J. Chem. Soc., Faraday Trans. 1, 1984, **80**, 831–839

Aldol Condensation of Butan-2-one and Pentan-3-one on an Activated Alumina as Monitored *via in-situ* Carbon-13 Nuclear Magnetic Resonance Spectroscopy

By VALERIE A. BELL, ROBERT F. CARVER, CECIL DYBOWSKI AND HARVEY S. GOLD*

Center for Catalytic Science and Technology, Department of Chemistry,
University of Delaware, Newark, Delaware 19716, U.S.A.

Received 22nd June, 1983

Conventional ^{13}C nuclear magnetic resonance spectroscopy is used to monitor the reactions of butan-2-one and pentan-3-one adsorbed on alumina. Both reaction sequences proceed *via* successive aldol condensations. The products observed for butan-2-one (5-methyl-4-hepten-3-one and 4-hydroxy-4-methylpentan-2-one) are those expected for homogeneous base catalysis. A *J*-modulated spin–echo sequence demonstrates that 5-ethyl-4-methyl-5-hepten-3-one, the β,γ condensation product, is obtained using pentan-3-one. The results demonstrate that conventional ^{13}C n.m.r. can be effectively used to distinguish reaction pathways and products for surface-catalysed reactions.

Nuclear magnetic resonance (n.m.r.) spectroscopic studies of species adsorbed on solids are becoming increasingly common, particularly in the area of catalyst characterization. At present, n.m.r. of adsorbed-state species may be accomplished using one of three techniques. These are (1) conventional n.m.r., (2) solid-state, broad-line n.m.r. and (3) magic-angle spinning (m.a.s.) n.m.r. Broad-line n.m.r. is limited with respect to resolution and is therefore constrained to studies of systems with a minimal number of species present. M.a.s. n.m.r. requires a carefully balanced sample rotor, which limits the sample preparation procedure.

Use of conventional n.m.r. to study compounds on solid supports has proved to be a viable alternative to infrared (i.r.) and gas-chromatographic (g.c.) methods. The traditional limitation of n.m.r. to study interactions of reacting adsorbates on supports can easily be overcome, as has been demonstrated by Derouane and coworkers in the context of product formation and kinetics,[1–8] and by Bell and Gold in the study of acetone on alumina.[9] Conventional ^{13}C n.m.r. studies of reactive systems include methanol on H-ZSM-5 zeolite,[10] the isomerization of but-1-ene to but-2-ene using alumina,[11] CaNaY-type zeolite[12] and tin–antimony oxide,[13] propene dimerization on NiO/SiO_2[14] and formic acid dehydration on TiO_2.[15] In general, peak widths have been found to vary according to the surface area of the support, the inherent inhomogeneities of the instrumentation and of the particular sample, the degree of attachment of the adsorbate to the support, the number of monolayers or pore fillings present and the temperature of the system. These experimental variables must be carefully considered when n.m.r. of physisorbed species is contemplated.

In the present study the use of conventional ^{13}C n.m.r. is extended to butan-2-one and pentan-3-one on γ-alumina. Aluminas are extensively used as catalysts, as well as supports for catalysts. Indeed, the alumina-catalysed dehydration of ethanol was recognized as early as 1797.[16] While alumina is generally classified as alpha, eta or gamma, a range of catalytic activity is encountered within each crystalline form. In the case of γ-alumina eight distinct forms have been reported, although no general agreement regarding individual structures yet exists.[16] A criterion for selection of a particular sample of γ-alumina for use in n.m.r. studies is the absence of iron and other paramagnetic impurities, which contribute to n.m.r. relaxation processes and attendant line broadening.[17]

Use of conventional ^{13}C n.m.r. is broadly applicable to adsorbed-state heterogeneous catalytic reactions. Although species which are tightly adsorbed (chemisorbed) to the surface are not readily monitored *via* this method, owing to the relaxation times involved, species which are less tightly adsorbed are easily observed. Application of this technique to both the butan-2-one and the pentan-3-one/alumina reactions revealed unexpected reaction products; butan-2-one reacts *via* the less hindered reaction mechanism, and pentan-3-one reacts to form a β, γ unsaturated ketone.

