

QUALITATIVE ANALYSIS OF CHEMISORBED MOLECULAR SPECIES VIA ^{13}C NMR

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Chemical reactions in which the surface of a solid phase is modified are important *inter alia* in (a) the bonding of polymer to filler in composite materials [1], (b) the modification of chromatographic supports [2], (c) the binding of enzymes to solid substrates [3], (d) the poisoning of catalysts [4], and (e) the very chemistry of heterogeneously catalyzed industrial reactions [5]. Although NMR spectroscopy is in principle a tool for the analysis of such systems [6,7], is only with the advent of ^{13}C spectroscopy, for which chemical shifts are much larger than for protons and internuclear dipolar broadenings much less, that any practical advance has been made [8–11]. Nevertheless, for the chemisorbed species, which are relatively immobile, the proton–carbon dipolar interaction is still large; this however can be removed in double resonance experiments under strong proton radiation, and such irradiation also offers the possibility of enhancing the relatively weak ^{13}C signal [11].

In order to make some prototype studies of chemisorption systems we have chosen systems in which the lifetime of the chemisorption complex is essentially infinite; the result of a chemical reaction. Specifically we report herein the spectra of certain organic derivatives of chrysotile asbestos namely the trimethyl–silyl [12], the vinyl [13], and the (proposed) allyl derivatives [13]. These materials are useful in polymer composites. As a result of the preparation procedure all three derivatives contain methyl groups. Because of the reaction stoichiometry the specimens contain almost 15% by weight carbon, which is certainly of benefit from the point of view of sensitivity.

The purpose of this research is thus the application of proton enhanced ^{13}C NMR spectroscopy [11] as an analytical tool in surface chemistry. For the modified chrysotile asbestos specimens we are able in two cases to confirm and in another to deny the validity of reported [12,13] synthetic procedures.

Specimens were ground and formed into cylindrical pellets 7 mm in diameter, of weight 0.3 g, and containing about 2×10^{19} ^{13}C nuclei. The spectrometer is described elsewhere [14]. The one contact proton enhancement technique was used [11]; this technique enhances the ^{13}C signal by a factor of four by the transfer of proton magnetization to the ^{13}C nuclei; contact between the two systems was established according to the Hartman–Hahn criterion. The spectra recorded in fig. 1 are fast fourier transforms of the enhanced free induction decays which were recorded under proton decoupled conditions at 26.7 MHz.

The spectra are recorded in fig. 1. The shift of liquid tetramethylsilane with respect to liquid methanol is 49 ppm [15]; at this point there is in each of the observed spectra a sharp line indicative of methyl groups bound to silicon atoms. These are expected from the synthesis of the chrysotile derivatives. Referred to methanol the shift of liquid benzene is

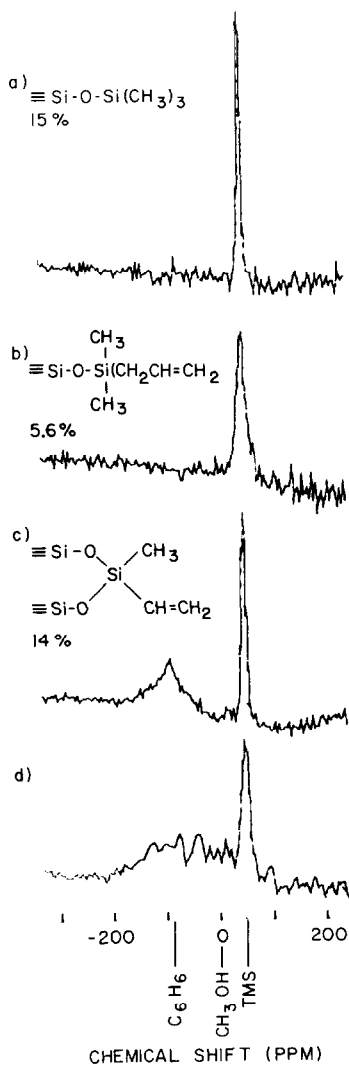


Fig. 1. Proton enhanced ^{13}C spectra of organic derivative of chrysotile asbestos: (a) trimethylsilyl derivative; room temperature signal; accumulation time is 1 hr (4096 scans); repetition rate, 1 s^{-1} ; mixing time 1 msec; (b) allyl derivative; accumulation time 8 hr; repetition rate 0.167 s^{-1} ; other conditions same as in (a); (c) vinyl derivative; accumulation time 8 hr; repetition rate 1 s^{-1} ; other conditions same as in (a); (d) vinyl derivative; 100°K ; accumulation time 30 min; other conditions same as in (a). The spectra are referred to methanol; the positions of benzene and tetramethylsilane are indicated. The proposed structures of the modifying functional groups are indicated as is the percent by weight carbon.

—80 ppm; in this aromatic region should appear the spectra for the doubly bonded carbon atoms of the allyl and vinyl derivatives. It is clear that the vinyl group is indicated as present, but the allyl group is not. Nor are there any indications of oxidation products of the allyl group. These analytical results are the principle conclusions of this paper. In conjunc-

tion with this work, a chemical search for the allyl group was also undertaken; no oxidation with permanganate occurred [16]. It was further found that in the synthesis of this derivative, propylene was given off [16]. In assessing the value of the NMR result note that infra-red evidence for the existence of olefins in these materials was not conclusive [13].

