metal complexes revealed no enhanced intensity in this spectral region. Interestingly, however, a new, strong absorption is noted in the 1520–1570-cm^{-1} region for various oxidized metallooctaethylporphyrins. It should be noted that weaker bands of variable intensity are also seen in this region for oxidized TPP derivatives. A 10-cm^{-1} shift associated with meso deuteration in [Fe(OEP)][ClO$_4$]$_2$ (see Table I) once again serves to indicate assignment to a vibration within the macrocycle. Absence of an enhanced intensity band near 1280 cm^{-1} most likely reflects molecular structural differences rather than electronic configuration differences for OEP vs. TPP compounds. Examination of oxidized [Co(OEP)][X]$_2$ complexes, representation of both the $^2A_{1u}$ and $^2A_{2u}$ radical states,[17] seems to indicate no particular association of radical type with IR spectral type.

In summary, the empirical observation of an IR-active porphyrin ring mode at ~1280 cm^{-1} in TPP$^{+\cdot}$ complexes and at ~1550 cm^{-1} in OEP$^{+\cdot}$ complexes offers an apparently unique criterion for formulating the electronic structures of oxidized metalloporphyrins. The seemingly unambiguous choice between *either* metal-centered *or* porphyrin-centered oxidation in highly oxidized metalloporphyrin complexes can be rationalized by their orbital symmetries. Neither the a_{1u} nor a_{2u} porphyrin HOMO's have the correct symmetry to overlap with any of the metal d orbitals, and this excludes resonance formulations which might lead to ambiguous averaged valencies. Understanding the nature of the highest occupied orbital is probably important for explaining the diverse reactivity patterns of oxidized metalloporphyrins toward nucleophiles or the sites of electron transfer.[9,17] The ~1550-cm^{-1} band of OEP$^{+\cdot}$ complexes may be usefully diagnostic of radical cations in oxidized hemoproteins.[22]

Acknowledgment. Support from NSF grants, CHE 79-10305 (H.M.G.) and CHE 80-26812 (C.A.R.), and NIH grant, GM 28831-01 (H.M.G.), is gratefully acknowledged.

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Carbon-13 Cross-Polarization Magic-Angle-Spinning NMR Study of *n*-Butylamine Adsorbed on γ-Alumina: Characterization of Surface Acid Sites

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The question of surface acidity of aluminum oxides, silicates, and mixed alumina silicates is one of long-standing interest.[1] The problem is one of both practical and theoretical concern. Many industrially important catalytic reactions are based on these materials and, their reactivity is determined to a large extent by the nature of surface acid sites.[1,2] It is of prime interest to identify these catalytically active sites to ascertain whether they are of Brönsted or Lewis type and to determine their relative acidity.

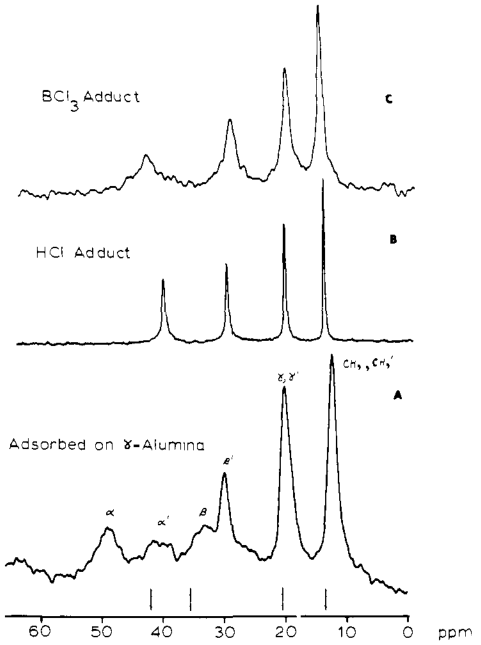

Figure 1. Carbon-13 CP–MAS spectra of *n*-butylamine.[9-11] (a) Adsorbed to the surface of γ-alumina (38 000 accumulations). The vertical bars indicate carbon chemical shifts for liquid-phase *n*-butylamine given in ref 12b; (b) Solid HCl adduct (46 accumulations); (c) solid BCl$_3$ adduct (212 accumulations).

Several methods have been used to study surface acidity, including the most straightforward approach of direct titration with acid–base indicators.[3] Infrared spectroscopy has been extensively employed to examine those interactions involving surface hydroxyl groups.[4] Widespread use of the IR method stems from its sensitivity and adaptability to a variety of adsorbate–adsorbent systems. Proton NMR spectroscopy has similarly provided valuable information that is both quantitative and sensitive to the motions of the adsorbed species.[5] More recently, ^{13}C NMR spectroscopy has been used to advantage.[6,7] For example, Gay and co-workers have employed ^{13}C NMR spectroscopy as a means of following the titration of surface acid sites with aromatic nitrogen bases.[6] To date, such studies have employed standard high-resolution NMR techniques which are able to yield spectra with suitable resolution only in cases where the molecules are undergoing rapid motion on the surface. For the case of strongly adsorbed species, it has been necessary to study the samples at elevated temperatures in order to induce enough motion to sharpen the resonances. This approach represents a serious limitation to investigating the nature of surface–adsorbate interactions by NMR spectroscopy. The recently developed technique of magic-angle spinning in conjunction with dipolar decoupling[8] provides an alternative method of narrowing the lines and avoids this limitation. We report here our cross-polarization magic-angle spinning (CP–MAS) results for *n*-butylamine adsorbed on γ-alumina.[9]

The spectrum of *n*-butylamine on γ-alumina is shown in the Figure 1a.[10,11] There are six prominent resonances, two of which

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(9) The carbon-13 CP–MAS experiments were conducted at 50.3 MHz by using a modified Bruker WP200-WB spectrometer. The single-contact pulse sequence used 50-kHz matching, a contact time (unoptimized) of 1 ms, and a recycle time of 1 s.

are readily assigned to the γ-methylene and methyl carbons by comparison with the liquid-phase spectrum. These resonances are only slightly shifted upon adsorption. The remaining four resonances arise from the two α- and β-methylene carbons, from which we conclude that a least two types of chemically different butylamine species are present on the surface.

