J. Chem. Eng. Data **1995,** *40,* 417–418

Thermochemistry of Charge-Transfer Complexes of 7,7,8,8-Tetracyanoquinodimethane with Benzene and Its Chloro Derivatives

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The enthalpies of formation of charge-transfer complexes of benzene, chlorobenzene, and 1,3-dichlorobenzene as donors with 7,7,8,8-tetracyanoquinodimethane as acceptor were determined. The thermochemical data show an increased stability of charge-transfer complexes of donors with permanent dipole moment. The results confirm the importance of electrostatic forces in bonding and stabilizing weak complexes. The approximate formation constants of the complexes are also reported.

Introduction

There has been a continued interest in the study of charge-transfer (CT) complexes following the classical work on benzene–iodine by Benesi and Hildebrand (*1*, *2*). Benesi–Hildebrand, Rose–Drago (*3*), Scott (*4*), and related equations have been developed for the spectroscopic study of the thermochemistry of CT complexes. Because of the problems associated with the use of these equations (*5*, *6*), Morales *et al.* (*7*) proposed a method for the determination of the enthalpy of formation of weak complexes. According to this method if A_{CT} is the absorbance due to the CT complex, an apparent enthalpy of formation is defined as

$$\Delta H_{app} = -R[d(\ln A_{CT})/d(1/T)] \qquad (1)$$

where ΔH_{app} is related to the initial molar concentration of the donor $C(D_0)$ by the equation

$$\Delta H_{app} = \Delta_f H\,(1 - KC(D_0)) \qquad (2)$$

where $\Delta_f H$ is the real enthalpy of formation and K is the approximate formation constant of the CT complex. Hence, the plot of ΔH_{app} vs $C(D_0)$ in the limit of ideal solution condition would give a method for the evaluation of $\Delta_f H$ and K.

Although 7,7,8,8-tetracyanoquinodimethane (TCNQ) is known to form CT complexes with many aromatic hydrocarbons, there is no report on its CT complexes with benzene and its chloro derivatives.

Experimental Section

All of the reagents were purified according to standard procedures (*8*, *9*). TCNQ was obtained from Merck-Schuchandt and was purified by repeated recrystallization from acetonitrile. Absorbance was measured on a Hitachi 200-20 UV–vis spectophotometer with a temperature-regulated (±0.1 K) cell holder. The temperature regulation was done using a Haake E8, EK 51-1 bath system. Chloroform was used as the solvent. Concentration of TCNQ was kept at 1.96×10^{-4} M for all absorbance measurements with donor concentration varying in the range 1–3.5 M. The ratio $C(D_0)/C(A_0)$ was of the order of thousands in all cases. All absorbance measurements were done in an optimum wavelength range of 465–435 nm, where absorbance due to TCNQ alone was small relative to that of the CT complex. Solvent chloroform and all of the donors used were transparent in this wavelength range.

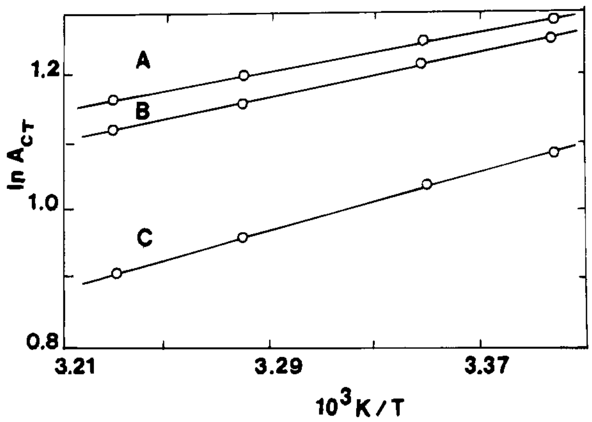

Figure 1. Plot of ln A_{CT} against $1/T$; $C_{TCNQ} = 1.96 \times 10^{-4}$ M: (A) benzene (2.70 M); (B) chlorobenzene (2.65 M); (C) 1,3-dichlorobenzene (2.63 M).

