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An NMR Investigation of the Adsorption of Acetaldehyde and Acetone Vapors on Silica (Cabosil)

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Abstract

The adsorption of acetaldehyde and acetone vapors on silica (Cabosil) has been investigated by ^{1}H NMR spectroscopy. The chemical shifts of both acetaldehyde and acetone adsorbed on Cabosil are shown to be upfield of those in the pure liquids. The reasons for this are discussed.

INTRODUCTION

This paper describes an NMR investigation of the nature of the adsorbed phase with systems involving organic vapors adsorbed on a high surface area solid (silica). The interaction of complex organic molecules with a silica surface by means of functional groups such as –CHO is of particular importance in the field of chromatographic separations. This is because the mechanism of the adsorption process is probably controlled by the functional group.

High resolution proton NMR studies of liquids including acetaldehyde and acetone adsorbed on Cabosil M5 have previously been carried out by Pickett and Rogers (*1*), who found that high resolution spectra could be obtained for a variety of organic molecules adsorbed on a pyrogenic silica. They reported that chemical shifts in the adsorbed state on Cabosil at low surface coverage were the same within ±0.1 ppm as for the pure liquid. Geschke (*2*) found that proton resonance shifts at monolayer coverage of molecules adsorbed on silica gels are in the direction to higher fields compared with the free liquid. Subsequently (*3*), Pickett and Rogers reported that the resonance positions of a variety of organic molecules adsorbed on silica at monolayer coverage were upfield by 40 to 60 Hz from those of the pure liquid. At the same time, in a further paper (*4*), they reported when studying the adsorption of a variety of organic molecules including acetone on silica and desilanized silica that contrary to Geschke's results they found no large upfield shifts; in fact, acetone showed a downfield shift compared to the free liquid.

Gay (*5*) has studied the adsorption of various organic vapors including acetaldehyde and acetone on silica gel using ^{13}C NMR. He found that methyl group chemical shifts were invariably upfield of those in the pure liquid, whereas carbons adjacent to a probable hydrogen bonding site suffered a downfield shift compared to the free liquid.

We report here the results of ^{1}H spectroscopy of acetaldehyde and acetone adsorbed on Cabosil, a high surface area pyrogenic silica.

EXPERIMENTAL

The adsorbent used was Cabosil, a submicroscopic fire-dry fumed silica. The adsorbates were acetone and acetaldehyde, both of B.D.H. lab reagent grade. The adsorbent was outgassed in an NMR tube before use for a minimum of ~11 hr or in a large tube for a longer period of time before being transferred to an NMR tube and then outgassed for at least a further 100 min. The adsorbates were cooled in liquid nitrogen and outgassed for a few minutes before use. A conventional vacuum pumping system was used with a backing pump and a mercury diffusion pump. Pressures were measured on a mercury vacustat. Adsorption was carried out by exposing an NMR tube containing the evacuated Cabosil to degassed vapor-phase adsorbate. The system was left under vacuum to equilibrate at room temperature for about 3 to 5 days. The minimum equilibration time was 1 day and the maximum 35 days. The masses of the NMR tubes, large tubes, adsorbate tubes, and their contents were determined before outgassing and after adsorption equilibration by direct weighing in order to determine the amount of vapor adsorbed. The quantities adsorbed by the various samples are shown in Table 1. The specific surface area (*6*) of the adsorbent was assumed to be 162 m^2/g. Coverages for adsorbed molecules were calculated by deriving an effective radius from the liquid density on the assumption of spherical shape (*7*, *8*). While this is a rather crude estimation, it does lead to a coverage of reasonable magnitude. Calculated values

