a nonequilibrating carbocation. In superacid solutions, the trivalent carbons of nonequilibrating ions have ^{13}C chemical shifts in the vicinity of 320 ppm. We have not observed a resonance at a chemical shift higher than 250 ppm in any of several hundred NMR spectra of dozens of propene–HY samples. The 70-ppm discrepancy between the observed shift of 250 ppm and the results in superacid solution was explained in ref 6 by invoking a nonbonding interaction between the carbocation and framework oxygens. Indeed, carbocations of the type RC^+OH are known to have ^{13}C chemical shifts approximately 80 ppm lower than the corresponding alkyl cations.[21] But the results of the in situ VT-MAS experiments have shown that the interaction between unstabilized "incipient carbocations" and the framework oxygens of the zeolite is so strong that the word carbocation is inappropriate, and the long-lived intermediate is better described as an alkoxy species. We conclude that in order for a free carbocation to exist as a long-lived species in the highly nucleophilic interior of the zeolite, it must be incapable of coordinating to framework oxygens, and it must be stabilized in some fashion. Scheme II shows how free carbocations can be formed in the zeolite, which is consistent with all of the available evidence.

Olefins such as VI–VIII are assumed to undergo hydride abstraction and deprotonation to yield dienes such as IX which then undergo hydride abstraction and cyclization. Scheme II is essentially identical with the well-known process of conjunct polymerization of alkenes, which involves the formation of alkanes at the expense of hydrogen from the olefins, the latter being converted to cyclopentenyl cations.[22] Scheme II is, therefore, a very attractive explanation for the 250-ppm resonance observed in our studies of propene-*1*-^{13}C or propene-*2*-^{13}C on HY. Alkyl-substituted cyclopentenyl cations (e.g., XV) have been studied


XV


XVI

by solution-state NMR by Deno[23] and co-workers and Olah and co-workers.[24] The ^{13}C chemical shift of C-1 and C-3 of XV was reported to be 249 ppm and the C-2 resonance was reported to be at a chemical shift of 158 ppm,[24c,25] a value that would put it on the low-shielding side of the olefinic carbon envelopes in ^{13}C spectra of the 1-^{13}C or 2-^{13}C isotopomers of propene on HY at room temperature. It should, therefore, be possible to resolve this resonance and correlate its intensity with that of the 250-ppm peak. The intensity of the 250-ppm resonance is variable depending on propene loading and adsorption temperature, suggesting a procedure for identifying the species proposed in Scheme II. Figure 8 shows the low-shielding regions of ^{13}C CP/MAS spectra of various samples prepared by adsorbing labeled propene on HY at or near room temperature. A close examination of these spectra reveals a resonance at 158 ppm[26] whose intensity correlates with that of the 250-ppm resonance. Furthermore, the ratio of the integrated intensities of these features (approximately 2:1) is consistent with the prediction for an equilibrium mixture of ions like XIII and XIV. The NMR results are, therefore, consistent with Scheme II. Further evidence for this assignment is that alkyl-substituted cyclopentenyl carbocations are known to be remarkably stable[27] and are frequently observed as the endproducts of many complex reactions of olefins in strongly acidic solutions. For example, XVI is formed in a concentration equal to that of its equilibrate diene in a 35% solution of sulfuric acid, and concentrated solutions of XVI are stable in 96% sulfuric acid solution for months.[27]

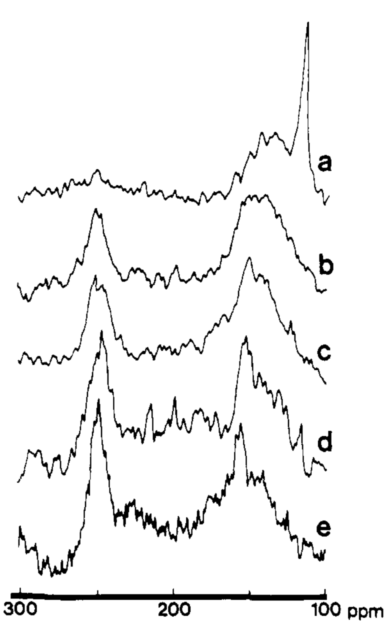


Figure 8. 25.02-MHz ^{13}C CP/MAS spectra of several preparations of propene-*1*-^{13}C or propene-*2*-^{13}C on HY at or near room temperature. The low-shielding region is emphasized to show the relationship between the 250- and 158-ppm resonances.

Finally, the positive charge in alkyl-substituted cyclopentenyl ions is delocalized and sterically inaccessible to framework oxygen atoms, so it is reasonable that these species should exist as long-lived free carbocations in the zeolite at room temperature. All of the available evidence strongly supports Scheme II as the source of long-lived carbocations on HY catalyst at or below room temperature.

Conclusions

The mechanisms by which propene reacts at 313 K and below on zeolite catalyst HY have been studied by in situ variable-temperature ^{13}C CP/MAS NMR. These studies find evidence for long-lived intermediates that are believed to be alkoxy species (possibly alkyl silyl ethers) formed by the covalent bonding of "incipient carbocations" to framework oxygen sites. No simple

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[20] Zilm, K. W.; Conlin, R. T.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6672.

