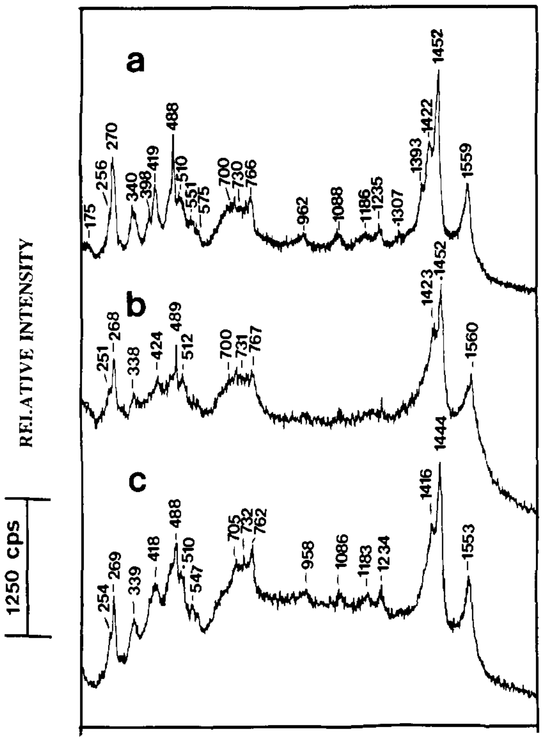

Figure 1. Surface-enhanced Raman spectrum of C_{60} coated on a gold electrode immersed (a) in pure water with no applied potential, (b) in 0.1 M aqueous KCl at +0.200 V vs SCE, and (c) in 0.1 M KCl at −0.600 V vs SCE. No SER scattering is observed above 1800 cm^{-1}.

This is not to suggest that C_{60} has been transmuted to C_{70} on the gold surface! Rather, we propose that C_{60} in the interfacial environment has decreased symmetry, which causes new modes to become Raman active. The chemical similarity between C_{60} and C_{70} leads us to predict that many of the normal modes and vibrational frequencies of these spheroidal carbon clusters will be similar. The higher frequency modes will be dominated by bond-stretching motions (changes in edge lengths), while the lower frequency modes are expected to involve radial distortions to a more ellipsoidal shape.[14] We have obtained a preliminary SER spectrum of C_{70}, and indeed the band positions in the 1000–1600-cm^{-1} region are similar to those observed in the SER spectrum of C_{60}, although the relative intensities more closely match those of the bulk C_{70} spectrum.[15] We cannot yet say whether adsorbed C_{60} distorts to a C_{70}-like ellipsoidal shape, or whether the symmetry is reduced to C_{5v} or even lower due to adsorbate–surface interactions. We are currently performing a more detailed analysis of the C_{60} and C_{70} SER spectra and normal modes.

The seven strongest bands in the C_{60} Raman spectrum (at 1575, 1470, 1428, 774, 496, 437, and 273 cm^{-1}) have analogues of comparable relative intensity in the SER spectrum, but the SER bands are shifted to lower frequency. (Some of the weaker Raman bands are also shifted slightly, and some have different relative intensities in the SER spectrum.) The frequency shifts are similar to those observed for other aromatic molecules upon adsorption on gold[16] and are interpreted as evidence for a change in the electronic structure of the adsorbate. Donation of π electron density to the metal, or back-donation from the metal d orbitals to the molecular π^* orbitals, results in a decrease in the adsorbate C–C bond strength, and thus a decrease in the molecular force constants and vibrational frequencies. In the case of C_{60}, its high electron affinity[17] suggests that metal-to-molecule back-donation may be the more important of the two mechanisms.