TABLE 1

Amount of solid/g $\times 10^{-4}$	Amount of adsorbed vapor/g $\times 10^{-4}$	Equilibration time (days)	Estimated no. of layers	Reference	Line width/ppm (FWHM)		Chemical shift (ppm)	
					CHO	CH_3	CHO	CH_3
67	35	1	10	None	0.35	0.4	—	—
1572	398	1	5	None	—	0.4	—	—
1432	415	4	5.5	SUB	—	—	+0.44	+0.46
67	—	4	—	SUB	—	—	+0.28	+0.30
67	—	4	—	EXT	—	0.18	—	+0.90
1281	688	35	10	SUB	—	0.5	+0.8	0.86
1281	688	35	10	EXT	—	0.40	—	+0.65
67	79	35	22	SUB	0.48	0.45	+0.76	+0.75–0.8
67	79	35	22	EXT	—	0.43	—	+0.67
150	134	5	17	TMS	0.35	0.44	—	—
—	192	5	—	SUB	0.22	0.21	+0.77	+0.80
226	47	3	4	INT	0.23	—	+1.25	—
239	—	3	—	None	0.40	0.39	—	—
229	517	3	42	None	0.24	0.24	—	—
275 acetone	—	3	—	SUB		0.3–0.45		+0.21
249 acetone	283	3	20	SUB		0.42		+0.46 −0.83

for the number of adsorbed layers were higher than expected (in general, values up to 5 are more likely).

NMR measurements were performed at 60 Hz on an R10 NMR spectrometer. Liquid samples and solid samples containing an external or internal reference liquid were spun to average out field inhomogeneities perpendicular to the direction of spinning. Spinning had no effect on the spectra of solid samples. Uncertainties of chemical shift arising from field drifts and uncertainty in locating the center of fairly broad peaks were estimated to be ±0.05 ppm. Since proton decoupling was not available on the spectrometer, the pure liquid spectra showed multiple structure due to direct C–H coupling. Line widths were reported as the full width at half the maximum height (FWHM). Various referencing techniques were tried.

Substitution referencing was tried for both acetaldehyde and acetone. The sample and standard were placed in separate NMR tubes of the same size and recorded separately in the order standard, sample, standard, sample, standard so that field drift measurements could be observed and allowed for. External referencing was tried for acetaldehyde. A standard sealed in a capillary tube was placed coaxially in the sample tube and the spectrum was recorded. Tetramethyl silane (TMS) was dissolved in acetaldehyde and a spectrum was recorded. The solution was then degassed after cooling in liquid nitrogen and the vapor allowed to adsorb onto the Cabosil. The spectrum of the adsorbed phase was then recorded (TMS was handled in the refrigeration room due to its extreme volatility). Two methods of internal referencing were tried with acetaldehyde: (1) some of the degassed acetaldehyde was added directly to the sample dropwise after adsorption and the spectrum recorded, and (2) after adsorption of the acetaldehyde the NMR tube was removed from its outer tube, cooled in liquid nitrogen, replaced in the outer tube, and reconnected to the vacuum line. The outer tube was cooled in Dry Ice and both tubes were outgassed for a few minutes until a steady minimum pressure was achieved. The tube of acetaldehyde used for adsorption was then heated by placing it in a Dewar of warm water and left for a few hours for the acetaldehyde to condense inside the NMR tube. The condensed liquid acted as an internal reference when the NMR spectrum was recorded.

RESULTS

In the earlier experiments it was found that the NMR signal from the adsorbed phase was much stronger when the acetaldehyde was adsorbed directly onto the solid in the NMR tube than when it was adsorbed onto the solid in the large tube and a smaller sample transferred to an NMR tube. Therefore later experimental work was restricted to adsorption directly onto the solid contained in NMR tubes.

Various types of referencing techniques described previously were tried when recording the spectra. Pure liquid acetaldehyde gives a quartet at low field due to irradiation of the aldehyde proton and a doublet at high field due to irradiation of the methyl protons. Pure liquid acetone gives a singlet at high field due to irradiation of the methyl protons.

When a spectrum of the adsorbed phase was recorded using a capillary of acetaldehyde as an external reference (Fig. 1), only three peaks were observed. Two of the peaks were the signal from the pure liquid and the third peak was probably the signal from the methyl protons of the adsorbed phase. No signal could be detected for the aldehyde proton of the adsorbed phase, probably because the signal was not strong enough.

