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Carbon-13 Nuclear Magnetic Resonance Studies of the Aldol Condensation Products of Acetone on an Activated Alumina Catalyst

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The aldol condensation of acetone adsorbed on alumina is monitored with C-13 NMR. The detectability of the major reaction products, diacetone alcohol, mesityl oxide, phorone, isophorone, and mesitylene, is compared to that previously observed using infrared and gas chromatographic methods.

INTRODUCTION

Conventional carbon-13 nuclear magnetic resonance (NMR) spectrometry is being used increasingly for the study of compounds on solid supports (*1–11*). It shows promise as a valuable supplemental technique to the more widely used gas chromatographic (GC) and infrared (ir) methods of analysis, with the ultimate advantage being its ability to monitor the motions of adsorbed molecules over a wide range of frequencies (rates) using relaxation time studies. This feature should reveal information regarding both the nature of adsorption and the reaction mechanisms.

Many conventional C-13 NMR studies have been performed in order to elucidate the details of adsorption using nonreacting adsorbates on a variety of supports. Typical information obtained in these studies includes surface acid site concentration (*12–17*), energy barriers for mobility of adsorbed molecules (*18*), and the extent of interaction of the adsorbates with magnetic and paramagnetic centers in the support (*18–20*). Studies of acetone on SiO_2 have focused upon the interaction of the carbonyl group with different types of adsorption sites (*16, 17*). To date, published C-13 NMR studies of reacting adsorbates have dealt primarily with product formation and kinetics, with the majority of these studies having been reported by Derouane and coworkers (*4–11*).

In the present study, the aldol condensation of acetone on alumina, as monitored by conventional C-13 NMR, is reported. The detectability of the various products formed at each stage of the reaction is considered, and compared to similar studies which used ir (*21*) and pulse microreactor GC (*22*). This information is required prior to attempting to look at the adsorbate–support interactions via an NMR relaxation study.

METHODS

Al_2O_3. The alumina used was Catipal γ-Al_2O_3 (Conoco) chosen for its exceptionally low iron content (0.005%). Iron and other paramagnetic impurities contribute to NMR relaxation processes, thereby causing line broadening (*18*). Surface area, as measured by BET isotherms with N_2 gas, was found to be 219 ± 10 m^2/g. The Catipal was heated to 775 K for 24 h in a flow of oxygen (630 ± 10 Torr, 83.979 ± 1.333 kN/m^2) to burn off hydrocarbon impurities, then transferred to a 9-mm-o.d. NMR sample tube and degassed at 773 K and 3×10^{-5} Torr (4×10^{-2} N/m^2) for 20 h. After vapor

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deposition of acetone, the tube was sealed off with a flame.

Acetone. Spectral-grade acetone (Fisher Scientific) was degassed by several freeze–thaw cycles, then vapor-deposited on alumina spread along the length of a horizontally positioned NMR tube. Deposition required approximately 20 min. Quantization was done by measuring the pressure difference in the vacuum line and employing Van der Waals gas law. On silica gel, acetone is known to deposit in clusters (*17*); however, it is not known whether deposition occurs as uniform monolayers or as clusters on alumina. Methanol has been observed to form clusters on silica gel, but monolayers on alumina (*23*). In the present study, one monolayer of uniformly deposited acetone is equivalent to a loading of 8.7×10^{-4} mole/g. A total of 4.4 statistical monolayers was deposited to minimize the total spectral scanning time required in order to achieve acceptable signal to noise.

The sample was maintained at 77 K during deposition since at room temperature the heat of adsorption is sufficient to cause the reaction to proceed almost instantaneously, resulting in formation of an unidentified yellow compound. Subsequent to sealing, the tube was agitated gently while warming toward room temperature, then quickly returned to liquid nitrogen to promote even distribution of the acetone without rapid reaction. This procedure was repeated five times, then the sample was placed in liquid nitrogen for storage until being placed in the magnet for spectral studies.

Instrumental. All spectra were acquired on a Bruker WM-250 Fourier transform NMR spectrometer operating at 62.9 MHz, at a sweep width of 16,000 Hz (220 ppm from tetramethylsilane, TMS) with proton decoupling. Relaxation delay times varied from 1.0 to 7.0 s. An external deuterobenzene lock solvent was used to shim all samples. The magnetic susceptibility correction was determined using the method of Gay and Kriz (*24*), by adsorbing TMS on the alumina in a separate experiment. Relative to a benzene standard in a coaxial tube, the TMS shift was determined to be 0.586 ± 0.005 ppm. However, in the condensation reaction sequence, interaction of the various compounds occurs ("solvent shift"), so that chemical shift values are probably not accurate to more than ±5 ppm, depending upon which peaks are being observed, the number of monolayers, and the stage of the reaction. The correction for magnetic susceptibility is thus not generally significant at the present stage of experimental development.