EXPERIMENTAL

Butan-2-one (Burdick and Jackson, spectral quality) was used as received following a ^{13}C n.m.r. determination of purity. Pentan-3-one (Alpha/Ventron) was distilled before use. The alumina used was Catapal γ-Al_2O_3 (Conoco), a product selected for its exceptionally low iron content (0.005%). The alumina was calcined at 775 K in a flow of oxygen for 24 h, and subsequently degassed at 673 K and 1×10^{-3} Torr (*ca.* 1.33 N m^{-2}) for 0.5 h. The details of sample preparation and instrumental operating parameters have been described previously.[9] All spectra were acquired at 295 K using a Bruker WM 250 n.m.r. spectrometer operating at 62.9 MHz, with proton decoupling (1 W) and an external deuterobenzene lock solvent. The *J*-modulated spin–echo sequence used is that found in the Bruker instrument manual; however, the value of $1/2J$ was assumed constant at 0.008 s (where J equals the carbon–proton coupling constant). *J*-modulated spin–echo sequences cause resonances corresponding to carbons with an odd number of attached protons to be inverted. The use of the *J*-modulated spin–echo sequence for adsorbed-state species was verified *via* use with the known butan-2-one/alumina reaction mixture before use with the pentan-2-one/alumina reaction mixture.

Two distinct types of butan-2-one samples were prepared and monitored. Samples I and II each contain 3×10^{-3} mol (2.5 statistical monolayers based upon a surface area of 280 ± 10 m^2 g^{-1} for the alumina) of butan-2-one vapour deposited at 77 K utilizing an external liquid-nitrogen bath. Sample I was flame-sealed and kept at 77 K until inserted into the n.m.r. probe. Sample II was warmed to 295 K with gentle mixing. After 20 min the sample was cooled in liquid nitrogen and 0.8 statistical monolayer of water was added to the sample. It too was kept at 77 K until being inserted into the n.m.r. probe.

The procedure used for the pentan-2-one sample parallels that for sample I of butan-2-one.

RESULTS

BUTAN-2-ONE

SAMPLE I

Within 30 min of removal of the sample from the liquid nitrogen, reaction products were readily apparent. Fig. 1 shows the spectrum resulting from the coaddition of 75 scans taken over the first 25 min that the sample was in the n.m.r. probe at 298 K. The original butan-2-one resonances at δ 8, 29, 37 and 209 ppm are evident, along with new resonances at δ 19, 123, 159 and 203 ppm, with a shoulder at δ 13 ppm.

SAMPLE II

Fig. 2 shows the spectrum which results immediately upon insertion of the sample into the probe, and shows strong new resonances at δ 73 and 52 ppm, produced by

