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The ^{13}C Chemical Shifts of Pyridinium Ion in the Adsorbed State

In a previous publication from this laboratory (*1*) we have suggested that surface concentrations of protonic acid may be determined using ^{13}C nmr. Various aromatic and heterocyclic amines undergo large changes of chemical shift on protonation, and apparently only rather small ones upon interaction with surface Lewis acids (*1*). Our proposal involved two assumptions: that observed shifts were average values over both protonated and nonprotonated amine molecules, and that the shift of a protonated molecule was the same as that observed in acidic solution. The first of these assumptions seems reasonable in view of the facts that we have never observed separate lines for protonated and nonprotonated species, and that the motional frequencies must be rather high. In order to observe chemical shifts at all, it is necessary that molecular motions be fast enough to average the C–H dipolar linewidth to at least a few hundred hertz. This requires rotational correlation times of not more than about 10^{-5} sec. Under these conditions a lifetime of $\sim 10^{-3}$ sec or less for exchange between protonated and nonprotonated species seems very reasonable, and would produce the proposed averaging of shifts. The second assumption is rather more questionable, since one might imagine that the difference in dielectric constant of the environment might produce shifts upon ion formation on a surface which were different from those found in solution.

In the present communication we examine both of these hypotheses in a simple and relatively well-defined system. It has been shown by Kiviat and Petrakis (*2*) that pyridinium ion may be formed on surfaces by the interaction of adsorbed pyridine with gaseous HCl. Infrared spectroscopic observation of the pyridinium ion formed by this method does not reveal any qualitative differences from that formed by interaction of pyridine with SiO_2–Al_2O_3 catalysts (*2*, *6*, *7*). We have therefore prepared pyridinium ion on a rather inert surface (silica gel) using this reaction, and have observed its ^{13}C chemical shifts. By using less HCl than pyridine, it is possible to prepare a surface layer containing both pyridine and pyridinium, and to examine the hypothesis of average shifts.

The silica gel used was Davison 923 grade, having a surface area of 560 m^2/g. Samples were degassed for 5–16 hr at 250°C before experiments. This should remove H_2O molecules, but leave a virtually complete layer of SiOH groups (*3*). No effects were observed due to variation of degassing time in the range stated. Reagent grade pyridine was dried over molecular sieves and vacuum degassed before use. Matheson HCl of 99% minimum purity was vacuum distilled.

Samples were prepared by degassing the SiO_2 in a 12 mm nmr tube, and then distilling in a measured quantity of pyridine. For the present experiments, a coverage of $3.7 \pm 0.1 \times 10^{-6}$ moles of pyridine/m^2 of SiO_2 were used. This corresponds to a coverage of 0.7 monolayer, based on an area of 32 $Å^2$/molecule. The equilibrium pressure after adsorption was less than 0.1 Torr at room temperature. A measured amount of HCl was then

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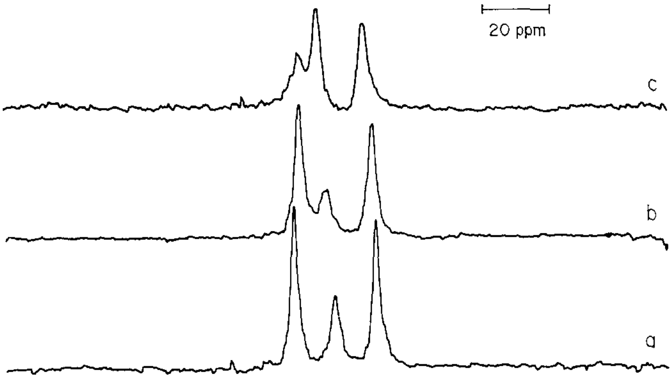

FIG. 1. Spectra obtained with HCl/pyridine ratios of (a) 0; (b) 0.25; and (c) 1.01. Recorded with 4096, 4096 and 2048 scans at temperatures of 110, 120, and 130°C, respectively. In (a) and (b) the lines, reading from left to right, arise from C-2, C-4, and C-3, respectively. In (c) the C-2 and C-4 lines have crossed over.

adsorbed from the gas phase, using conventional gas-volumetric techniques. The equilibrium pressure after this adsorption was less than 1 Torr, except for the two highest HCl coverages (HCl/pyridine = 1.23 and 1.42) where it was 13 and 54 Torr, respectively.