Spectra b and c of Figure 1 are SER spectra obtained with 0.1 M KCl as the electrolyte at +0.200 and −0.600 V. The similarity of spectra b and a shows that Cl^- does not perturb the adsorbed C_{60}. Applying a more negative potential (Figure 1c) causes the three highest frequency bands, which arise from normal modes involving bond stretching,[14] to shift downward significantly, as expected if metal-to-molecule back-donation contributes to the adsorbate–substrate interactions. Similar negative frequency shifts are observed for these bands in the Raman spectra of C_{60}^- and alkali-metal-doped C_{60} films.[18] A potential of −0.600 V is not sufficient to reduce C_{60} in water with KCl as the electrolyte (no current is passed).[4,19] Applying a more negative potential is likely to result in the formation of the fulleride anion on the surface. This may provide a method for fabricating metal–semiconductor Schottky barriers that can exploit the unique electronic properties of the fulleride salts.[6] The electrochemical data also suggest that the C_{60} anion undergoes Jahn–Teller distortion,[4,5] which may make its symmetry and vibrational spectrum quite similar to those of neutral C_{60} on gold at negative applied potentials, shown here. Further vibrational spectroscopic studies of adsorbed neutral C_{60} and fulleride salts are under way.

Acknowledgment. This work was supported by NSF Grants CHE89-21133 (to F.N.D. and R.L.W.) and DMR84-51962 (to R.L.G.) and NIH Grant GM42977 (to R.L.G.). We thank Lexel Laser, Inc., for use of the RamanIon laser.

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NMR Observation of Trimethyloxonium Formation from Dimethyl Ether on Zeolite HZSM-5

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The reaction of methanol to gasoline (MTG) on zeolite HZSM-5 is central to what is probably the most successful synthetic fuels process.[1] This process accounts for a substantial part of New Zealand's gasoline supply. Despite extensive study of the methanol/HZSM-5 system, the mechanism for the formation of the first C–C bond is still disputed.[1,2] The most popular[1] of the proposed reaction mechanisms involves the formation of trimethyloxonium (**1**) followed by deprotonation by an unspecified basic site to yield methylenedimethyloxonium ylide (**2**). The ylide is then assumed to either abstract a methyl group to form dimethylethyloxonium, which undergoes β-elimination to yield ethylene and dimethyl ether, or to undergo a Stevens-type rearrangement to form methyl ethyl ether (Scheme I).[3,4] A detailed

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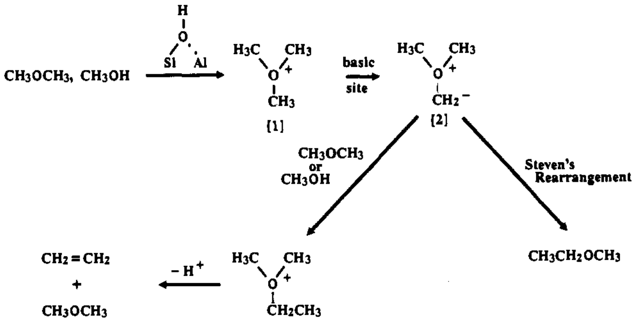
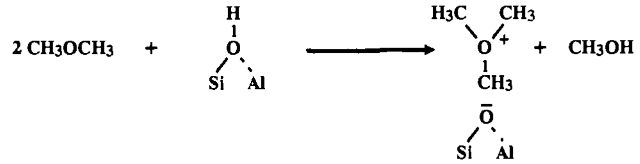
Scheme I



Scheme II



analysis of the possible reactions of **2** has been published by Olah, et al.[3,5] A main problem with these mechanisms is that neither **1** nor **2** has been observed to form in zeolite HZSM-5 from a known intermediate in the MTG process. For example, in their FTIR studies of the reactions of methanol and dimethyl ether on HZSM-5, Forester and Howe did not observe spectral features that could be assigned to **1**.[6] In a similar fashion, **1** was not observed in any of several ^{13}C solid-state NMR studies of methanol on HZSM-5.[2] In this communication we report the observation by ^{13}C magic-angle spinning (MAS) NMR of significant quantities of trimethyloxonium in HZSM-5 formed by the reaction of dimethyl ether, a known intermediate in the MTG process.

