High-resolution Nuclear Magnetic Resonance Evidence of Conformational Preference at a Solid Interface

By F. F. L. HO* and G. A. WARD

(*Research Center, Hercules Incorporated, Wilmington, Delaware*, 19899)

Summary From a study of the effect of temperature and surface coverage on the proton–proton spin coupling constant, the conformational preference of 1,1,2-trichloroethane adsorbed on pyrogenic silica has been determined.

N.M.R. has been established to be a powerful tool in studies of molecular conformation,[1] especially because of the known angular dependence of vicinal spin–spin coupling.[2] The utility of n.m.r. in studies of molecules adsorbed at solid interfaces has been widely recognized,[3,4] but it has usually been limited to the measurement of relaxation times by the spin–echo technique. Although adsorbed molecules generally give broad n.m.r. signals because of restricted molecular motion and/or interactions with surface constituents, high-resolution spectra of low surface coverages of organic liquids on pyrogenic silica have been observed recently.[5,6] We report here the first application of this technique to the determination of the conformation of molecules absorbed at a solid interface.

The n.m.r. spectrum of 1,1,2-trichloroethane absorbed on Cab-O-Sil EH-5 (Cabot Corp., Boston, Mass.) at a coverage of three monolayers is shown in Figure 1, together with the representation of the major rotamers. From expanded scale spectra of the proton groups shown in Figure 1, the vicinal proton–proton coupling constant J was measured as a function of temperature at several levels of surface coverage, and on silicas of different surface hydroxyl content. Some pertinent data are summarized in the graph in Figure 2. The J values were obtained on a Varian A-60A spectrometer using a sweep width of 1 Hz/cm and a sweep rate of 0·20 Hz/s, and are averaged over four separate scans. The uncertainty in J is estimated at ±0·2 Hz. The uncertainty in temperature is less than ±2°. Two important conclusions can be drawn from these data. First, the initial layer of absorbed trichloroethane molecules prefers the *gauche* conformation, which recently was reported to have an energy content higher than that of the *trans* rotamer. The energy difference was estimated to be 1·93 kcal/mole from a calculation based on a classical model of nonbonded interaction,[7] and to be 1·2 kcal/mole based on n.m.r. data observed in n-octane solution.[8] Second, the conformational preference lessens as the monolayer coverage increases. These conclusions are in good agreement with the results of a study of the conformation of 1,2-dichloroethane on silica, based on i.r. spectroscopy.[9]

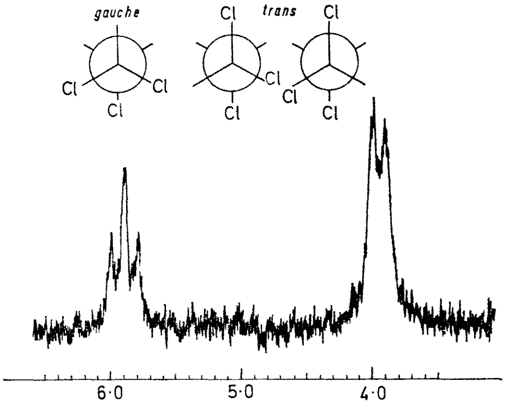

FIGURE 1. *High-resolution n.m.r. spectrum of* 1,1,2-*trichloroethane adsorbed on Cab-O-Sil EH-5 at three monolayers coverage at* 50°.

The data obtained show that the observed J at the interface is consistently smaller than that obtained in n-octane solution, with the value at single monolayer coverage the smallest. Several authors have shown that the *gauche* rotamer has a higher dipole moment and is more stabilized in polar solvents, resulting in a smaller J for solvents with a higher dielectric constant.[8,10] Nevertheless, a J of 4·5 Hz measured in this study at a single monolayer coverage on the "as received" silica at 40° is smaller than observed in any solvents reported.[8,10] It is also significant that the J is smaller for molecules adsorbed on the "as received" silicas than on the annealed and rehydrated adsorbent. The i.r. spectra of the silicas showed much stronger broad bands at 3650 and *ca.* 3400 cm^{-1} for the "as received" sample, indicating the presence of a significantly higher concentration of surface hydroxyls. This suggests that the conformational preference is caused by the interaction of the polar halogen substituents with the surface hydroxyls. The J at the interface increases with temperature, in contrast to that observed in n-octane solution, which also suggests a preference for the *gauche* form at the interface.