The existence of well-resolved resonances demonstrates that if surface diffusion is occurring, then the rate is not comparable to the spinning rate (~3.2 kHz).[13] Further, if site exchange is occurring, then the rate must be slow compared to the chemical-shift difference between the two species on the surface. Therefore, this spectrum is consistent with a picture whereby the nitrogen of the *n*-butylamine is firmly anchored to the surface. In all probability the system is executing rapid albeit limited angular diffusion about the bond axis connecting the surface to the nitrogen, with the motion of the alkyl chains increasing as one moves away from the surface.

The appearance of four resonances in the region expected for the two α and β carbons of the alkyl group is consistent with there being two quite different sites available to the amine. Two candidates are the classic Lewis and Brönsted sites. In order to check this possibility we obtained the CP-MAS ^{13}C spectra of two solid adducts of *n*-butylamine (Figure 1b,c). Those resonances for the solid HCl adduct match closely to four of the resonances for the surface adsorbed species. The resonances corresponding to the α and β carbons of the solid BCl_3 adduct are deshieled relative to the corresponding carbons within the HCl adduct but shielded relative to the analogous carbons of the adsorbed amine. Hence, we conclude that the most deshielded set of resonances correspond to the *n*-butylamine which is attached to the surface via Lewis bonds to an aluminum atom. That the chemical shifts of this species are deshielded relative to those of the BCl_3 adduct we attribute to the fact that the acid site in this surface is a stronger Lewis acid than BCl_3.

The breadth of the resonances for the α and β carbons may arise from several factors. An important consideration for the α carbon is the presence of nitrogen-14 dipolar coupling. The fact that we do not observe "well-resolved" doublets[14] for this carbon may be due in part to the angular diffusion of the molecule and/or the strength of the applied magnetic field relative to the nitrogen-14 quadrupolar coupling constant. Perhaps of equal importance to the line width is a heterogeneity of the acid sites on the surface of the alumina. The presence of a distribution of site acidities would lead to a corresponding distribution of chemical shifts and hence appear as a line-broadening mechanism.

In summary, it is clearly evident that ^{13}C NMR spectroscopy in conjunction with CP-MAS methods can be used to probe the interactions between small molecules and surfaces even when the surface is of moderately low specific area. Compared to other spectroscopies carbon-13 CP-MAS NMR spectroscopy appears to provide a facile method to distinguish between different types of surface bonding sites and their relative acidity. Within the limitations of cross-polarization dynamics the relative populations of these sites can be quantified.

Acknowledgment. We thank Z. Szafran for his assistance in preparing the amine and F. D. Doty for the MAS probe design used for this work. We are indebted to Dr. R. C. Schoening for his useful advice. The encouragement and support of the management of union Carbide Corporation is gratefully acknowledged. The use of the facilities at the University of South Carolina Regional NMR Center, funded by the National Science Foundation Grant CHE78-18723, is acknowledged.

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(10) The γ-alumina (SA = 220 m^2/g) employed in this study was pretreated at 350 °C in vacuum. The *n*-butylamine was laid down on the surface by using entrainment in a helium flow. The basis of a weight increase of approximately 0.5%, the surface covered by the butylamine is estimated to be 10 m^2/g or roughly one-twentieth of a monolayer. Operating under a dry nitrogen atmosphere the granular alumina sample was packed into an aluminum oxide NMR rotor.

(11) An important experimental difficulty that had to be overcome with these relatively dilute samples (typically 40 mM in amine based on the total volume of the NMR rotor) was the carbon background signal from the NMR probe. We accomplished this using sample machined from aluminum oxide and a stator from Macor. The Delrin end caps of the rotor leave a small signal at 90 ppm which we use for reference.

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Laser Photochemical Production of Vitamin D[†]

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The complex photochemistry of 7-dehydrocholesterol (7-DHC) and ergosterol (E) is now moderately well understood due, in large part, to the elegant studies of Havinga and co-workers.[1-9] Table I shows how the distribution of products depends on photolyzing wavelength.[10] Photolysis in the range 270–310 nm gives relatively high yields of previtamin D (P); shorter wavelengths lead to a predominance of tachysterol (T) and longer wavelengths to lumisterol (L).[11] The interrelations between the various products are shown in Figure 1.

Using laser photolysis, we have confirmed the main aspects of the dependence of the product array on wavelength and have gone further by demonstrating that by a two-stage photolysis we can "engineer" a desirable product distribution with improved yields. This approach may offer an attractive alternative to the commercial method of vitamin D production, which requires a number of fractional crystallizations.[15]

Photolysis at KrF (248 nm) and XeCl (308 nm) wavelengths was carried out with an excimer laser (Lumonics Research Limited, Model 861), which gives average powers in the 1–10-W range. Photolysis at 337 nm used a nitrogen laser (Molectron, Model UV 1000) with an average power of 0.2 W while at 353 nm a YAG laser (Molectron, Model MY 34) with an average power of 0,4 W was used. The reaction mixtures were analyzed by high-performance LC[20] (Varian 8500) on a silica Si-5 column (5

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