

Investigation of Surface Acidity by ^{13}C NMR Adsorption of Amines on Silica, Alumina, and Mixed Silica-Alumina

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^{13}C NMR spectra have been obtained for several amines, notably pyridine, aniline, and some derivatives of these, adsorbed on SiO_2 , Al_2O_3 , and mixed SiO_2 - Al_2O_3 . On SiO_2 , only weak interactions with surface hydroxyl are observed. An anomalous case is *N,N*-diethylaniline which shows an unaccountably large C-2 chemical shift. On Al_2O_3 , much stronger interactions are observed. There is no evidence, however, of large chemical shifts such as occur on protonation of the corresponding amines in aqueous acids. It is shown that the strong acid sites on Al_2O_3 are sterically hindered. On SiO_2 - Al_2O_3 , chemical shifts due to protonation are observed. It is shown that ^{13}C NMR can be used to estimate the concentration of surface proton acids.

INTRODUCTION

The catalytic importance of acidic sites on solid surfaces has long been recognized, and has led to many efforts at determining the number and nature of such sites (1). One of the most fruitful techniques has been the spectroscopic observation of adsorbed amines, which has led to the recognition on solid surfaces of both protonic and Lewis acid sites, and to semi-quantitative measurement of their concentrations. Following Parry (2), most workers have used infrared spectroscopy, although a few studies by ultraviolet spectroscopy exist (3, 4).

It has recently been shown (5-8) that ^{13}C NMR spectroscopy is capable of resolving chemical shift differences between free and adsorbed molecules, and is therefore potentially able to indicate the state of adsorbed species. In the particular case at hand, it is known that rather large chemical shifts occur upon protonation of aromatic and heterocyclic amines in aqueous solution (9), and ^{13}C NMR might

therefore be a useful means of studying surface proton acids. A further benefit of NMR spectroscopy is that information about the motional state of adsorbed species is fairly directly available (10) from linewidth and relaxation measurements. We have therefore undertaken ^{13}C NMR observations of various amines on SiO_2 , Al_2O_3 , and mixed SiO_2 - Al_2O_3 surfaces, with a view to observing the interactions between the adsorbed species and surface acid sites.

EXPERIMENTAL

All NMR measurements were performed at 25.2 MHz on a Varian XL-100 spectrometer with TTI Fourier transform modification. Proton noise decoupling was used in all experiments. Normally an 18 μs (approx $\pi/3$) pulse was used at a repetition rate of 5 per second. Between 10^3 and 2×10^5 scans were taken for each spectrum, depending on concentration and linewidth. Chemical shifts were measured relative to external samples of the neat liquid amine,

using susceptibility corrections determined from ^1H spectroscopy of physically adsorbed tetramethylsilane (8).

Spectra were run at temperatures from ambient (approx 28°C) to 90°C . In general, narrower lines could be achieved at the higher temperatures, but too high a temperature resulted in distillation of adsorbate to the cooler regions of the sample tube. The measurement temperature was always at least 20°C below the temperature at which visible liquid condensate appeared on the cool portions of the sample tube.

Samples for NMR measurement were prepared in 12-mm (o.d.) Pyrex tubes, which were then sealed off. Adsorbents were degassed *in vacuo* at various temperatures, noted below, and the required quantity of amine adsorbed from the vapor phase. In the case of the more volatile amines, this was achieved with a conventional gas-volumetric apparatus. In the case of amines having less than about 20 Torr vapor pressure at room temperature, a different technique was used. Measured samples of adsorbent and adsorbate were degassed and sealed in opposite ends of a two compartment tube. The compartments were then brought into communication by breaking a breakseal, and the whole apparatus placed in an oven at a temperature (usually about 100°C) at which the adsorbate had a vapor pressure of 10 to

100 Torr. The apparatus was left in the oven for some hours and then allowed to cool. In no case was any liquid amine visible after this treatment, and since the amount of gas phase amine would be negligible, even at the vapor pressure of the liquid, we assume that essentially all of the amine was adsorbed on the solid sample. Water-poisoned samples were prepared by the same technique, a measured amount of H_2O being added to the same compartment as the amine.