Zeolite NH_4ZSM-5 (obtained from UOP Corporation, Si/Al = 38) was activated by a multistep activation procedure,[7] transferred to a zirconia rotor under a nitrogen atmosphere, and loaded into a glass version of our CAVERN apparatus[7,8] prior to adsorption. Typically, 2.5 mmol of dimethyl ether[9] per gram of catalyst was adsorbed onto the catalyst via standard vacuum-line techniques. All ^{13}C NMR spectra were obtained at 50.06 MHz on a modified Chemagnetics CMC-200 spectrometer using cross polarization (contact time = 2 ms, pulse delay = 1 s, 400 transients) or single pulse excitation (pulse delay = 2 s, 100 transients) with proton decoupling and MAS at approximately 4 kHz.

The first step in the MTG reaction is the condensation of methanol to form dimethyl ether and 1 equiv of water. Since large concentrations of water and/or methanol could be expected to shift equilibria or otherwise mask possible intermediates, we were motivated to study in detail the reaction of dimethyl ether on HZSM-5. One set of experiments involved adsorption at cryogenic temperatures followed by warming in the MAS NMR probe during spectral acquisition.[10] Parts a–c of Figure 1 show ^{13}C CP/MAS NMR spectra of dimethyl ether-*1*-^{13}*C* on HZSM-5 as the sample was heated to room temperature following adsorption at 173 K. In the spectrum at 173 K (Figure 1a) there is one peak at 60 ppm, indicating that the dimethyl ether had not yet reacted. Following warming to 233 K (spectrum not shown), the characteristic trimethyloxonium resonance appeared at 80 ppm.[11] This assignment is within 1 ppm of the reported literature values for **1** in solution or ion exchanged into HZSM-5.[12] The 80-ppm signal continued to grow following warming to 293 K and for several hours thereafter (Figure 1b,c).

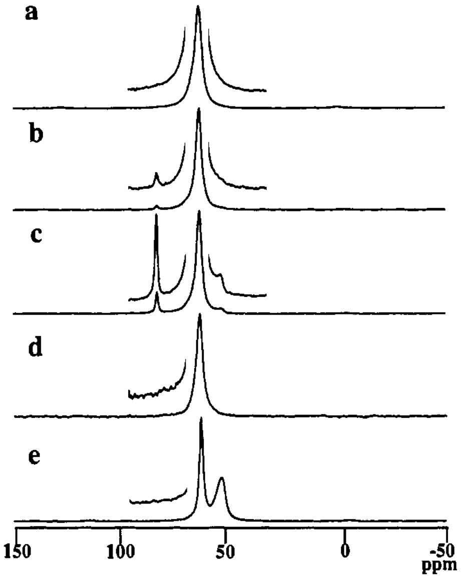


Figure 1. ^{13}C CP/MAS NMR spectra (50.06 MHz) showing the chemistry of dimethyl ether on zeolite ZSM-5. Spectra a–c are from a low-temperature CAVERN experiment in which dimethyl ether was adsorbed on HZSM-5 at 173 K prior to warming in the MAS probe: (a) at 173 K, showing unreacted dimethyl ether; (b) at 293 K, showing a clear signal from trimethyloxonium at 80 ppm; (c) after 10 h at 293 K, showing peaks due to trimethyloxonium and methanol (50 ppm) in a 3:1 intensity ratio; (d) control experiment on NaZSM-5 (293 K); (e) spectrum at 293 K following coadsorption of dimethyl ether and a comparable amount of methanol (see text).

The balanced reaction for the disproportionation of dimethyl ether in HZSM-5 (Scheme II) requires a stoichiometric number of Bronsted acid sites and produces 1 equiv of methanol. The conjugate base of the acid site serves as the counteranion for the trimethyloxonium cation. When care is taken to ensure quantitation, we always observe a methanol signal at 50 ppm at $^1/_3$ the integrated intensity of the trimethyloxonium resonance (see Figure 1b,c). The yield of **1** is always a fraction (typically ≤0.2) of the number of acid sites. Further evidence for the role of the acid sites was obtained in control experiments using inactive NaZSM-5[13]: **1** never formed on the inactive samples (see Figure 1d). The properties of HZSM-5 responsible for the MTG process are thought to be its shape selectivity and its exceptionally strong acid sites. Interestingly, no **1** formed when analogous experiments were performed on zeolite HY (spectrum not shown).

