Fluorine Nuclear Magnetic Resonance Determination of the Association Constant of an Organic Electron-donor–Acceptor Complex

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RECENTLY a nuclear magnetic resonance method for determining the association constant (K) of electron-donor–electron-acceptor interactions has been described.[1] The chemical shift (Δ) of a nucleus in the electron acceptor A is measured in a series of solutions containing different concentrations of the electron donor D, in all of which solutions $[D] \gg [A]$. It may be shown that:

$$\Delta/[D] + \Delta K = \Delta_0 K \qquad (1)$$

whence a plot of $\Delta/[D]$ against Δ should be a straight line with gradient $-K$, where $K = [AD]/[A][D]$ and Δ_0 is the chemical shift for the particular acceptor nucleus in the pure complex.

The method has been used to obtain K for several complexes from proton chemical shifts.[1]

The association constant for the complex between 1,3-difluoro-2,4,6-trinitrobenzene and hexamethylbenzene in chloroform has now been evaluated from measurements of the chemical shift of both the *proton* absorption and the *fluorine* absorption of the acceptor in such a series of solutions. From the proton chemical shift measured at 40 Mc./sec., $K = 0{\cdot}47 \pm 0{\cdot}02$ kg./mole (kg. solution per mole), and $\Delta_0 = 93{\cdot}2$ c./sec. From the fluorine chemical shift (measured at 37·6 Mc./sec.) $K = 0{\cdot}45 \pm 0{\cdot}02$ kg./mole, and $\Delta_0 = 140{\cdot}7$ c./sec. Thus the two determinations give the same value of K within experimental error. The fluorine absorption appears as a doublet ($J_{F-H} = 8{\cdot}2$ c./sec.) and the proton absorption as a triplet with the same coupling as in 1,3-difluoro-2,4,6-trinitrobenzene when dissolved alone in chloroform.

The large value of Δ_0 for the fluorine resonance and the absence of overlapping absorptions from the donor or solvent molecules which frequently occur when a proton absorption is being observed makes the fluorine measurements attractive. Although fluorine is a highly electronegative element, the presence of fluorine atoms in some potential electron-acceptor molecules does not appear significantly to enhance their electron-accepting capabilities, presumably because of the $+M$ effect. In this respect the chemical shift of fluorine in hexafluorobenzene as a solution in carbon tetrachloride shows no significant change when the electron-donor hexamethylbenzene is added. Optical measurements of hexafluorobenzene–hexamethylbenzene mixtures in solvents of low dielectric constant down to 220 mμ indicate no absorption in excess of the sum of the two components measured separately. If an electron-donor–acceptor complex had been formed, an intermolecular charge-transfer absorption band might have been expected in this region.

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[1] R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, **1965**, **61**, **1626**.