

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:

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

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., $K = 0.47 \pm 0.02$ kg./mole (kg. solution per mole), and $\Delta_0 = 93.2$ c./sec. From the fluorine chemical shift (measured at 37.6 Mc./sec.) $K = 0.45 \pm 0.02$ kg./mole, and $\Delta_0 = 140.7$ c./sec. Thus the two determinations

give the same value of K within experimental error. The fluorine absorption appears as a doublet ($J_{F-H} = 8.2$ 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 m μ 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.