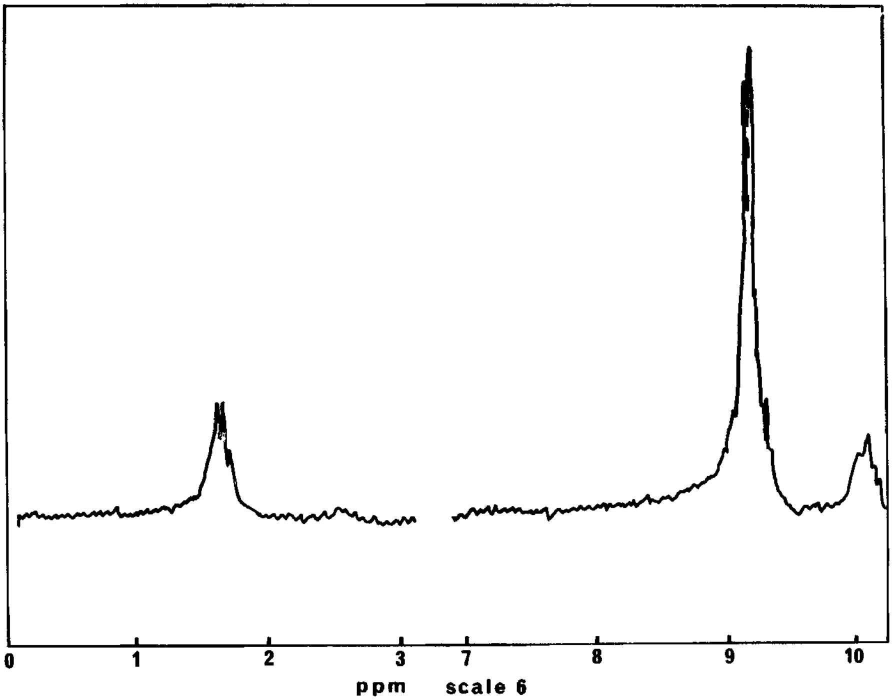

FIG. 1. ^1H NMR spectrum of CH_3CHO adsorbed on Cabosil at 298 °K using an external reference. Scale factor: 6 Hz per unit.

However, the position of the methyl group proton resonance was found to be 0.90 ppm upfield of that for the pure liquid. Corrections for the diamagnetic susceptibility of the medium were not made since they were estimated to be ±0.05 ppm, which is not significant. When a spectrum of liquid acetaldehyde/TMS was run, three separate signals due to the acetaldehyde and TMS protons were observed although the TMS signal was of low intensity. However, in the spectrum of the adsorbed phase the TMS signal was not detectable. TMS is so volatile it may well have evaporated before adsorption took place or else insufficient TMS to give a detectable signal may have been adsorbed.

Internal referencing by adding liquid acetaldehyde dropwise directly to the sample after adsorption was unsuccessful. It was difficult to establish how much liquid to add, and a trial and error process had to be used. In general, too much liquid was added and the adsorbed vapor signal was not detectable. When internal referencing by condensing liquid acetaldehyde inside the tube containing the adsorbed phase was tried, the spectrum (Fig. 2) showed two distinct peaks due to the acetaldehyde liquid. On either side of the peak due to the CH_3 group resonance there were several smaller peaks, the two largest of which were roughly symmetrically similar to each other. It was uncertain whether or not any of these peaks were due to the adsorbed phase or merely spinning sidebands. Upfield of the CHO group liquid resonance was a small fairly broad peak which could have been due to the adsorbed species. The position of the peak varied from 1.1 to 1.4 ppm upfield of the pure liquid in the two spectra recorded.

For acetaldehyde, substitution was the most successful referencing technique of all those tried, e.g., on one day each standard spectrum recorded showed two sharp peaks, a quartet at 0.59 ppm and a doublet at 8.15 ppm, which did not alter their positions with time during the experiment so it was assumed that field drift effects on the chemical shift values could be ignored in comparing the resonance positions of the adsorbed phase and free liquid. The resonance shifts of the protons in the adsorbed molecules were found to be upfield of those in the pure liquid by +0.79 to 0.80 ppm (Fig. 3).