The silica used was B and A chromatographic grade, and had a surface area of $250\text{ m}^2/\text{g}$. Alumina and mixed silica-alumina were prepared by hydrolysis of aluminum isopropoxide or a mixture of this with silicon ethoxide in isopropanol or benzene solution. The resulting precipitates were dried and ignited in air at 550 to 700°C . After ignition samples were rehydrated at 100% relative humidity. Different preparations had areas ranging from 100 to $200\text{ m}^2/\text{g}$ as determined by the BET method using nitrogen.

RESULTS AND DISCUSSION

Silica

All amines adsorbed on silica showed fairly narrow lines and rather small chemical shifts relative to the liquid amine. A typical spectrum, that of pyridine, is shown in Fig. 1a. The chemical shifts rela-

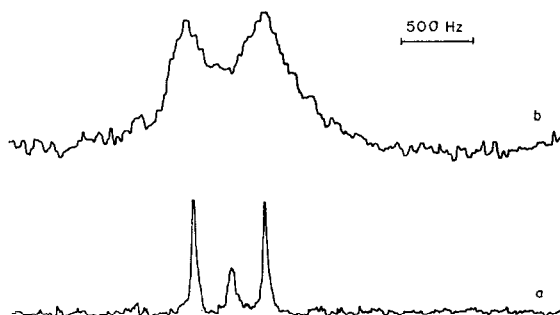


Fig. 1. ^{13}C NMR spectra of pyridine. (a) On SiO_2 degassed at 250°C . Fractional coverage 0.77. Spectrum recorded at 28°C , 10^4 scans. (b) On Al_2O_3 degassed at 250°C . Fractional coverage 0.86. Spectrum recorded at 60°C , 2.6×10^5 scans.

TABLE 1
Chemical Shifts of Amines on SiO₂^a

Amine	Coverage ^b	Monolayers ^c	Carbon atom	Shift ^d
(CH ₃) ₃ N	2.51	0.51	CH ₃	+2.0
C ₂ H ₅ NH ₂	4.14	0.70	CH ₃	+3.5
			CH ₂	+1.2
(C ₂ H ₅) ₂ N	2.54	0.61	CH ₃	+4.3
			CH ₂	+2.3
pyridine	3.56	0.77	2	+1.1
			3	0.0
			4	-0.2
2-methyl pyridine	3.50	0.77	CH ₃	+2.4
			2	+0.8
			3	unresolved
			4	-0.6
			5	unresolved
			6	+0.5
4-methyl pyridine	4.15	0.91	CH ₃	+1.5
			2	unresolved
			3	-0.3
			4	unresolved
2,6-dimethyl pyridine	3.29	0.81	CH ₃	+1.4
			2	-0.6
			3	-0.5
			4	-0.5
3,5-dimethyl pyridine	3.20	0.78	CH ₃	+1.3
			2	+1.6
			3	-0.8
			4	-0.4
pyrrole	5.30	0.91	2	+0.1
			3	+1.1
aniline	2.65	0.51	1	+2.2
			2	-2.1
			3	+0.8
			4	-1.6
<i>N,N</i> -diethyl aniline	2.24	0.70	CH ₃	+3.0
			CH ₂	-2.5
			1	-0.4
			2	-9.0
			3	+0.4
			4	unresolved

^a All measurements at 28°C.

^b In micromoles per square meter.

^c Calculated from liquid density, assuming spherical shape.

^d With respect to neat liquid. Positive shifts upfield. Susceptibility corrections included.

tive to the liquid for the various amines adsorbed on silica are shown in Table 1.