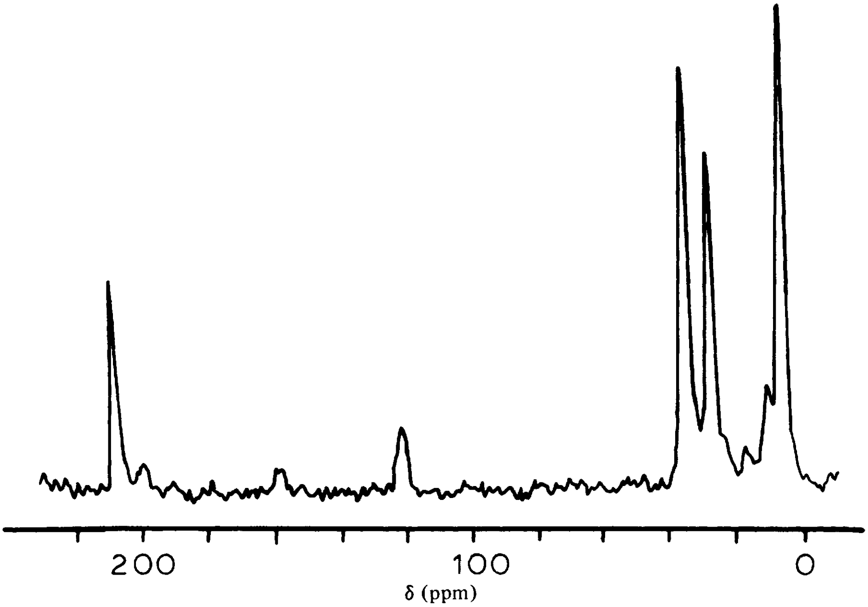

Fig. 1. ^{13}C n.m.r. spectrum of butan-2-one reacted on alumina for 30–35 min after removal from liquid nitrogen (sample I). The spectrum represents the coaddition of 75 scans, using a relaxation delay of 20 s. Chemical shifts are relative to tetramethylsilane (TMS).

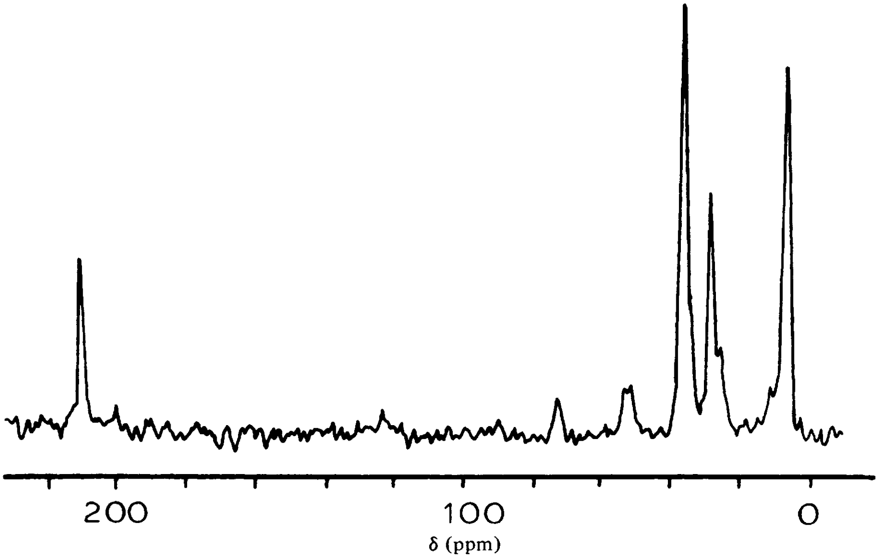

Fig. 2. ^{13}C n.m.r. spectrum of butan-2-one reacted on alumina wherein the reaction has been quenched by addition of 0.8 statistical monolayer of water (sample II). The intermediate ketol is desorbed. Chemical shifts are relative to TMS.