The adsorbed phase of acetone gives a single peak broader than that in the free liquid and of greater intensity than that observed for adsorbed acetaldehyde (Fig. 4). Successive spectra appeared to indicate that field drift effects were shifting the resonance peak in both the free liquid and the adsorbed phase to lower field with increasing time during the experiment. However, the resonance position of the adsorbed phase was still

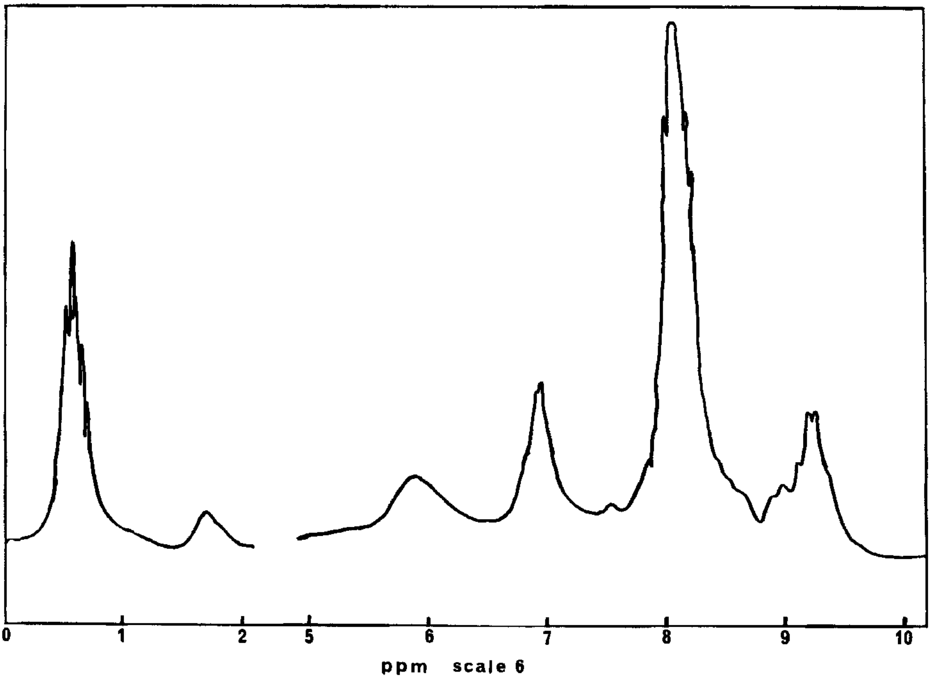

FIG. 2. ^1H NMR spectrum of CH_3CHO adsorbed on Cabosil at 298 °K using an internal reference. Scale factor: 6 Hz per unit.

upfield of that for the pure liquid. The difference in chemical shift between the pure liquid and the adsorbed phase increased from 0.46 to 0.83 ppm for the 1st sample tube and remained approximately constant for the 2nd sample tube. The contents of the 2nd tube looked slightly wet whereas the 1st tube appeared to contain a fine dry white powder. The difference in appearance was probably due to condensation of a small amount of acetone vapor in the 2nd NMR tube at the beginning of the adsorption equilibration.

Although substitution referencing was the most successful referencing technique, a different method would have been preferable as allowances have to be made for field drift effects in substitution referencing and these are not always uniform. It would have been better anyway to have the signals due to the adsorbed phase and free liquid recorded directly on the same spectrum for comparison. Even if external referencing had been successful, a correction would have to be applied due to the different volume