The narrowness of the observed lines, ranging from 30 to 80 Hz shows that the adsorbed amines are in a state of rather rapid motion on silica. An evaluation of

the strength of the ¹H-¹³C dipolar interaction allows an estimate to be made of the motional correlation time. Interpretation of the linewidths in terms of simple motional narrowing models (11) indicates effective correlation times of not more

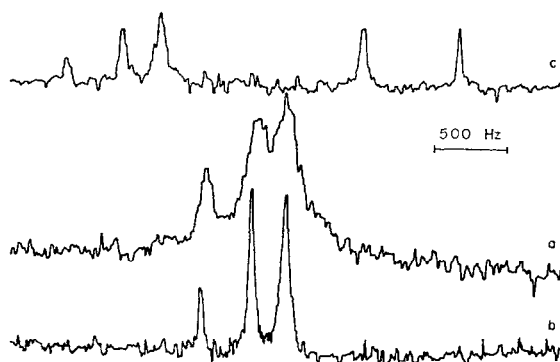


FIG. 2. (a) Aniline on Al_2O_3 degassed at 250°C . Fractional coverage 0.9. Spectrum recorded at 80°C , 6×10^4 scans. (b) Aniline on H_2O -poisoned Al_2O_3 . Fractional coverage 0.9. Spectrum recorded at 60°C , 3×10^4 scans. (c) *N,N*-diethylaniline on Al_2O_3 degassed at 150°C . Fractional coverage 0.6. Spectrum recorded at 80°C , 6×10^3 scans. The spectrum in (c) is displaced 940 Hz upfield with respect to (a) and (b).

than about 10^{-6} sec. This may of course represent a weighted average of molecules bound with differing mobilities, but it is clear that the majority of adsorbed molecules are in fairly rapid motion, at least rotationally. This fact, together with the small chemical shifts, supports the generally held view (2, 3) that weak bases on SiO_2 do not suffer interactions stronger than hydrogen bonding, and are comparatively weakly held.

The one exception to this trend is *N,N*-diethylaniline; as can be seen from the table, an abnormally large shift (-9.0 ppm) is recorded for C-2. This appears entirely out of line with the other data in the table; in particular, no such shift is found for aniline. Protonation with aqueous HCl produces the large shift of -10.4 ppm in this carbon, but also produces a shift of $+10.8$ ppm at C-1, and it is clear that such a C-1 shift does not occur on SiO_2 , thus apparently ruling out protonation by the surface hydroxyls. On the other hand, the shift can be reduced through thermal dehydroxylation of the surface. The data in Table 1 are for SiO_2 vacuum degassed at 250°C . Raising this temperature to 650°C reduces the C-2 shift to -6.4 ppm with no change greater than ± 0.9 ppm for any other line. Observa-

tion of the spectrum at 60°C narrows the lines sufficiently to resolve the C-4 carbon. This is also found to have a large downfield shift, about $\frac{3}{4}$ that of C-2. A small reduction in C-2 shift, to -7.6 ppm, is also observed on measurement at 60°C . These observations would seem to imply a rather specific interaction of *N,N*-diethylaniline with surface hydroxyls. The detailed nature of the interaction, however, and the reasons for its absence with other amines is by no means clear.¹

Alumina

The spectra of many amines on Al_2O_3 display much broader lines than on SiO_2 . This is illustrated in Fig. 1b which shows the spectrum of pyridine on Al_2O_3 at 60°C . Computer least-squares fitting of this poorly-resolved spectrum, assuming Lorentzian lines of equal width, yields a full width at half height of 430 ± 20 Hz. The C-2 line is well located by the fit and has a shift of $+0.2 \pm 0.3$ ppm with respect to

¹ It has been pointed out to us by a referee that a similar pattern of shifts occurs in *N,N*-dimethylaniline derivatives when an ortho substituent prevents coplanarity of the ring and the *N,N*-dimethylamino group (18). It is possible that a similar explanation can be given here; i.e., that adsorption forces are such as to destroy coplanarity in *N,N*-diethylaniline.

