Tetrahedron Letters No.56, pp. 4935-4936, 1970. Pergamon Press. Printed in Great Britain.

SOLVENT EFFECTS ON THE ASSOCIATION OF BENZENE WITH 2,4,6-TRINITROTOLUENE

K. Barnes and C.H.J. Wells

School of Chemistry, Kingston Polytechnic, Kingston upon Thames

(Received in UK 26 October 1970; accepted for publication 5 November 1970)

The association constant for the formation of a 1:1 molecular complex between electron donor and electron acceptor species can be measured by a number of methods[1]. Of these, the n.m.r. method developed by Hanna and Ashbaugh[2] and modified by Foster and Fife[3] has been extensively used in recent years. Under the appropriate concentration conditions the n.m.r. method has been shown to give results which are internally consistent[4] and, also, results which are in reasonable agreement with those derived by optical methods[5]. However a recent communication[6] on association constants obtained by n.m.r. for a number of donor - acceptor systems reported that the value obtained is dependent on the particular nucleus in the acceptor upon which measurements are made. Carbon tetrachloride was used as solvent in the study, and since the results for the benzene-2,4,6-trinitrotoluene system conflicted with our findings for this system in 1,2-dichloroethane[7] we have now investigated the effect of solvent on the association constant for the interaction of benzene with 2,4,6-trinitrotoluene.

Chemical shift measurements were made on the aliphatic and aromatic protons of 2,4,6-trinitrotoluene(A) in the presence of excess benzene(D), and the values of the association constants, K^{AD}, were derived from a plot based on the equation

$$\Delta/D_o = K^{AD}\Delta_o - K^{AD}\Delta$$

where D_o is the initial concentration of donor D, Δ is the difference between the chemical shift of one of the acceptor proton types in the presence and absence of donor, and Δ_o is the difference between the chemical shift of the acceptor protons in the pure complex and in the uncomplexed acceptor. The values of the association constants in the different solvent systems are summarised in the Table.

It can be seen from the Table that there is a marked difference between the values of the association constants derived from measurements on the aliphatic and aromatic protons in the non-polar solvents carbon tetrachloride, carbon bisulphide, cyclohexane and n-hexane. As would be expected the values are lower in the relatively more polar solvents chloroform, Association constants (K^{AD}) for the benzene(D)-2,4,6-trinitrotoluene(A) system under the condition $D_o \gg A_o$ and at 33.5°.

Solvent	K^{AD} (kg. mol^{-1})[a] Aliphatic protons	Aromatic protons
Carbon tetrachloride[b]	0.35	0.42
Carbon bisulphide	0.28	0.32
Cyclohexane	0.27	0.35
n-Hexane	0.23	0.31
Chloroform	0.20	0.22
1,2-Dichloroethane	0.14	0.13
Dichloromethane	0.12	0.14

[a] The error in the quoted values is ± 0.01 in each case. [b] Previous literature values for the aliphatic and aromatic protons in this solvent are 0.21 and 0.42 kg. mol^{-1} respectively[6].

1,2-dichloroethane and dichloromethane. As the values drop so the difference between the association constant within a system becomes masked. Since the differences are more marked in the non-polar set of solvents it would suggest that solute-solvent interaction is not the underlying cause of the anomaly in the values. It has been suggested previously[6] that the differences might arise from the presence in the system of isomeric 1:1 complexes or additional complexes in which the stoicheiometry is not confined to 1:1. The present results taken in conjunction with the previous findings indicate that association constants for weak interactions between donor and acceptor species must be viewed with caution.

REFERENCES

1. R. Foster, "Organic Charge-Transfer Complexes", Academic Press, London and New York, pp. 125 - 178 (1969)
2. M.W. Hanna and A.L. Ashbaugh, J. Phys. Chem., **68**, 811 (1964)
3. R. Foster and C.A. Fyfe, Trans. Faraday Soc., **61**, 1626 (1965)
4. Reference 1, p. 144
5. P.H. Emslie, R. Foster, C.A. Fyfe and I. Horman, Tetrahedron, **21**, 2843 (1965)
6. M.I. Foreman, R. Foster and D.R. Twiselton, Chem. Comm., 1318 (1969)
7. E. Shilton and C.H.J. Wells, J. Chem. Soc. (B), in press