Nuclear Magnetic Double Resonance Study of Chemical Exchange: Effect of Spin–Spin Coupling

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IN a two-spin (AX) system, with nucleus A in chemical exchange with another nucleus (C) not coupled to the AX system, strong irradiation at the resonance frequency of C may cause A to be saturated indirectly. As a result, the n.m.r. signal of A is partly or completely removed from the spectrum, depending upon the lifetime τ and spin–lattice relaxation in time T_1 of the nuclei at the exchanging sites.[1] Although the spin states of A are saturated, one would expect the splitting pattern of X by A to be preserved. The same argument holds for AX_2 or more complex spin systems. If the chemical shift, δ_{AX}, is comparable to the coupling constant, J_{AX}, the situation is more complicated; this will be discussed elsewhere.

Figure 1A shows the n.m.r. spectrum of diphenylmethanol and t-butyl alcohol in CS_2.[2] The phenyl protons (not shown) gave a singlet at $-6{\cdot}80$ p.p.m. from the methyl protons of t-butyl alcohol. When the OH signal of diphenylmethanol was irradiated, the CH doublet was decoupled, and the OH signal of t-butyl alcohol almost completely disappeared (Figure 1B). When the OH signal of t-butyl alcohol was irradiated, the OH signal of diphenylmethanol was saturated indirectly, while the CH doublet was preserved (Figure 1C). Change of radio frequency amplitude of the irradiating field, H_2, from 100 to 300 mv had no influence on the

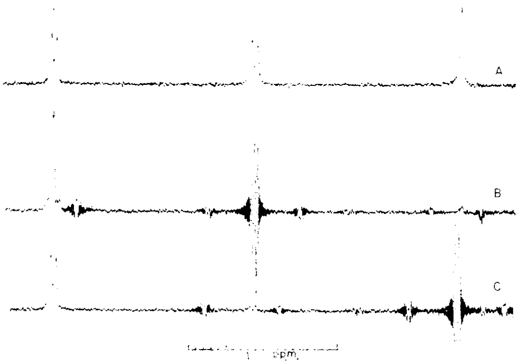

FIGURE 1. *N.m.r. spectra of diphenylmethanol* (0·60 *molal) and t-butyl alcohol* (0·58 *molal) in* CS_2 *at* 25° *and* 100 *Mc./sec.* (A) *The* CH *and* OH *protons of diphenylmethanol and the* OH *proton of t-butyl alcohol.* (B) *The effect of irradiating the* OH *proton of diphenylmethanol.* (C) *The effect of irradiating the* OH *proton of t-butyl alcohol.*

splitting pattern. A similar result was observed for benzyl alcohol and t-butyl alcohol in CS_2 (Figure 2).*

For compounds with protons which may undergo rapid exchange, such as polyhydroxy-compounds, two common methods have been used to record simplified n.m.r. spectra. First, a catalyst may make exchange so rapid that all exchangeable protons experience the same average environment during the n.m.r. transition and a single sharp peak is observed. Second, all exchangeable protons may be replaced by deuterium. Both of these methods eliminate the possibility of observing coupling between exchangeable protons and neighbouring protons, such as AX coupling of secondary alcohols (Figure 1) and AX_2 coupling of primary alcohols (Figure 2).

The saturation technique, illustrated here, allows simplification of n.m.r. spectra by taking advantage of relatively long relaxation times of exchanging protons under conditions where exchange is occurring slowly on the time scale of the n.m.r. transitions. As in the case where exchangeable protons are replaced by deuterium, exchangeable proton signals are eliminated. However, their coupling (a source of structural information)[2] is preserved, and both the original and simplified spectra may be recorded directly from the original sample, as in Figures 1 and 2.

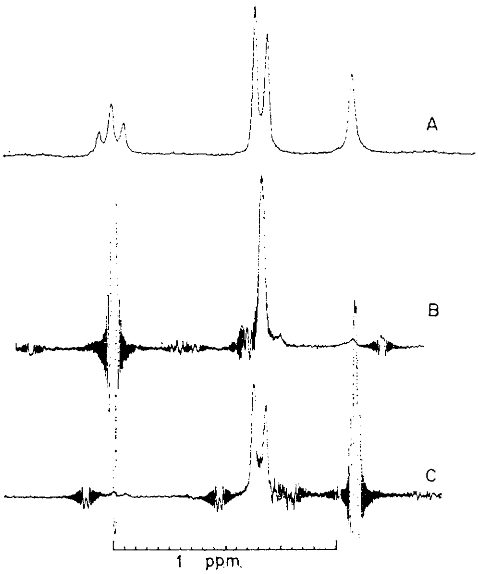

FIGURE 2. *N.m.r. spectra of benzyl alcohol* (0·85 *molal*) *and t-butyl alcohol* (0·74 *molal*) *in* CS_2 *at* 20° *and* 100 *Mc./sec.* (A) *The* CH_2 *and* OH *protons of benzyl alcohol and the* OH *proton of t-butyl alcohol.* (B) *The effect of irradiating the* OH *proton of benzyl alcohol.* (C) *The effect of irradiating the* OH *proton of t-butyl alcohol.*

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* N.m.r. spectra were recorded with a Varian HA-100 spectrometer in the frequency-sweep mode, locked on the methyl proton signal of t-butyl alcohol.

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[2] J. J. Uebel and H. W. Goodwin, *J. Org. Chem.*, 1966, **31**, 2040.