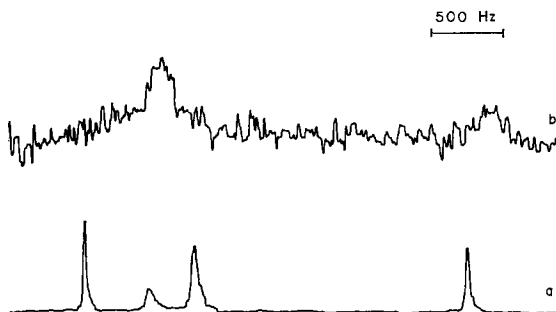


FIG. 3. (a) 2,6-Dimethylpyridine on Al_2O_3 degassed at 250°C . Fractional coverage 0.95. Spectrum recorded at 60°C , 1.8×10^4 scans. (b) 3,5-Dimethylpyridine, same conditions. Fractional coverage 0.73, 8.5×10^4 scans.

the liquid. The C-4 line can be located with equally good fit above or below the C-3 line, resulting in an uncertainty of ± 14 ppm for the position of this line, and an uncertainty of ± 3 ppm in the position of C-3, the midpoint of this range lying 2 ppm to low field of the liquid line.

It thus appears that pyridine is not a suitable molecule for investigation of strong interaction with acidic surfaces, since the line most strongly shifted in aqueous acids (12), C-4, is essentially unlocatable. We note, however, that the well-located C-2 line does not show the 7.8 ppm upfield shift (12) observed in acid solution. A reasonable explanation would be that the shift in aqueous acid is caused by protonation which does not occur on Al_2O_3 where most strong bonding sites are Lewis acids (2, 13).

The spectrum of pyridine on Al_2O_3 at 28°C shows a single featureless peak, indicative of about twice the linewidth displayed in Fig. 1b. Thus, we conclude that pyridine is much more tightly bound on Al_2O_3 , and must exhibit a motional correlation time at least an order of magnitude greater than on SiO_2 .

The spectrum in Fig. 1b was obtained on a sample degassed at 250°C . Degassing at 150°C gives a similar spectrum. On a sample degassed at 450°C , a further increase in linewidth is observed. This probably indicates that adsorbate mole-

cules are exchanging between weakly and strongly binding sites, and that the number of the latter increases with increasing evacuation temperature. It might well be possible to establish a quantitative relationship between linewidth and site concentration, but this could be more economically pursued via ^1H NMR spectroscopy.

A more suitable molecule for chemical shift observation in strongly interacting situations is aniline. This has nearly the same base strength in aqueous solution as does pyridine (14) and on protonation has its largest ^{13}C chemical shift change at C-1 which is well separated from the other peaks.

Figure 2a shows the spectrum of aniline on Al_2O_3 , and Fig. 2b on H_2O -poisoned Al_2O_3 , the added H_2O amounting to $4.4 \mu\text{mole}/\text{m}^2$. As can be seen, the lines are again broad on the unpoisoned Al_2O_3 but the low-field C-1 line is resolved from the remainder. Because of the broadness, the position of this line cannot be measured with high accuracy. We find it to be 0.6 ± 0.5 ppm upfield of the liquid line. There is no evidence of a large upfield shift such as is observed on protonation in acid solution (15). On the water-poisoned alumina, we find much narrower lines but again no significant C-1 shift. We measure 0.0 ± 0.2 ppm with respect to the liquid.

Steric Effects on Alumina

Figure 2c shows the spectrum of *N,N*-diethylaniline on alumina. It is immediately apparent that the lines are considerably narrower than those of aniline, and hence that *N,N*-diethylaniline is in more rapid motion. This is at first glance surprising, since the latter molecule is a considerably stronger base (14). The most plausible interpretation would be that the presence of the ethyl groups hinders the access of the nitrogen atom to the surface acid sites. A better test of the geometric accessibility of acid sites results from a comparison of the spectra of 2,6-dimethylpyridine and 3,5-dimethylpyridine. These spectra are shown in Figs. 3a and 3b, respectively. As can be seen, a narrow line spectrum is obtained from the 2,6 isomer, while the 3,5 isomer displays a line of about 250 Hz width for the nonprotonated C-3 superimposed upon lines of the other ring carbons, which are so broad as to be nearly unobservable under our experimental conditions. Since these isomeric amines are of essentially the same base strength (14), it is clear that we have a pronounced steric effect, and that the strong acid sites on Al_2O_3 are relatively inaccessible. A similar conclusion has been reached by Knozinger and Stolz (16) from a comparison of the relative ease of mutual

displacement of pyridine and 2,4,6-trimethylpyridine on Al_2O_3 .