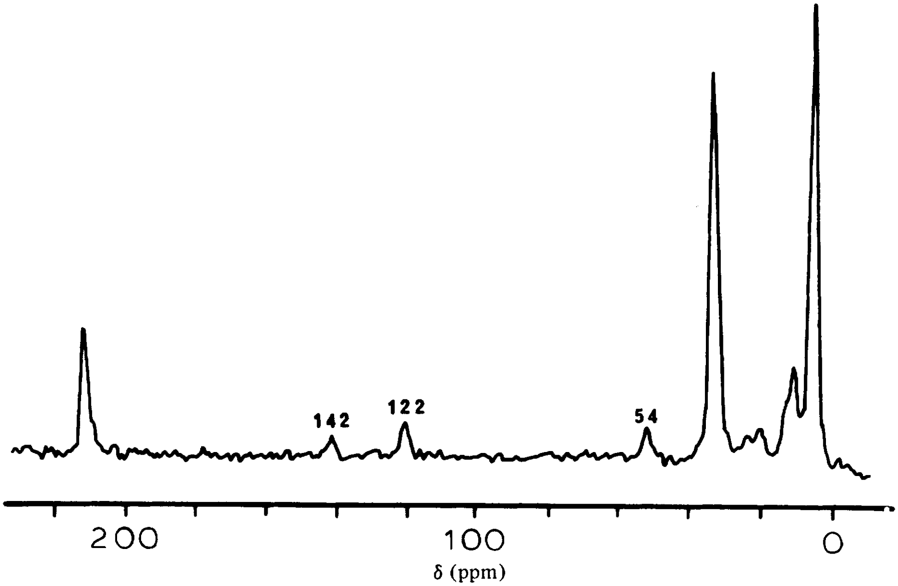

Fig. 3. ^{13}C n.m.r. spectrum of pentan-3-one reacted on alumina after standing for 6 days at 298 K. Chemical shifts are relative to TMS. The spectrum represents the coaddition of 116 scans, using a relaxation delay of 20 s and a 45° pulse.

compounds which were desorbed upon addition of water because of competition for surface sites on the alumina.*

During the time it takes to acquire the spectrum of fig. 1, the reaction has gone almost to completion, as evidenced by the fact that a spectrum acquired 2 h later reveals little change. A spectrum acquired 6 days later shows additional resonances at δ 46 and 54 ppm, both of which are believed to be due to secondary condensation products, paralleling the behaviour observed for acetone.[9] Following this, the overall relative intensities changed little over the course of 1 month at 298 K.

PENTAN-3-ONE

Initial pentan-3-one resonances are observed at δ 8, 36 and 211 ppm. The reaction is observed to occur much more slowly than the corresponding butan-2-one reaction. A shoulder appears on the downfield side of the δ 8 ppm resonance after 3 h, and two resonances at δ 54 and 122 ppm appear simultaneously after 6 h, together with additional resonances in the methyl resonance region. Heating the sample to 350 K in the probe did not produce any additional detectable products. After 6 days at room temperature the spectrum of fig. 3 was obtained, in which there is sufficient intensity to identify an additional resonance at δ 142.5 ppm. Addition of 0.8 statistical monolayer of water did not produce any additional resonances. A similar sample (containing no added water) kept at room temperature for one month showed no additional resonances, although the relative intensities of the δ 54, 122 and 142.5 ppm resonances were much greater. This sample was used in the J-modulated spin–echo sequence experiment.

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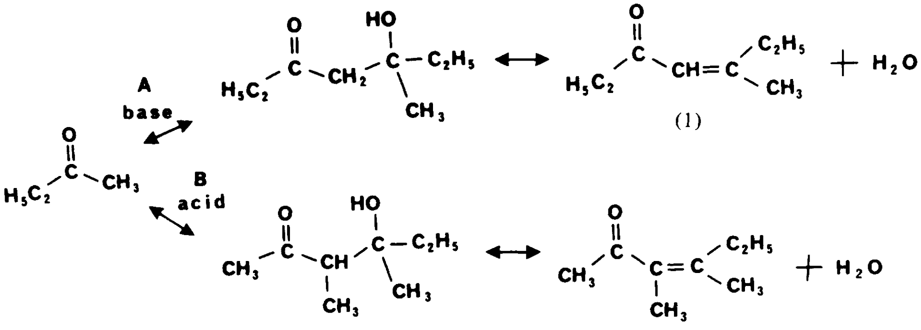
* This competitive process effectively quenches the reaction and allows observation of tightly bound products.