[21] Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; pp 225–227.

[22] See: Reference 1b, p 41.

[23] Deno, N. C.; Richey, H. G., Jr.; Hodge, J. D.; Wisotsky, M. T. *J. Am. Chem. Soc.* **1962**, *84*, 1498.

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[25] Young, R. N. *Prog. NMR Spectrosc.* **1979**, *12*, 261.

[26] This 158-ppm resonance was assigned to an equilibrating secondary carbocation in ref 6.

[27] For a review, see: Deno, N. C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. 2, Chapter 18.

secondary or tertiary carbocations were detected by NMR, even at reduced temperatures.[28]

Long-lived alkyl-substituted cyclopentenyl cations are proposed to form from propene in HY by deprotonation of oligomeric dienes. Such ions apparently have no catalytic role. It is significant that the only free carbocations observed in this work are those that are incapable of bonding to the framework as alkoxy species. However, the alkoxy intermediates identified in this contribution are likely to be labile at higher temperatures, and a small concentration of (momentarily) free ions could be invoked to rationalize scrambling of isotopic labels[29] or cracking of alkanes[30] on solid acid catalysts at elevated temperatures.

One implication of this investigation is that the role of the zeolite framework in stabilizing alkoxy intermediates should be considered in future efforts to develop new catalysts. Also, the novel experimental methodology introduced in this contribution should be useful in the study of many highly reactive catalyst/adsorbate systems. Several analogous investigations are underway in our laboratory.

Acknowledgment. This research was funded by the National Science Foundation (Grant CHE-8700667). We thank Ray Gorte of the University of Pennsylvania for sharing with us some of his results on 2-methyl-2-propanol on ZSM-5 prior to publication and Jack Lunsford for his comments on the draft of this paper.

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(28) Yannoni and co-workers have shown that carbocations generated in the solid state by codeposition of alkyl chlorides and SbF_5 can be observed by ^{13}C CP/MAS NMR at temperatures comparable to those used in the present study. For example, see: Yannoni, C. S.; Myhre, P. C. *J. Am. Chem. Soc.* **1981**, *103*, 230.

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Solid-State Chemistry of Molecular Metal Oxide Clusters. Ortho Metalation and Hydrogen Transport in $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ Probed by ^{31}P NMR Long-Range Deuterium Isotope Effects

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Abstract: Deuterium isotope effects on ^{31}P shielding that are large relative to the accuracy with which they can be measured are reported. In $(Ph_3P)_2IrH_2(dmf)_2^+$, substitution of one ^2H for one ^1H at the Ir–*H* or at the ortho position in the Ph_3P ligand leads to two- and three-bond isotope shifts of +0.094 and −0.110 ppm, respectively, with the effect being defined as $[\delta(^2H\ \text{form}) - \delta(^1H\ \text{form})]$. The ortho-deuterium effects on ^{31}P for Ph_3P, Ph_3PO, $Ph_3PMe^+I^-$, and $(Ph_3P)_2Ir(C_8H_{12})^+$ are −0.110, −0.096, −0.035, and −0.077 ppm, respectively. These long-range isotope effects are used to demonstrate a thermally activated, solid-state exchange of deuterium between iridium and only the ortho positions of the Ph_3P ligands in $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$. There occurs, additionally, an intermolecular hydrogen–deuterium exchange process. Slow exchange with c-C_6D_{12} leads to incorporation of the deuterium label in the Ph_3P rings.

We are developing the solid-state physical and reaction chemistry of materials derived from molecular metal oxide clusters of the Keggin-ion type, exemplified by $PW_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$.[1-8] An issue of particular interest is the reactivity of coordinatively unsaturated organometallic cations that can be stabilized as interstitial species in lattices comprised of such oxide cluster anions. The compound $[(Ph_3P)_2IrH_2]_3PW_{12}O_{40}$ (**1**) participates in unusually facile intermolecular C–H activation processes,[5,6] but this reactivity can be modulated by phenomena peculiar to the solid state. In this paper, we describe long-range deuterium NMR isotope effects on ^{31}P chemical shielding and then use these to probe *intra*molecular C–H activation in **1**. This chemistry can readily occur in the solid state because ligand phenyl groups in the lattice have sufficient motional freedom to participate in an ortho- or cyclo-metalation reaction. In addition, the data indicate that intermolecular, intralattice hydrogen transport is also involved in redistribution of the deuterium label, a process that, to our knowledge, is without precedent in homogeneous organometallic chemistry.

Long-Range NMR Deuterium Isotope Effects. We begin by describing some effects of substituting deuterium for hydrogen at positions two and three bonds removed from a magnetically active nucleus, here ^{31}P. These effects, though perhaps deceptively small, are quite large relative to the experimental errors associated with determining ^{31}P NMR chemical shifts at high magnetic fields. Furthermore, although the absolute magnitude of ^{31}P chemical shifts, expressed relative to a reference material (85% H_3PO_4), can be solvent and concentration dependent, these factors affect all isotopomers equally to within experimental error so that *relative* magnitudes of the isotope-induced shifts can readily be determined with high accuracy.[9] Consequently, these isotope effects can be very useful in determining how a deuterium label in a molecule

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