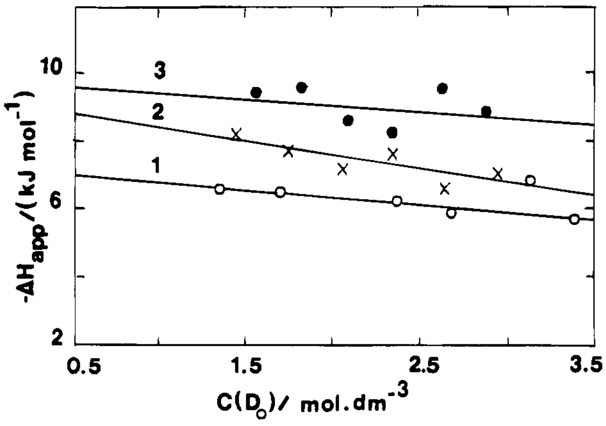

Figure 2. Plot of $-\Delta H_{app}$ against $C(D_0)$: (1) benzene; (2) chlorobenzene; (3) 1,3-dichlorobenzene.

Absorbance measurements were done at seven wavelengths spaced at 5 nm increments at various temperatures, viz. 21.2, 25.2, 31.4, and 36.1 °C. Results were reproducible within 1%. For each experimental data set the logarithm of the sum of the absorbances at seven experimental wavelengths (corrected for TCNQ absorption) was plotted vs $1/T$ (Figure 1). Using the slope m (by method of least squares), ΔH_{app} was evaluated by eq 1. The slope and intercept of the plot of ΔH_{app} vs $[D]_0$ (Figure 2) gave K and $\Delta_f H$. The results are given in Table 1.

0021-9568/95/1740-0417$09.00/0

Table 1. Enthalpy of Formation ($\Delta_f H$) and Approximate Formation Constant (K) for CT Complexes of TCNQ with Benzene and Its Chloro Derivatives

donor	$C(D_0)$/(mol dm^{-3})	m	$-\Delta H_{app}$/(kJ mol^{-1})	$-\Delta_f H$/(kJ mol^{-1})	$K \times 10^2$
benzene	1.352	797	6.626	7.0 ± 0.3	4.0
	1.690	788	6.551		
	2.366	759	6.310		
	2.705	713	5.928		
	3.043	833	6.925		
	3.381	683	5.678		
chlorobenzene	1.475	988	8.214	9.3 ± 0.3	9.0
	1.770	932	7.748		
	2.064	864	7.183		
	2.359	924	7.682		
	2.654	796	6.618		
	2.949	848	7.050		
1,3-dichlorobenzene	1.557	1139	9.470	9.9 ± 0.4	4.0
	1.840	1160	9.644		
	2.013	1040	8.646		
	2.365	990	8.231		
	2.628	1150	9.561		
	2.891	1067	8.871		

Results and Discussion

The $\Delta_f H$ values show that TCNQ forms weak CT complexes with weaker aromatic π systems of relatively higher ionization potentials as donors. These complexes belong to the "sacrificial" bπ−aπ type of Mulliken's classification (*10*). This was verified by a linear Scott plot (*4*). The magnitude of $\Delta_f H$ increases from benzene to mono- and dichlorobenzene, implying higher stability of complexes. It can be explained by classical electrostatic theory of bonding in weak CT complexes advocated by a host of authors such as Dewar (*11, 12*), Hanna (*13, 14*), Mulliken (*15*), and Qureshi (*16*). The electrostatic interaction of the dipole-induced dipole type of chloro- and dichlorobenzene (with dipole moments of 1.69 and 1.72 D, respectively) with TCNQ will be much higher compared to that of benzene (zero dipole moment).

Acknowledgment

We express our sincere gratitude to UGC, Government of India, for the award of a Teacher Fellowship under FIP to C.G.R.

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Received for review July 20, 1994. Revised December 12, 1994. Accepted December 15, 1994.[⊗]

JE940146B

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.