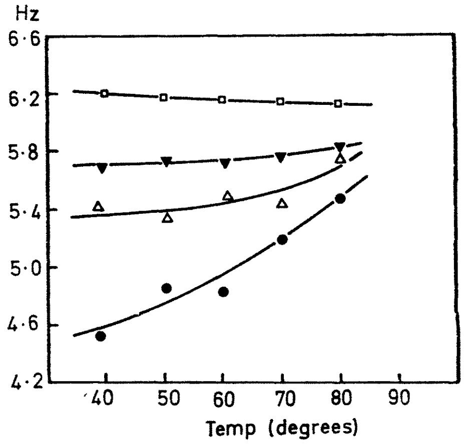

FIGURE 2. *Temperature dependence of* J: ● *a single monolayer coverage* ($\theta = 1$) *on the "as received" silica* △ $\theta = 1$ *and* ▼ $\theta = 3$ *on the annealed and rehydrated silica*; □ *data in n-octane taken from Fig.* 5 *of ref.* 8.

Some mechanisms other than that suggested above, which might lead to the observed variation of J have also been considered. The effect of temperature on the intrinsic values of J_t and J_g has been studied by other workers.[8,11] The observed values of the temperature coefficients of J_t and J_g were less than ±0·15 Hz per 100°, which would not be sufficient to account for the changes in J observed in our work. The dependence of J_t and J_g on the change in electronegativity of the Cl substituents due to the effect of the surface must also be small since, for example, J_g only changes from 2·3 Hz in 1,1,2-trichloroethane to 2·4 Hz in 1,1,2-tribromoethane.[8] This is certainly a much larger change in substituent electronegativity than would be experienced on changing the solvent sphere of the substituent. Finally, the variation of J with the dielectric constant (ϵ) of the medium must also be considered. Abraham and Cooper[10] have calculated that even if ϵ approached infinity, J for 1,1,2-trichloroethane would be only 5·72 Hz, corresponding to 25% of the *gauche* conformer. Our observed value for the "as received" silica is much less than this, indicating a greater preference for the *gauche* conformer than possible even in the most polar medium. To confirm this experimentally we have measured J in n-propanol ($\epsilon = 22{\cdot}2$) and methanol ($\epsilon = 31{\cdot}8$) and observed values of 5·68 and 5·60 Hz, respectively. Moreover, J has a temperature dependence in n-propanol different from that on the silica surface, varying from 5·68 at 43° to 5·62 Hz at 92°. We feel that these electric field effects in solution are similar to those which would be experienced by the molecule adsorbed on the silica surface, even though the field at the surface is large and directional, because the adsorbed molecule is not tightly held in a fixed orientation on the surface. The latter fact is shown by the fact that the observed n.m.r. spectra indicate that the adsorbed 1,1,2-trichloroethane is rotating rapidly and exchanging between the surface layer and adjacent layers. The correlation time for molecules adsorbed on silica has been previously measured by others[3,12] and is estimated to be on the order of 10^{-10} to 10^{-7} s.

Because a knowledge of the conformation of adsorbed molecules is important in understanding the interactions involved in surface reactions, these results suggest that high resolution n.m.r. is a powerful new tool for the study of heterogeneous systems.

(*Received, October 12th,* 1970; *Com.* 1755.)

---

[1] A. A. Bothner-By, *Adv. Mag. Resonance*, 1965, **1**, 195.
[2] M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2870.
[3] K. J. Parker, *Progr. NMR Spectroscopy*, 1967, **3**, 87.
[4] H. A. Resing, *Adv. Mol. Relaxation Processes*, 1967, **1**, 109.
[5] G. Karagounis, *Nature*, 1964, **201**, 604.
[6] J. H. Pickett and L. B. Rogers, *Separation Sci.*, 1970, **5**, 11; J. H. Pickett, C. H. Lochmuller, and L. B. Rogers, *ibid.*, p. 23.
[7] R. J. Abraham and K. Parry, *Chem. Comm.*, 1969, 963; *J. Chem. Soc.* (*B*), 1970, 539.
[8] F. Heatley and G. Allen, *Mol. Phys.*, 1969, **16**, 77.
[9] A. V. Kiselev, V. I. Lygin, and M. F. Moskovskaya, *Russian J. Phys. Chem.*, 1966, **40**, 1247.
[10] R. J. Abraham and M. A. Cooper, *J. Chem. Soc.* (*B*), 1967, 202.
[11] J. C. Schug, P. E. McMahon, and H. S. Gutowsky, *J. Chem. Phys.*, 1960, **33**, 843.
[12] D. Michel, *Z. Naturforsch.*, 1968, **23a**, 339.