As stated earlier, the reason that prior attempts to observe trimethyloxonium formation in HZSM-5 have been unsuccessful may be the masking effect of water or methanol. Indeed, no **1** formed following coadsorption of dimethyl ether and methanol in HZSM-5 (see Figure 1e).

When samples of dimethyl ether on HZSM-5 were heated to 423 K, consumption of **1** and hydrocarbon synthesis were observed. The product distribution was similar to that in previous in situ studies of methanol on HZSM-5 with the same in situ NMR protocol.[2a] These observations do not prove that **1** is a key in-

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(9) Dimethyl ether-*1*-^{13}*C* (90% ^{13}C) was obtained from Merck Isotopes and used without further purification. Methanol-^{13}*C* (99% ^{13}C) was obtained from Cambridge Isotopes and purified via several freeze–pump–thaw cycles.

(10) The procedures used to perform the low-temperature in situ experiments including the method of rotor sealing are described in ref 7.

(11) The 80-ppm resonance met all of the standard tests for the proposed structure including its response to interrupted decoupling.

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(13) NaZSM-5 was prepared by ion exchanging 10 g of HZSM-5 twice with 1 M $NaNO_3$, washing with distilled water, and activating via the multistep activation procedure described in ref 7.

termediate in MTG chemistry, but the observation that **1** can form in HZSM-5 from a known MTG intermediate removes a major objection to mechanisms such as those in Scheme I. Furthermore, with the ability to generate significant quantities of **1** in HZSM-5, it should be possible to further explore these mechanisms.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8918741). Stable-isotope chemicals were purchased with funds provided by the Robert A. Welch Foundation, and the NMR instrument was upgraded with funds provided by the Texas Advanced Technology Program. E.J.M. is a National Science Foundation Predoctoral Fellow.

Helix-Sense Reversal of Isotactic Chloral Oligomers in Solution[1]

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We report the observation of helix-sense reversal of linear chloral oligomers (degree of polymerization, DP = 4–6) in solution by NMR spectroscopy and determination of the inversion barrier, which has been found to be dependent on DP.

Some synthetic polymers such as polychloral,[2] poly(triphenylmethyl methacrylate),[3] and poly(*tert*-butyl isocyanide)[4] are known to show optical activity arising entirely from conformational asymmetry (macromolecular asymmetry) when the polymers are prepared by helix-sense selective polymerization. The helix of the optically active polymers seems to be rigid in solution[5,6] or slowly undergoes racemization to a nearly 1:1 mixture of the right- and left-handed helices.[7] The helical conformation of polyisocyanates is less stable, and consequently, right- and left-handed states exist in equilibrium.[8] Although the one-handed helicity of the polymers is apparent from their optical activity, it has been difficult to determine the helical polymer structures and thermodynamic parameters for the helix–helix transition; one reason for the difficulty is that those polymers are, as usual synthetic macromolecular compounds are, mixtures of very similar but not identical molecules (distribution of DP, slight difference in tacticity, etc.).

Recently, we were able to resolve the *tert*-butoxy-initiated, acetate end-capped, purely isotactic pentamer of chloral **1** into the two enantiomers (*R,R,R,R,R* and *S,S,S,S,S* isomers) by HPLC using a chiral stationary phase.[9] The (*R,R,R,R,R*)-(−)-**1**[10] was found to adopt the right-handed 4_1-helical conformation in solution at 35 °C[11] *as well as* in the crystalline state.[12] This conclusion is based on the dihedral angle dependence of $^3J_{\mathrm{COCH}}$ coupling constants obtained from the ^{13}C NMR spectrum. The helical-sense preference was ascribed to the conformational energy difference (ΔE) between the right-handed and left-handed helical states, which was estimated as 2.7 kcal/mol[13] by molecular mechanics calculation.[14,15]

