Nuclear Magnetic Resonance Measurement of Organic Charge-transfer Complexes over a Temperature Range

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DETERMINATIONS of equilibrium constants for organic electron-donor–acceptor (charge-transfer) complexes[1,2] have now been extended over the temperature range $-5°$ to $+45°$. The method of evaluation described previously has been used.[2] Good straight lines of log K against $1/T$ are obtained, confirming the 1 : 1 stoicheiometry of the complexes. Values of enthalpy (ΔH_0) and entropy (ΔS_0) of formation for complexes of a series of methylbenzenes with the acceptors 1,3,5-trinitrobenzene and with fluoranil in carbon tetrachloride are given in the Table.

The ^{1}H resonance of 1,3,5-trinitrobenzene only varies within 2 c./sec. in the range $-5°$ to $+45°$. The chemical shift of the ^{1}H in the acceptor moiety of the pure complex in carbon tetrachloride relative to the chemical shift of ^{1}H in free acceptor in the solvent (Δ_0) is also effectively constant. This

TABLE

Thermodynamic constants[a] *for charge-transfer complexes of a series of donors with fluoranil* (FA) *and* 1,3,5-*trinitrobenzene* (TNB) *in carbon tetrachloride*

Donor	FA		TNB	
	ΔH_0 (kcal./mole)	ΔS_0 (e.u.)	ΔH_0 (kcal./mole)	ΔS_0 (e.u.)
Benzene	$-2{\cdot}0_4$	$-7{\cdot}4$	$-1{\cdot}9_5$	$-7{\cdot}8$
Toluene	$-2{\cdot}3_0$	$-7{\cdot}5$	$-2{\cdot}1_9$	$-7{\cdot}9$
p-Xylene	$-2{\cdot}7_3$	$-8{\cdot}0$	$-2{\cdot}52_2$	$-8{\cdot}2$
Mesitylene	$-3{\cdot}0_3$	$-8{\cdot}1$	$-2{\cdot}8_5$	$-8{\cdot}8$
Durene	$-3{\cdot}9_2$	$-9{\cdot}6$	$-3{\cdot}0_7$	$-8{\cdot}5$
Pentamethylbenzene	$-4{\cdot}4_3$	$-10{\cdot}1$	$-3{\cdot}3_9$	$-8{\cdot}6$
Hexamethylbenzene	$-5{\cdot}4_1$	$-12{\cdot}2$	$-3{\cdot}6_9$	$-8{\cdot}8$

[a] based on association constants measured in kg. solution/mole.

would seem to rule out important solvent effects in these complexes. The ^{19}F resonance of fluoranil, however, is temperature dependent, (36 c./sec. within the range $-5°$ to 45°). The Δ_0 values for the fluoranil complexes are also temperature dependent to about the same extent as free fluoranil. However the trend of Δ_0 with association constant for the various fluoranil complexes is maintained at any given temperature.

With the exception of the mesitylene complexes the values of ΔH_0 for each series of complexes shows a regular variation with increasing methylation of the benzene ring of the donor. A similar behaviour in ΔS_0 is also observed (Table). The variation of ΔH_0 with ΔS_0 for each series is consequently regular.

(*Received, January 11th*, 1967; *Com.* 034.)

[1] M. W. Hanna and A. L. Asbaugh, *J. Phys. Chem.*, 1964, **68**, 811.
[2] R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, 1965, **61**, 1626.