(2)

Fig. 4. The acid- and base-catalysed reaction pathways of butan-2-one in solution.[11]

DISCUSSION

BUTAN-2-ONE

The aldol condensation of butan-2-one has two possible pathways, each involving an enol intermediate, as shown in fig. 4. Steric hindrance would be expected to cause a preference for pathway A, wherein the attacking carbanion is the more exposed α-carbon. Abbott *et al.*[18] have characterized this reaction as catalysed by homogeneous acids or bases. All ketones except butanone are found to react *via* pathway A, the sterically favoured pathway, for both acid and base catalysis.[19] Butanone, however, is found to react *via* pathway B, the hindered mechanism, when a homogeneous acid catalyst is used.

To determine the major product obtained in the presence of an alumina catalyst, the characteristic resonances of sample I at δ 123 and 159 ppm must be assigned. These resonances correspond to the olefinic carbons. For compound (2) (3,4-dimethylhex-3-en-2-one), the resonance of C3 occurs at δ 134 ppm and of C4 at δ 145 ppm.[20] For compound (1) (5-methylhept-4-en-3-one), peaks can be assigned by analogy to adsorbed mesityl oxide[9] and by comparison with the shifts of similar unsaturated ketones upon substitution.[21] Thus the resonance of C4 is determined to be δ 124 ± 3 ppm. The resonance of C5 is determined to be δ 159 ± 3 ppm. The resonances observed in fig. 1 indicate formation of product (1), the base-catalysed product. This agrees with the product identified by Kozima and Katsuno using i.r. detection of the desorbed products of the same reaction of butan-2-one on γ-alumina.[21] Resonances at δ 54 and 73 ppm in fig. 2 can be assigned by analogy to the spectrum of diacetone alcohol (4-hydroxy-4-methylpentan-2-one) adsorbed on alumina, which has resonances at δ 54 and 69 ppm. Thus the resonances at δ 54 and 73 ppm are assigned to the C4 and C5 carbons, respectively, of the ketol (5-hydroxy-5-methylheptan-3-one) formed in pathway A.

The products found are those expected for a homogeneous base catalyst. This is of interest, since Lewis-acid sites are the most commonly cited cause of catalytic reactions on alumina.[22] Ketones are known to interact with Lewis-acid sites *via* the carbonyl group.[22] Also, for the aldol condensation of acetone on rutile, Griffiths and Rochester[23] reported evidence of attachment of the carbonyl group to the exposed titanium ion, and concluded that this Lewis-acid site was the catalyst for the condensation. In the butan-2-one system the product formed indicates that the catalyst is a basic site in the alumina. This cannot be definitely concluded, however,

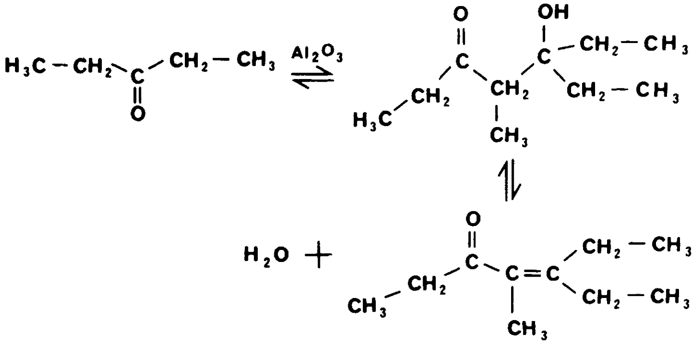


Fig. 5. Reaction sequence showing the condensation of pentan-3-one to yield α,β-conjugated unsaturated ketone.

since catalysis on alumina includes the additional consideration of increased steric hindrance due to the alumina surface. It may be that the reaction on alumina is in fact catalysed by an acid site, but that the acid catalysis follows a different mechanism than that found in solution, resulting in the product expected for basic catalysis. Thus it may be that the relative steric hindrance of the two α-carbons is the governing factor when catalysis is carried out on a surface. Unfortunately other ketones cannot be used for comparison, since all other ketones react *via* the less hindered α carbon for either acid or base catalysis.