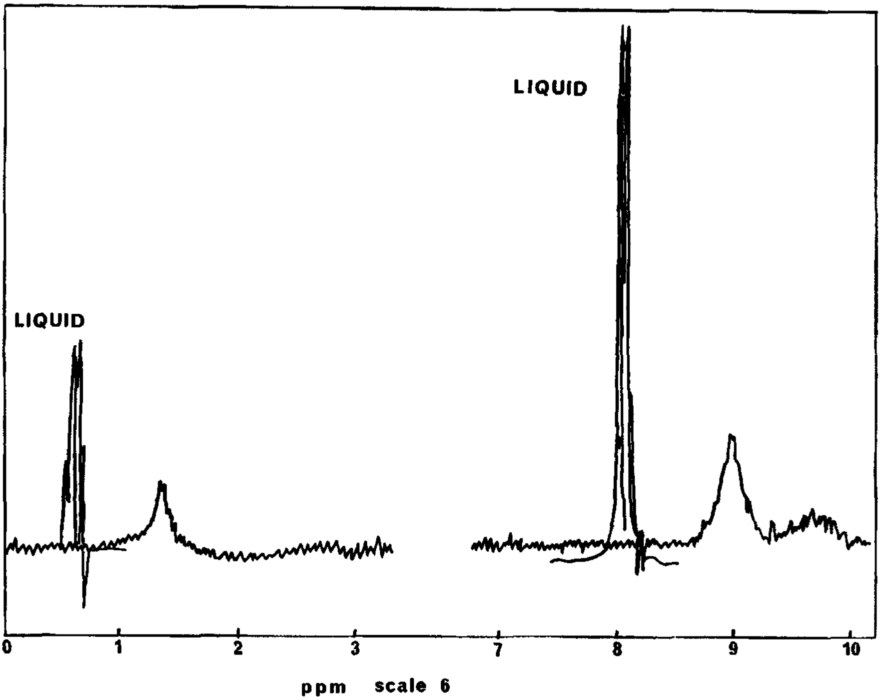

FIG. 3. ^1H NMR spectrum of CH_3CHO adsorbed on Cabosil at 298°K with spectrum of liquid CH_3CHO substitution reference superimposed. Scale factor: 6 Hz per unit.

magnetic susceptibilities of sample and standard. Referencing using TMS was unsuccessful due to the volatility of TMS and the difficulty in handling it. Although internal referencing by adding liquid directly to the sample was unsuccessful, the condensation method showed considerable promise although due to lack of experimental data it is uncertain whether or not the technique would have eventually proved successful.

^1H NMR spectra for acetaldehyde and acetone adsorbed on Cabosil using different referencing techniques and varying adsorption times were recorded and the results collected in Table 1. From the results obtained, no correlation could be found between the weight of acetaldehyde adsorbed and the weight of adsorbent or the equilibration time. There did not appear to be any relation between the number of layers of vapor adsorbed and the equilibration time.

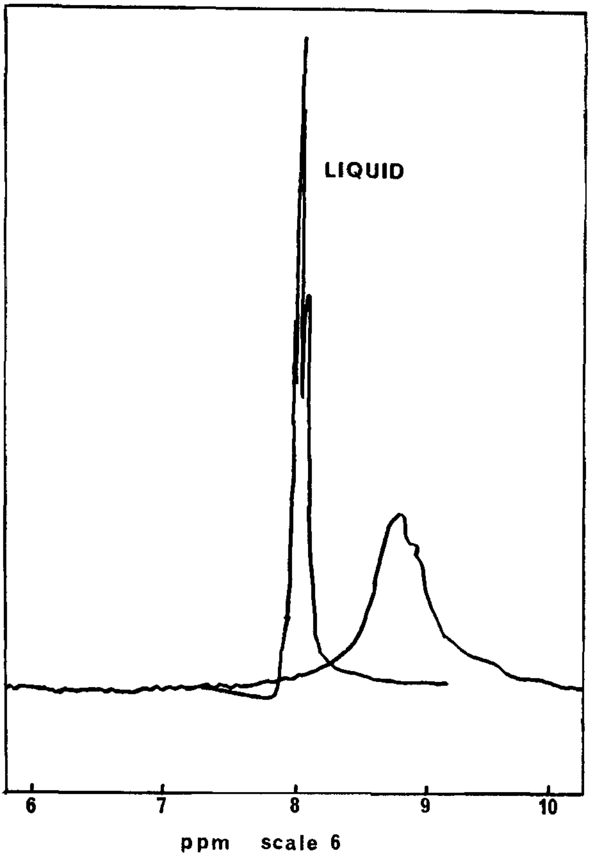

FIG. 4. ^{1}H NMR spectrum of $(CH_3)_2CO$ adsorbed on Cabosil at 298 °K with spectrum of liquid $(CH_3)_2CO$ substitution reference superimposed. Scale factor: 6 Hz per unit.

It was not possible to draw conclusions about the relationship of line broadness or the increase in chemical shift in going from the free liquid to the adsorbed phase to the surface coverage. In general, for the adsorbed state there was an absence in the spectra of molecules of fine structure due to spin-spin coupling. Line widths varied from (0.21 to 0.48) ppm (FWHM) for aldehyde protons and (0.18 to 0.5) ppm (FWHM) for methyl protons of acetaldehyde. For acetone, line widths varied from (0.30 to 0.45) ppm (FWHM). For acetaldehyde, the chemical shift of the adsorbed phase was upfield of the free liquid by +(0.21 to 1.4) ppm for aldehyde protons and +(0.3 to 0.9) ppm for methyl protons. For acetone, the adsorbed signal resonance varied from +(0.21 to 0.83) ppm upfield of that of the pure liquid.