In this type of NMR spectroscopy the chemical shift anisotropy is the major source of line width. The carbon-proton nuclear magnetic dipolar interaction is averaged away by the proton decoupling field [19]; for non-decoupled spectra the dipolar linewidth in fig. 1 would correspond to about 10^4 ppm, which would of course render resolution of chemical shifts impossible. The shape of this decoupled line has essentially three limiting cases [9]: the full anisotropy powder pattern; the axially symmetric powder pattern (due either to rotation of the molecule or submolecular group about a single axis or to accidental equivalence of two of the principle values of the chemical shift tensor); and the isotropic line (due either to some isotropic molecular motion or to an isotropic shift tensor). In this context, then, the observed methyl group lines are somewhat narrower (~ 20 ppm) than those for methyl groups in solids [11] (~ 60 ppm). For the trimethylsilyl group this motional narrowing is consistent with its freedom of movement; there are three (non-orthogonal) rotation axes aligned along the bonds (a) lattice silicon-oxygen, (b) oxygen-silicon, and (c) silicon-carbon. This in contrast to a normal solid in which the methyl group would have only one rotation axis. On the other hand the vinyl-methyl derivative should have only a single axis for methyl rotation, so the narrow methyl line here is not understood; it may be indicative of long siloxane polymer linkages to the surface, rather than a monomer doubly bonded to the surface. Such linkages have been proposed [13]. Likewise the olefinic part of the vinyl spectrum at room temperature does not have the expected powder pattern shape [11]. There are two different ^{13}C giving rise to this spectrum, one bound to silicon, the other terminating the vinyl group. This, combined with the possible motion of the long siloxane polymer may give rise to the partially averaged spectrum of fig. 1c. The broadening of the olefinic spectrum at low temperatures confirms the motional narrowing at room temperature. The reader will have noted that motional narrowing enhances spectral resolution, and that resolution is indeed limited by chemical shift anisotropy. It is possible to motionally narrow away the chemical shift anisotropy by an artificial molecular motion, namely by spinning at the magic angle [19]; this offers the possibility both for better spectral resolution and better signal-to-noise ratio.

The ultimate usefulness of ^{13}C NMR spectroscopy as an analytical tool in surface chemistry depends on the range of surface areas, surface coverages, and functional groups which may be investigated. Certainly, with the solid state powder spectra expected from rigid chemisorbed species, the spectra of the various functional groups will overlap, so that a specimen rich in variety of adsorbed species will be difficult to unscramble unless there is sufficient motional narrowing to yield sharp peaks. The broadness of the spectra also decreases sensitivity. The specimens used here have relatively large specific areas (ca. $200\text{ m}^2/\text{g}$) and practically monolayer coverages; they represent the maximum signals available from chemisorbed specimens. And the spectrometer used is not far from the ultimate in sensitivity. Therefore the signal accumulation time of 8 hr cited for the proposed allyl specimen (fig. 1b) appears rather formidable. Signal-to-noise may be increased (accumulation time reduced) somewhat by (a) working at higher frequencies, (b) working at lower temperatures, (c) using the multiple contact technique, and/or (d) accumulating data at

the optimum rate (one spectrum per T_1 period). For instance, the proton relaxation time for the trimethylsilyl derivative is 30 msec, so that the spectrum of fig. 1a might have been gathered, in principle, in three minutes instead of an hour.

Because of the relation of relaxation to the rate of molecular motion and because of the dependence of rates of motion on temperature, there exists an optimum temperature at which data accumulation may be done most rapidly. But because of differences in relaxation times from specimen to specimen depending on the respective structure and molecular motion the accumulation time and hence the analytical sensitivity will vary greatly from specimen to specimen, especially at a given temperature. For instance, the spectrum of a silica gel modified with γ -amino propyl groups [20] (3% C), could not be obtained at room temperature; T_1 was only 3 msec; because $T_{1\rho}$ (the spin lattice relaxation time in the rotating frame), which is essentially the lifetime of the signal must be $\leq T_1$, 3 msec was not sufficient time for the experiment. For the routine analysis of a given material the optimum conditions might be determined once and for all. The most promising avenue for further increase in sensitivity is the development of an extremely low temperature spectrometer so that the proportionality of signal strength to inverse temperature may be gainfully employed; liquid helium temperature gains almost a factor of 100. Further gains may be obtained by pre-polarization in higher magnetic fields [11], multiple contact enhancement [11] and perhaps sample rotation to sharpen the lines and enhance resolution.

In conclusion, proton enhanced ^{13}C NMR spectroscopy is expected to be useful in the qualitative analysis for organic functional groups in selected surface systems. Prospects for improving the technique are good.

J.J. CHANG and A. PINES

Department of Chemistry, University of California, Berkeley, California, U.S.A.

J.J. FRIPIAT*

*Institut des Sciences de la Terre, Université Catholique de Louvain,
Heverlee 3030, Belgium*

and
H.A. RESING**

*Chemistry Division, Naval Research Laboratory,
Washington, D.C. 20375, U.S.A.*

* Present address: CNRS-CRSOCI, 45045 Orleans-la-Source, France.

** From whom reprints should be requested.

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