PENTAN-3-ONE

The aldol condensation of pentan-3-one on alumina to form an unsaturated ketone[22] would occur by the pathway shown in fig. 5. The dehydration of the ketol (5-ethyl-4-methyl-5-hydroxyheptan-3-one) occurs *via* an enol intermediate.[24] Characteristic shift assignments for this product can be obtained by analogy with published values for 3,4-dimethylhex-3-en-2-one, and are 134 ± 5 ppm for C4 and 145 ± 5 ppm for C5.[25] The spectrum obtained (fig. 3) shows resonances at δ 54, 122 and 142.5 ppm. Thus the conjugated α,β-unsaturated ketone is not the product obtained when pentan-3-one reacts on γ-alumina. Evidence suggests that alumina stabilizes the enol configuration. If a dehydration product is formed in which the enol intermediate is conjugated, the final unsaturated ketone is the β,γ-unsaturated ketone (shown in fig. 6). Abbott and coworkers found that the β,γ-product is preferred in homogeneous catalysis when there is substitution α to the carbonyl in the original ketone.

Since literature values for the β,γ-product, 5-ethyl-4-methylhept-5-en-3-one, are unavailable, the expected characteristic chemical shifts were calculated. Using the Clerc and Pretsch[26] technique for saturated carbons, the shift for C4 is δ 55.1 ppm (*trans*). Using the method of Dorman[27] for acyclic alkenes, the shift for C5 is δ 142.5 ppm, and for C6 it is δ 115.7. These calculated values agree quite well with those observed experimentally in the cases of C4 and C5, but C6 is outside the range of uncertainty.

As an additional verification of resonance assignments, a *J*-modulated spin–echo sequence was used, yielding the spectrum in fig. 7. The inversion of the resonances at δ 54 and 122 ppm is in accord with the presence of a single proton attached to the corresponding carbons. Likewise, the lack of inversion of the resonance at δ 142.5 ppm indicates that an even number of protons is attached; in this case this is consistent with the presence of zero protons at the C4 position.

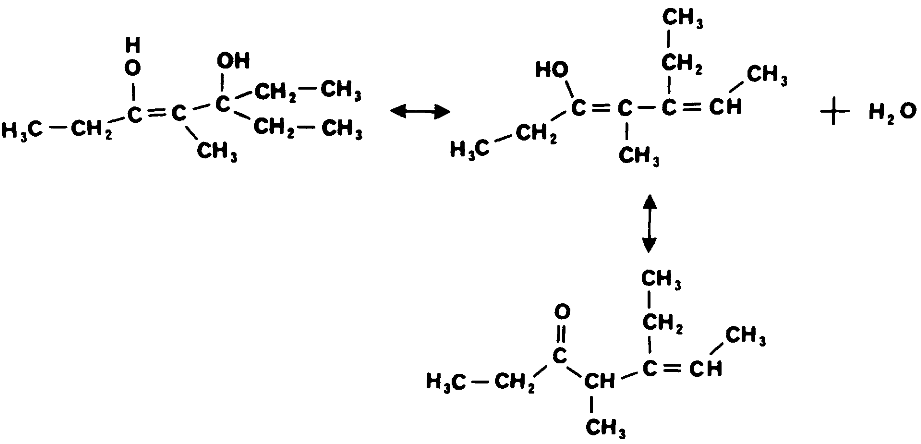


Fig. 6. Reaction sequence showing the condensation of pentan-3-one to yield a product corresponding to conjugation in the enol intermediate.