Nuclear magnetic resonance spectra were run at 25.2 MHz on a Varian XL-100 instrument, with TTI fourier transform modification. The external fluorine lock and proton noise decoupling were used for all spectra. In order to observe the small C-4 line in the vicinity of the larger C-2 and C-3 lines, it was necessary to record spectra at temperatures above 100°C. Most were run at 120 or 130°C. Some typical spectra are shown in Fig. 1. The C-2 and C-3 lines were resolved at 50°C and above, and there was no temperature-dependent change in the position of these lines up to the highest temperature used. There was also no evidence for distillation of adsorbate to the cooler parts of the sample tube at any of the temperatures used. A pulse length of 18 μsec (approx $\pi/3$) was used at a repetition rate of 2 Hz.

Our results are shown in Fig. 2. This shows the shift of each line in the adsorbed samples, with respect to neat liquid pyridine, as a function of the HCl/pyridine ratio. A susceptibility correction (*4*) of -0.6 ppm has been applied. The C-2 and C-4 lines change their relative positions as protonation proceeds, and cannot therefore be individually observed in the range of HCl/pyridine ratios from 0.5 to 0.8.

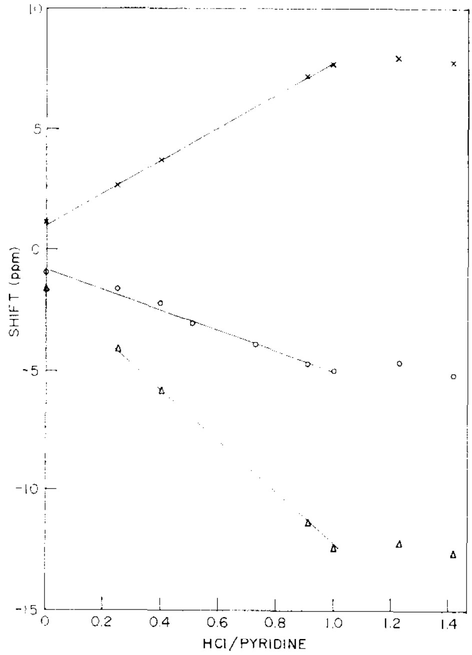

FIG. 2. Chemical shifts with respect to liquid pyridine (corrected) as a function of HCl/pyridine ratio. (×) C-2; (○) C-3, (△) C-4. Positive shifts are to higher field.

As can be seen from Fig. 2 there is a small shift for adsorption of pure pyridine on the SiO_2. Addition of HCl results in progressively larger shifts up to HCl/pyridine = 1.0, after which the shift no longer changes. The lines shown in Fig. 2 are least squares fits of the data in the range 0.0 to 1.0 of HCl/pyridine ratios. All of the points in this range lie within 0.25 ppm of these lines. The average shifts for our three points at HCl/pyridine $\geqslant 1$ are 7.8, −5.1 and −12.3 ppm for C-2, C-3, and C-4, respectively. These are in excellent agreement with the solution values (*5*) of 7.8, −5.0 and −12.4 ppm for the same lines.

Our present observations thus appear to support the assumptions made in Ref. (*1*). The chemical shifts for adsorbed pyridinium are the same, within experimental error as those found in solution, and the shifts for partially protonated layers are given by concentration-weighted averages of the protonated and nonprotonated shifts. It would appear, therefore, that our proposed method (*1*) of determining surface proton acids is valid. This method has the advantages over infrared measurements that formation of the sample into a wafer is not necessary, the spectroscopic cell is a simple cylindrical tube, and the surface proton concentration is determined from the position of a line, rather than from its intensity. Determination of position is always a much simpler spectroscopic procedure.

As pointed out in Ref. (*1*), pyridine is not the optimum molecule for such measurements because of the crossing over of the C-2 and C-4 lines. We are currently investigating whether other amines will be more suitable. A possible problem with this method is the interaction of the amine with surface Lewis acids. Although our previous results (*1*) show that such interaction produces little change in chemical shift on Al_2O_3, this may not be generally true. It may therefore be preferable to use a sterically hindered amine which would interact less well with Lewis acids and also yield narrower nmr lines (*1*). The possibilities of this approach are also being investigated in our laboratory.

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