RESULTS

The first spectrum, Fig. 1A, is the result of co-addition of 115 scans of the sample taken within 15 min of removal of the sample tube from liquid nitrogen. The temperature of the sample during this period was unknown, but was certainly increasing toward room temperature. Only acetone is observed during this sampling interval. Without gated decoupling and optimal delay times, peak intensities of neither liquid- nor adsorbed-state spectra are quantitative. No assumptions can be made regarding expected nuclear Overhauser enhancement factors since the system is not in the extreme narrowing limit.

After allowing equilibrium at a temperature of 295 K, the spectrum shown in Fig. 1B was obtained (706 scans). This spectrum reveals the first condensation product, mesityl oxide (2-methyl-2-penten-4-one), and lesser amounts of the intermediate diacetone alcohol (4-hydroxy-4-methyl-2-pentanone). Further condensation occurs at 295 K over a period of days, but no further detectable amount of reaction occurred over the 2 h during which spectra were run under various instrumental operating conditions.

Gradual heating in the probe to a maximum of 345 K over a period of 1.5 h induced the formation of the second condensation product, isophorone (3,5,5-trimethyl-2-cyclohexen-1-one). Fur-

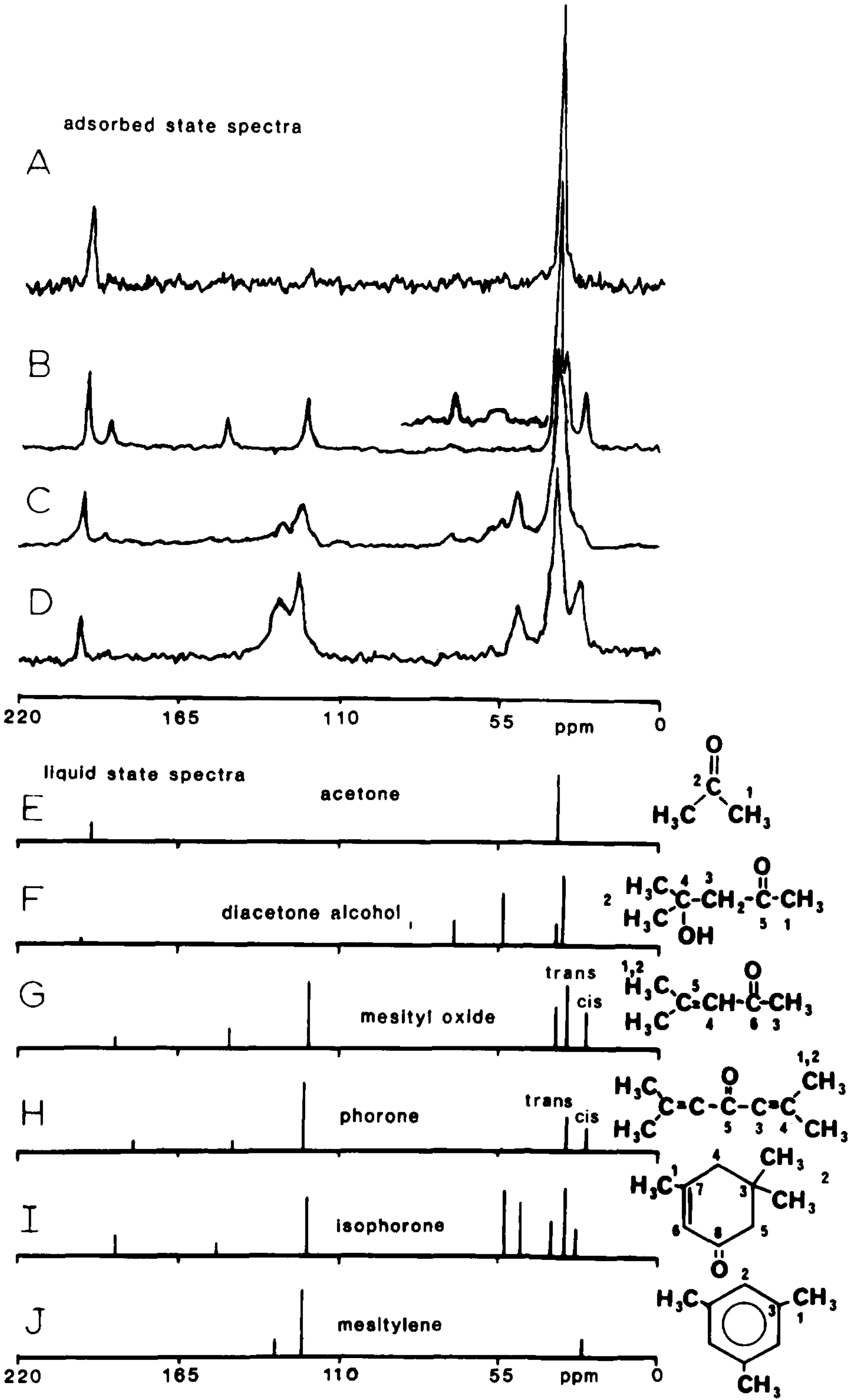

FIG. 1. (A) Adsorbed acetone at low temperature; (B) appearance of diacetone alcohol and mesityl oxide at 295 K; (C) appearance of isophorone at 345 K, followed by mesitylene at 460 K; (D) increase in relative amount of mesitylene after external heating to 575 K; (E) through (J) corresponding liquid-state reference spectra.