DISCUSSION

NMR studies of molecules adsorbed on solid surfaces have usually necessitated the use of broad line or spin-echo techniques because of short spin-spin relaxation times. The relatively narrow resonance lines observed for molecules adsorbed on pyrogenic silica in these experiments can be attributed to the nonporous surface, small particle size, and high purity of adsorbent. The line widths of solid samples may contain contributions from other factors as well as the nuclear relaxation of the adsorbate. The presence of paramagnetic ions in silica can cause an undesirable shortening of the spin-lattice relaxation time by electron spin-nuclear spin interactions. The resonance lines of the adsorbed molecules do not show any fine structure indicating a change in spin-spin interaction by adsorption. Poor resolution of fine structure could be due to small coupling constants and complex spin-spin interactions.

The results in Table 1 establish that the chemical shift of both the methyl and aldehyde protons in the adsorbed phase are upfield of those in the pure liquid. Geschke (*2*) found that although differences in the concentrations of paramagnetic impurities in the silica gel surface, different diamagnetic volume susceptibilities, and the relaxation process influenced the observed resonance shifts, the effects were small compared to the bonding and adsorption effects on these shifts. Pickett and Rogers (*4*) explained the downfield chemical shift compared to the pure liquid of acetone adsorbed on silica by the formation of hydrogen bonds with the surface silanols through the carbonyl group, resulting in a deshielding of the protons. They reported that the chemical shift for acetone was strongly influenced by hydrogen bonding but not by polarity changes. Gay (*5*), who established two trends of chemical shift behavior in ^{13}C NMR of adsorbed organic molecules, explained the upfield shifts of methyl groups compared to the liquid to be due to an effect of steric crowding. The downfield shift, compared to the liquid, of carbons adjacent to a possible hydrogen bonding site was attributed to withdrawal of electrons through formation of hydrogen bonds to the surface and consequent deshielding of adjacent carbons.

In the adsorbed phase one would expect a downfield shift compared to the free liquid for both acetone and acetaldehyde due to the formation of hydrogen bonds with the OH groups on the surface of the silica causing a deshielding of the protons in the adsorbed molecule, and hence a shift toward lower field as found by Pickett and Rogers (*4*). However, in contrast, a marked upfield shift exists compared to the free liquids.

There could be a small donation of unpaired spin density from the paramagnetic ion impurities in the silica to the bonding ligand atoms of the adsorbed molecule which is transmitted throughout the molecule by the so-called "contact" interaction. This results in an increase in shielding and hence a shift toward higher field. Karagounis (*9*) postulated that polarization alters the electrical charges locally within the adsorbed molecule, resulting in a shift to higher field. The CH_3 group chemical shifts in the adsorbed phase could be upfield of the pure liquid due to steric crowding. It is reasonable to suppose that molecules in an adsorbed layer are crowded or deformed relative to the same molecules in the liquid state. It is known (*10*) that ^{13}C NMR chemical shifts of methyl groups are upfield of what would otherwise be expected, but it is not clear that the same applies for ^{1}H NMR chemical shifts of methyl groups. The shift toward higher field indicates strong screening of the protons of the adsorbed molecule. A possible explanation is that the electron clouds of the adsorbate and surface atoms interact, increasing the electron density around the nuclei and hence producing a shielding effect of the protons which results in a shift to higher field.

If the anisotropic effect in the carbonyl group is reduced by hydrogen bonding to the surface, the protons lying in a cone extending above and below the aldehyde group will be less deshielded than in the free liquid, resulting in a shift to higher field. The anisotropic deshielding is greatest for an aldehyde proton directly bonded to a trigonally hybridized carbon atom. So if the anisotropic effect is reduced, the aldehyde proton might be expected to show the greatest upfield shift compared to the pure liquid since it was the most deshielded before hydrogen bonding. A combination of any of these factors could explain the observed resonance shift of the adsorbed molecules.

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