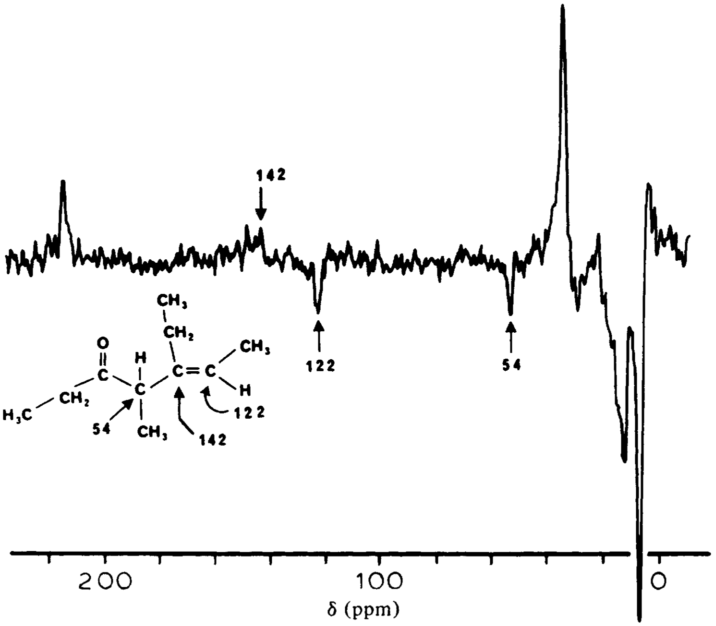


Fig. 7. ^{13}C n.m.r., *J*-modulated spin–echo sequence spectrum. Using this pulse sequence the resonances of carbons with an odd number of attached protons are inverted. The spectrum represents the coaddition of 405 scans. TMS was utilized as the chemical-shift reference.

A large number of other possible reaction products can be postulated. The expected chemical shifts of these theoretical products, including those resulting from rearrangements typical of ketone reaction intermediates and cyclics, were compared with the spectrum obtained. No other possible product agrees with this spectrum.

CONCLUSION

Conventional ^{13}C n.m.r. can thus be utilized effectively to distinguish reaction products and pathways for surface-catalysed reactions. This method benefits from the ease of sample preparation, which use of a standard n.m.r. tube attached to a vacuum manifold provides. The ability to control carefully surface conditions, sample loading and the introduction of other species (such as poisons) is crucial to elucidation of the catalytic system. Temperature and time may also be easily varied, making the conventional n.m.r. study of physisorbed molecules a valuable addition to surface analytical techniques.

The case of pentan-3-one is particularly interesting, since the chemical shifts, stability of the enol and the inversion spectrum all indicate that the β,γ-unsaturated ketone is the product obtained when pentan-3-one reacts on alumina. While it is indeed possible that differences in the reaction conditions used in this study (as compared with those of Kozima and Katsumo[21]) lead to formation of the β,γ-unsaturated ketone instead of the α,β-unsaturated ketone, both studies were performed at room temperature, and the calcining conditions for both are quite similar. It is unlikely, during the n.m.r. study, that the alumina contained adsorbed CO_2, since other work[28] indicates that any CO_2 initially present is desorbed when the sample is heated to 675 K under vacuum. In the case of the aldol condensation of acetone on Catapal, previous n.m.r. studies show that adsorption of CO_2 in amounts from 0 to 4 statistical monolayers before or after heating has no detectable effect upon the reaction. It therefore seems unlikely that adsorbed CO_2 would affect the pentan-3-one reaction.

In a recent publication Pines[29] discusses a significant difference in catalytic activity of two aluminas he has synthesized. One alumina was doped with potassium to a level of 0.08%: the other remained undoped. Despite this difference, conventional X-ray powder pattern analysis shows no significant differences and surface-area measurements were also quite similar for both.

The Catapal alumina (γ, neutral) used in this n.m.r. study may contain active sites other than the neutral γ-alumina used by Kozima and Katsumo, leading to differential stabilization of the enol intermediates. An intriguing possibility is that the low levels of paramagnetics and other foreign metal atoms present in other aluminas, but not in Catapal, may play a significant role.

The suggestions of Roger Crecely are greatly appreciated. This work was supported by the Center for Catalytic Science and Technology at the University of Delaware. Purchase of the Bruker WM 250 n.m.r. spectrometer was made possible by grant GM-27616 from the National Institutes of Health.

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