ther heating, to a maximum of 460 K, caused formation of a peak centered at 137 ppm. The spectrum shown in Fig. 1C was obtained at this point. Phorone (2,6-dimethyl-2,5-heptadiene-4-one), the precursor and structural isomer of isophorone, is not visible in these spectra, but a small peak at 190 ppm, believed to be phorone, has been observed in other spectra obtained in the course of these studies. Additional external heating at 575 K for 24 h caused an increase in the relative peak intensity for the species with a resonance at 137 ppm (Fig. 1D), in conjunction with a simultaneous increase in the peaks located at 128 and 21 ppm. These data point to mesitylene as yet another major reaction product. At this point in the reaction, however, a very large number of reaction products are possible since multiple reaction pathways are available. Most of the possible products are conjugated carbonyls, all of which have resonances centered around 130 ppm, and are thus presently unresolvable. These products would contribute to the resonance at 137 ppm, causing it to appear quite broad. Indeed, the peak at 137 ppm is observed experimentally to broaden considerably as a function of time.

DISCUSSION

The aldol condensation of acetone on various oxides has been reported previously in the literature, both as an intentional study of reaction mechanisms (*25*), and as an undesired artifact of chromatography (*26*). Infrared (*21*) and Raman (*27*) spectroscopies have been used to follow the formation of mesityl oxide from acetone on rutile. Griffiths and Rochester (*21*) utilized ir data to postulate an enolate ion intermediate between the acetone and mesityl oxide species. Lawrence *et al.* (*26*) identified the condensation products of acetone on alumina by using ir subsequent to elution with methanol. In that study, mesityl oxide, diacetone alcohol, triacetone alcohol, and phorone were identified.

The most detailed reported analysis of the oxide-catalyzed condensation is that done by Reichle using a gas chromatograph pulse microreactor (*22*). Using various catalysts, primarily LiAlMg(OH), the products obtained at 623 K upon injection of acetone were compared to those formed upon injection of several of the reaction intermediates. In all, 14 different products were reported, but the primary reaction sequence observed was acetone → mesityl oxide → phorone → isophorone. The yield of isophorone was approximately 40%, with approximately 40% of the acetone remaining. There were also small percentages of various other products present.

An alternate pathway results in 4,6-dimethyl-3,5-heptadiene-2-one, which, after an internal aldol condensation, results in mesitylene. When acetone was used as the starting material, only 1–2% yield of mesitylene was observed.

While the catalyst and the reaction conditions differ, the results obtained in the present study generally parallel those of Reichle. The NMR study demonstrates that formation of mesitylene is preferred at higher temperatures (575 K) and longer reaction times, while the reaction of acetone to form isophorone occurs at 345 K within minutes. Since 4.4 statistical monolayers were used, the final spectrum shows an excess of residual acetone. However, samples prepared using a single statistical monolayer of acetone and similarly studied resulted in the complete disappearance of the acetone peaks. This suggests that the water given off during the course of the condensation reaction deactivates the surface by competing for available reaction sites.

CONCLUSION

The results indicate that the attainable resolution of the spectra permits simultaneous detection of several compounds, even while these are adsorbed on the oxide surface. The data acquisition time required for detection of all species except diacetone alcohol was less than 10 min at a coverage of 4.4 statistical monolayers. Both of these factors indicate that performing various types of relaxation time studies is a reasonable undertaking, and should lead to valuable information regarding the nature of adsorption and reaction. In addition, varying experimental parameters, such as the relaxation delay between successive scans, may reveal the presence of additional species which are less mobile and therefore less efficiently relaxed than the compounds observed in the course of the current experiments wherein relaxation delays of not more than 7.0 s were used.

While conventional (as versus multipulse and/or magic angle spinning) NMR is not widely thought of as a surface analytical technique, it is nevertheless applicable to systems of physisorbed molecules. The present study has demonstrated an ability to use conventional NMR to probe a surface-catalyzed reaction as a function of temperature and time, without unreasonably long data collection times. This promises to be an entry point for the use of NMR to probe orientation at surfaces and reaction kinetics for this and other catalytic systems.

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