Association Constants of Organic Charge-transfer Complexes obtained from Nuclear Magnetic Resonance Measurements of Nonequivalent Nuclei

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Summary N.m.r. measurements on nonequivalent nuclei can give rise to widely differing values of association constant.

CHEMICAL-SHIFT data have been used by several groups of workers[1] to evaluate association constants (K) for charge-transfer complexes in solution. In various systems, measurements of nonequivalent nuclei in one component (usually the electron acceptor) have yielded values of (K) which are equal within experimental error.[2]

We now have results for a number of systems in which the value of K obtained is dependent on the particular nucleus measured. A selection of these results is given in the Table.

Earlier, Klinck and Stothers[3] reported that experimental values for the enthalpy of formation of the complex between 4-nitrobenzaldehyde and perdeuteriotoluene were somewhat dependent, on the nucleus measured. However, their results were based on the variation of the measured averaged chemical shifts with temperature and their results could

TABLE

Association constants (K) *for complexes between electron donors and electron acceptors calculated from chemical shift data of two or more magnetically nonequivalent nuclei in the acceptor at* 33·5°. *Solvent*: CCl_4

Donor	Acceptor	Nucleus[a] measured	K[b] (kg. mole^{-1})
HMB[c]	4-nitrobenzaldehyde	C*H*O	0·97 ± 0·05
		H (2,6)	0·72 ± 0·04
		H 3,5)	0·58 ± 0·04
HMB	4-chlorobenzaldehyde	C*H*O	0·55 ± 0·04
		H (2,6)	0·38 ± 0·04
		H (3,5)	0·32 ± 0·04
HMB	terephthalaldehyde	C*H*O	0·89 ± 0·05
		H (2,3,5,6)	0·61 ± 0·04
C_6H_6	2,4,6-trinitrotoluene	CH_3	0·21 ± 0·02
		H (3,5)	0·42 ± 0·02
HMB	2,4,6-trinitroanisole	OCH_3	0·79 ± 0·05
		H (3,5)	1·45 ± 0·05
HMB	3,5-dinitrobenzotrifluoride	*F*	1·47 ± 0·08
		H (2,6)	1·89 ± 0·08
		H (4)	1·90 ± 0·08
HMB	2,4,6-trinitrobenzotrifluoride	*F*	2·22 ± 0·08
		H (3,5)	2·96 — 0·08

[a] Numbers in parentheses indicate ring positions of protons. [b] Measured in kg. solution per mole. [c] Hexamethylbenzene.

have been explained in terms of temperature-dependence of the chemical shift of the pure complex. Obviously the present results based on data at a single temperature cannot be accounted for in this way.

The possibility that the results of Klinck and Stothers could be accounted for in terms of isomeric 1 : 1 complexes has been suggested.[4] Such an explanation by itself is not possible in the present work since the measured K should give a value for the sum of K values for all isomeric 1 : 1 complexes irrespective of the measured nucleus. The situation is analogous to that described by Orgel and Mulliken[5] for optical data. The model could be used, however, provided that the ratio of the two (or more) isomers was dependent on the concentration of the component present in excess. An argument on this basis has been used to rationalise the apparent wavelength-dependence of optically determined values of K for some tetracyanoethylene complexes.[6]

An alternative possibility is that the stoicheiometry of the complex species is not restricted to 1 : 1. Adequate evidence for the presence of termolecular species in these systems is, however, very difficult to demonstrate.[7]

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