Calorimetric Studies of π-Molecular Complexes: Tetracyanoethylene and Aromatic Donors

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Summary Thermodynamic parameters for tetracyanoethylene–aromatic donor complexes in CH_2Cl_2 solution have been determined calorimetrically.

EQUILIBRIUM constants for the formation of π-molecular complexes are usually determined by measuring the concentration-dependent intensity of an intermolecular charge transfer band. The equilibrium constants so determined often exhibit a significant dependence upon the initial donor [D] and acceptor [A] concentration[1] ($[D]_0 >> [A]_0$, $[D]_0 << [A]_0$, or $[D]_0 \approx [A]_0$). Equilibrium constants obtained by an n.m.r. method[2] are less dependent upon the initial concentrations of complexing molecules, but disconcerting variations in association constants have been observed, dependent upon the particular nucleus for which a concentration-dependent n.m.r. chemical shift is measured.[3] The accuracy of enthalpies and entropies calculated from the temperature dependence of equilibrium constants determined by spectroscopic or n.m.r. methods may therefore be questioned. For this reason we have undertaken calorimetric determinations of thermodynamic parameters for several series of π-complexes. This is a preliminary report of calorimetric experiments on tetracyanoethylene (TCNE)-aromatic donor complexes in CH_2Cl_2 solution at 25°.

Thermodynamic parameters for TCNE *complexes*

	Calorimetric results[a]			Spectroscopic results[b]		
	K	$-\Delta H^0$ (kcal mol^{-1})	$-\Delta S^0$ (cal mol^{-1} deg^{-1})	*K*	$-\Delta H^0$ (kcal mol^{-1})	$-\Delta S^0$ (cal mol^{-1} deg^{-1})
Benzene	0·108	3·158	15·02	0·129	2·54	12·6
Toluene	0·132	7·881	30·22	0·234	2·96	12·8
p-Xylene	0·252	9·935	36·07	0·491	3·61	13·5
o-Xylene	0·229	7·910	29·46	0·450	—	—
m-Xylene	0·221	9·428	34·62	0·386	—	—
Mesitylene	0·599	8·385	30·61	1·11	4·76	15·8
1,2,4-Trimethylbenzene	0·608	9·186	31·60	—	—	—
1,2,3,5-Tetramethylbenzene	1·220	9·378	31·06	—	—	—
Durene	1·150	8·953	29·75	—	5·32	15·4
1,2,3,4-Tetramethylbenzene	2·405	8·711	27·39	—	—	—
Pentamethylbenzene	4·358	6·981	20·49	7·91	7·21	20·1
Hexamethylbenzene	12·00	7·474	20·13	16·9	—	—
Naphthalene	0·247	4·364	17·41	0·752	—	—
Phenanthrene	1·874	11·34	36·79	—	—	—
Pyrene	0·888	4·530	15·43	1·90	—	—

[a] CH_2Cl_2 solution, 25°. [b] CH_2Cl_2 solution, 22°, ref.6.

The calorimeter used is similar to that described by Arnett, *et al.*[4] Aliquots of donor compound were added to solutions of TCNE in CH_2Cl_2, and the heat generated was determined by comparison with electrical calibrations. Several initial concentrations of TCNE were used, and many experiments were replicated over a period of three years. Equilibrium constants (K_C, in l mol^{-1}) and enthalpies of complexation, ΔH^0, were obtained from the experimental data by a computerized, least-squares criterion, simultaneous solution of the quadratic equilibrium expression involving K_C, $[A]_0$, $[D]_0$, and complex concentration [C], and the linear equation relating the heat produced to ΔH^0, [C], and the calorimeter constants. The concentrations of the donor and acceptor molecules were varied from 0·02—0·1 M with neither component in large excess. The precision of the data is relatively high. Conformity to the assumed 1 : 1 equilibrium is very likely since standard deviations in the calculated equilibrium constants are of the order of ±0·002 or less. The calculated heats of formation are correspondingly precise, errors of the order of 10 or less cal are found.

Our results are compared with spectroscopically determined values[6] in the Table. The calorimetric equilibrium constants are smaller in every case, and both ΔH^0 and ΔS^0 are much larger negative numbers than those measured by spectroscopic techniques. Among several possible explanations for the discrepancies, a contribution to the intensity of the charge-transfer band from "contact-charge-transfer"[7] can lead to a partial understanding of the results.

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