Multiple Association Constants of Electron-Donor–Acceptor Complexes

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Summary Evidence of 2 : 1 and 1 : 1 complexing has been obtained for mixtures of hexamethylbenzene and fluoranil in carbon tetrachloride solution, and association constants have been evaluated.

VARIOUS anomalies have been reported in the values obtained for the association constants (K) of interactions between organic electron-donors (D) and electron-acceptors (A), particularly where π-donors and π-acceptors are involved. These include the apparent dependence of K on: (*a*) the wavelength of measurement in the case of optical determinations;[1,2] (*b*) the nucleus measured in n.m.r. determinations;[3] (*c*) the relative concentration of donor and acceptor;[4] and (*d*) the physical property measured *e.g.* electronic absorption *versus* n.m.r. absorption.[4]

We have now measured the intensity of the intermolecular charge-transfer absorption band of the fluoranil (2,3,5,6-tetrafluoro-*p*-benzoquinone)–hexamethylbenzene complex under the condition $[D] \gg [A]$ for a wide range of donor concentrations. We have also measured the ^{19}F chemical shift of the fluoranil under similar conditions. The results have been analysed by a computer programme[5] based on the assumption that in these solutions there are two equilibria:

$$A + D \rightleftharpoons AD \qquad K_1 = [AD]/[A][D]$$
$$AD + D \rightleftharpoons AD_2 \qquad K_2 = [AD_2]/[AD][D]$$

The results are given in the Table. It is seen that there is good agreement between the two methods used for both K_1 and K_2. These results can be compared with those of earlier determinations involving relatively small concentration ranges. These experiments yielded data which were simply interpreted as involving only 1 : 1 associations, although the calculated association constants from n.m.r. measurements conflicted with those from optical measurements (Table).

The system has also been studied under the condition [D] = [A], which, under the experimental conditions used, if K_2 from the first experiment is correct, should yield negligible concentrations of AD_2. The results of association constant determinations under this condition (which should therefore yield independent values of K_1) for both optical and n.m.r. measurements are given in the Table. They are in good agreement with the K_1 values for the wide concentration-range determinations and provide confirmation of these values.

Measured properties of the hexamethylbenzene–fluoranil association in carbon tetrachloride at 33·5°

Method	rel. conc.	[D] range/M	K/l mol^{-1}	ϵ/l mol^{-1} cm^{-1}	Δ_0/Hz[a]
N.m.r.	$[D] \gg [A]$	0·034—0·74	$K_1 = 20 \pm 2$	—	174
			$K_2 = 3 \pm 1$	—	256
Optical	$[D] \gg [A]$	5×10^{-3}—0·7	$K_1 = 20 \pm 2$	2740	—
			$K_2 = 3 \pm 1$	4400	—
N.m.r.	$[D] = [A]$	0·011—0·022	$K_1 = 19{\cdot}2 \pm 2$[b]	—	195[b]
Optical	$[D] = [A]$	$2{\cdot}1 \times 10^{3}$—$5{\cdot}3 \times 10^{-3}$	$K_1 = 20{\cdot}8 \pm 2$	2700	—
Earlier values					
N.m.r.	$[D] \gg [A]$	0·5—0·7	$9{\cdot}8 \pm 0{\cdot}5$[c]	—	261[c]
Optical	$[D] \gg [A]$	6×10^{-3}—2×10^{-2}	$17{\cdot}1 \pm 2$[d]	3200[d]	—

[a] For ^{19}F measured at 56·462 MHz. [b] From R. Foster and D. R. Twiselton, *Rec. Trav. chim.*, in the press. [c] From N. M. D. Brown R. Foster, and C. A. Fyfe, *J. Chem. Soc.* (*B*) 1967, 406. [d] I. B. C. Matheson, Thesis, University of St. Andrews, 1967.

Also listed in the Table are the molar absorptivities (ϵ) and chemical shifts of the measured nucleus in the pure complex in solution relative to the chemical shift of the same nucleus in the pure acceptor in solution (Δ_0). It is seen that for both parameters the value for the 2 : 1 complex is considerably greater than that for the 1 : 1 complex. This largely accounts for the significant effect on the "apparent" experimentally-determined value of K when only a small concentration range is used.

The fluoranil–hexamethylbenzene complex is a typical π–π complex and it is to be expected that other similar complexes will behave in a like manner, and that many of the earlier published values, not only of association constants, but also the molar absorptivities are incorrect.

(*Received, September 25th*, 1970; *Com.* 1641.)

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[4] P. H. Emslie, R. Foster, C. A. Fyfe, and I. Horman, *Tetrahedron*, 1965, **21**, 2843.
[5] Devised by J. Gorton, University of Strathclyde.