Silica-Alumina

Mixed silica-alumina catalysts are well known to have appreciable surface concentrations of strong proton acid (2, 13). For the reasons noted above, we have used aniline as a test molecule to attempt to detect this acid. Figure 4a and b show spectra on $\text{SiO}_2\text{-Al}_2\text{O}_3$ (58 weight percent SiO_2) and on the same adsorbent after poisoning with 4.3 mole/ m^2 of H_2O . The linewidth on the unpoisoned surface is slightly narrower than on Al_2O_3 , and a further narrowing occurs on addition of H_2O . On both types of surface, there are substantial upfield shifts of the C-1 resonance. Our results regarding this shift are collected in Table 2. We also observe the remaining lines to behave in a way consistent with protonation. The C-3 line is essentially unshifted, while the unresolved peak due to C-2 and C-4 moves downfield by an amount smaller than the upfield shift of C-1. This shift pattern is the same as that observed on protonation in aqueous solution.

It will be noted in Table 2 that the C-1 shifts are smaller than in aqueous solution (15) and, for the H_2O -treated surface, vary with coverage. An obvious explana-

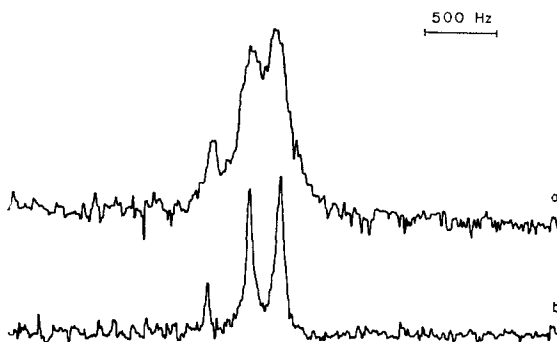


FIG. 4. (a) Aniline on $\text{SiO}_2\text{-Al}_2\text{O}_3$ degassed at 150°C . Fractional coverage 0.9. Spectrum recorded at 80°C , 6×10^4 scans. (b) Aniline on H_2O -poisoned $\text{SiO}_2\text{-Al}_2\text{O}_3$. Fractional coverage 0.9. Spectrum recorded at 60°C , 7×10^3 scans.

TABLE 2
C-1 Shifts for Aniline on SiO₂-Al₂O₃

Cover- age ^a	θ^b	H ₂ O poi- soned	Shift ^c	Frac- tional proton- ation ^d	Esti- mated H ⁺ ^{a,d}
4.84	0.90	No	4.4	0.25	1.2
2.47	0.46	Yes	5.5	0.31	0.7
4.84	0.90	Yes	3.4	0.19	0.8
6.46	1.20	Yes	3.5	0.20	1.2
8.06	1.50	Yes	2.3	0.13	0.95

^a Micromoles per square meter.

^b Monolayers.

^c Ppm upfield of neat liquid. Corrected.

^d See text.

tion of this is that the amounts of aniline exceed the amount of surface proton acid, and that the shift we observe is an average for aniline molecules which exchange readily between protonated and nonprotonated populations. If this explanation is accepted, we can estimate the amount of proton acid present assuming the fraction of aniline protonated to be equal to the observed shift divided by the shift resulting from complete protonation. Knowing the total amount of adsorbed aniline, we can then estimate the total amount of surface proton. These estimates are shown in Table 2, and are seen to increase slowly with coverage, apart from the point at $\theta = 1.2$ which appears to be in error.