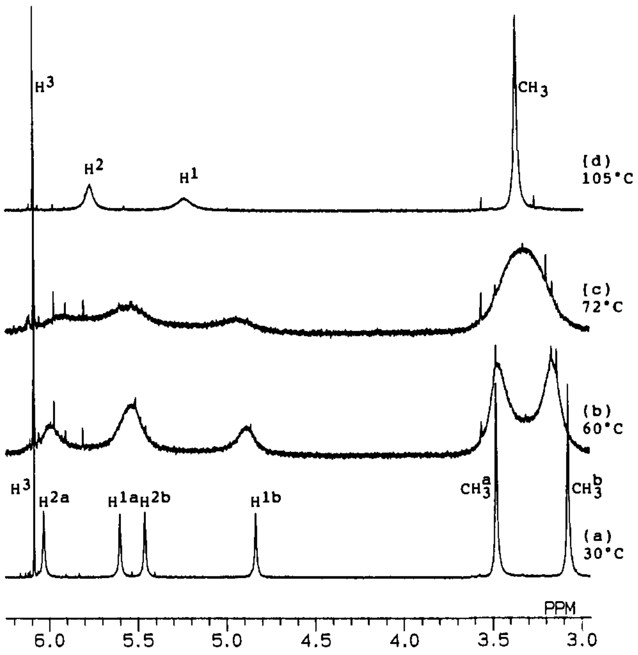
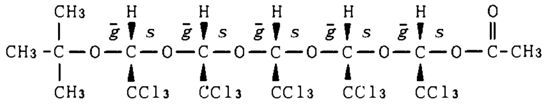
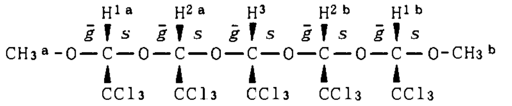


Figure 1. ^{1}H NMR spectra (500 MHz) of **2** in toluene-d_8 at (a) 30 °C, (b) 60 °C, (c) 72 °C, and (d) 105 °C.



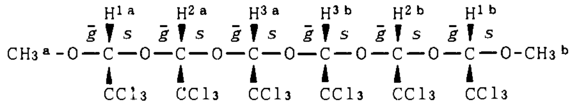
$$\mathrm{CH_3{-}}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{CH_3}$$

1



$$\mathrm{CH_3^{a}{-}O{-}}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{1a}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{2a}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{3}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{2b}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{1b}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O{-}CH_3^{b}}$$

2



$$\mathrm{CH_3^{a}{-}O{-}}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{1a}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{2a}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{3a}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{3b}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{2b}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O}{-}\underset{\mathrm{CCl_3}}{\overset{\bar{g}\,\overset{\mathrm{H^{1b}}}{\blacktriangledown}\,s}{\mathrm{C}}}{-}\mathrm{O{-}CH_3^{b}}$$

3

The purely isotactic and symmetrical pentamer carrying a methyl group at both ends, **2**, is the (*R,R,S,S*)-(±) isomer in which the right- and left-handed helical conformations are no longer

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[1] Haloaldehyde Polymers. 51.

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[12] Crystal data for (*R,R,R,R,R*)-(−)-**1** ($C_{16}H_{17}O_7Cl_{15}$): orthorhombic, $P2_12_12_1$, a = 16.354 (3) Å, b = 18.961 (4) Å, c = 10.767 (2) Å, Z = 4, D(calcd) = 1.698 g/cm^3. The 318 variables were refined with 3023 unique reflections (3° < 2θ < 55°) with $|F_o| > 3\sigma(|F_o|)$ to yield R = 5.65% and R_w = 6.94%. More complete crystallographic details will be described elsewhere: Ute, K.; Oka, K.; Matsuura, Y.; Hatada, K.; Vogl, O., to be submitted to *Polym. J.*

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