Since the number of surface protons should not vary with coverage of amine, it would appear that the above treatment is oversimplified. A clear flaw is the implicit assumption made above that the chemical shift for adsorbed nonprotonated molecules is zero. A more realistic treatment would admit of some (small) nonzero value for this shift. If this is done, and the model otherwise retained as above, we find after simple algebra

$$\delta_{\text{obs}} = \frac{n_+}{n_T} (\delta_+ - \delta_N) + \delta_N,$$

where δ_{obs} is the observed chemical shift, δ_+ the chemical shift of a protonated molecule, δ_N the chemical shift of a nonprotonated molecule, n_+ the number of protonated molecules, and n_T the total number of adsorbed molecules. Thus, a linear relationship between δ_{obs} and $1/n_T$ would be predicted if n_+ is constant due to an excess of amine over available proton sites. Such a plot of the data in Table 2 is, apart from the anomalous point at $\theta = 1.2$, linear within ± 0.2 ppm. Taking $\delta_+ = +17.5$ ppm (15), we find from the slope and intercept $\delta_N = +1.0$ ppm and $n_+ = 0.6 \mu\text{mole}/\text{m}^2$. The first of these is reasonable in view of the shifts reported above for aniline on SiO₂ and Al₂O₃, the second is close to the values which have been obtained (13, 17) by other techniques on SiO₂-Al₂O₃ of similar composition. Taking the value $\delta_N = +1.0$ ppm to apply also to the non-H₂O-poisoned surface, we recalculate the H⁺ concentration in this case to be $1.0 \mu\text{mole}/\text{m}^2$. This is somewhat at variance with the results of Schwarz (13) which indicate an increase in H⁺ on heating with H₂O. The difference may be that our SiO₂-Al₂O₃ was rehydrated at room temperature and 100% relative humidity, which may already develop the maximum proton acidity. The role of further water poisoning may be then to block both Lewis and proton acid sites, leading both to narrower lines and smaller shifts. It will clearly be desirable to check this by further measurements.

It may well be questioned whether the use of aqueous protonation shifts is appropriate when considering molecules adsorbed on a solid. In particular it might be wondered whether electrostatic effects due to the difference of medium would change the chemical shifts sufficiently to render the above type of calculation invalid. While there is no data to answer this type of question regarding the adsorbed state, it is possible to compare chemical shifts of ions in aqueous solution with

those of the same ions in the solid state. Thus, for CO_3^{2-} , the isotropic part of the chemical shift of ^{13}C in solid CaCO_3 is within 1 ppm of the value found for aqueous CO_3^{2-} (19). Further, in the series $\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- , $\text{C}_2\text{O}_4^{2-}$, the solid-state isotropic ^{13}C shifts are within 1.5 ppm of the aqueous values for all species (20, 21). Thus, it would appear that electrostatic medium effects are not likely to be too severe, and the calculations above are likely to contain only small errors from this source. More complete data involving the species studied in the present paper would obviously be desirable.

It is interesting to note that protonated aniline on the H_2O -poisoned surface has rather narrow lines, in spite of being bound electrostatically to the surface. Efficient narrowing requires at least that the C-H vectors be able to assume all orientations in space fairly rapidly; thus, simple rotation of the ring about the C-N bond is not sufficient to produce the present results. A motion which would seem reasonable would be the above rotation, together with a flopping motion of the C-N axis with respect to the surface normal. Such a motion would seem to be consistent with electrostatic attachment of the N to the surface, and is apparently less easy for amines coordinated to Lewis sites. In this connection we have made a few measurements of *N,N*-diethylaniline on H_2O -poisoned $\text{SiO}_2\text{-Al}_2\text{O}_3$. We find in this case that the ring lines are broader than in aniline, by a factor of about 2. This is in marked contrast to the results on Al_2O_3 . Our suggested explanation is that the proton acid sites are not sterically hindered to the extent Lewis sites are, and that the presence of the ethyl groups impedes the flopping motion mentioned above, leading to a less efficient motional averaging of the C-H dipolar interaction.

CONCLUSION

We have shown that ^{13}C NMR can lead to useful and interesting information about the state of amines adsorbed on solid surfaces. Interpretation of the results can further lead to estimates of the type and number of surface acid sites.

ACKNOWLEDGMENT

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