Tetrahedron Vol. 34, pp. 3201–3205
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0040-4020/78/1101-3201/$02.00/0

MOLECULAR COMPLEXES OF SEVERAL AROMATIC HYDROCARBON–KETONE SYSTEMS

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(*Received in USA* 28 *March* 1978; *Received in UK for publication* 26 *May* 1978)

Abstract—The association constants (K_{AD}) between several aromatic hydrocarbons and several ketones were determined by a NMR spectrometric method in carbon tetrachloride as a solvent. Thermodynamic parameters for the formation of complexes for benzene–acetone and benzene–actophenone are also reported. The effect of competing complexation with the solvent is discussed. A new equation, which was derived without assuming that the concentration of one solute is far greater than that of the other, was used for the computation of the K_{AD}-values.

The role of charge-transfer complexes in organic reactions is well-established and many investigators have attempted to correlate reaction mechanisms with this intermediate.[1–14] Especially in photochemical reactions, it has long been a question whether ground state aggregates or excited complexes (exciplexes) take part in a reaction, i.e.

$$D + A \rightarrow (D \cdot A) \xrightarrow{h\nu} (D^+A^-)^* \rightarrow \text{product} \qquad (1)$$

$$\text{or } D + A + h\nu \rightarrow {}^{1,3}D^* \text{ or } {}^{1,3}A^*$$

followed by

$${}^{1,3}D^* + A \rightarrow {}^{1,3}(D^+A^-)^* \rightarrow \text{product.} \qquad (2)$$

Generally it appears to be agreed upon that the ground state aggregates play an important role in some (2+4) cycloaddition reactions,[3,4] whereas exciplexes have been shown to be intermediates in some photochemical cycloaddition reactions.[15–23]

In the present paper, we report the formation constants and some thermodynamic properties of the charge-transfer (CT) complexes between several aromatic hydrocarbons and the aromatic ketones determined in carbon tetrachloride by a NMR spectroscopic technique. Aromatic ketones are important triplet sensitizers because of their high triplet population and convenient triplet energy levels. Our result in the present investigation indicates that there are very weak interactions between these two classes of compounds.

RESULTS AND DISCUSSION

The results reported here were obtained employing an equation,

$$\frac{1}{\Delta} \cdot \frac{[D]_0}{[A]_0 + [D]_0} = \frac{1}{K_c^{AD}\Delta_0^{AD}} \cdot \frac{1}{[A]_0 + [D]_0} + \frac{1}{\Delta_0^{AD}} \qquad (3)$$

where $[D]_0$ and $[A]_0$ are added concentrations of donor and acceptor molecules, Δ is the measured chemical shift for the solution in question, Δ_0^{AD} is the chemical shift for the supposedly pure complex relative to the shift for the pure molecule in solution, and K_c^{AD} is the association constant of the donor–acceptor complex in question. This equation is not based on the assumption, $[D]_0 \gg [A]_0$ as in Hanna's derivation.[24] Since the condition of $[D]_0 \gg [A]_0$ is not assumed in the derivation, one can use any concentration ranges. One then plots $[D]_0/\Delta([A]_0 + [D]_0]$ vs $1/([A]_0 + [D]_0)$ to obtain K_c^{AD} and Δ_0^{AD} from the slope and the intercept. Results are listed in Tables 1–3.

In order to check on this equation, two well established systems, i.e. maleic anhydride (MA)–benzene and 1,3,5-trinitrobenzene (TNB)–benzene systems were examined and the result was compared with a well established equation derived by Foster and Fyfe,[25]

$$\frac{\Delta}{[D]_0} = -\Delta \cdot K_c^{AD} + \Delta_0^{AD} \cdot K_c^{AD}. \qquad (4)$$

The results are listed in Table 1 and shown in Figs. 1 and 2. In Fig. 1, where Foster and Fyfe's equation used, one finds an apparent scatter in the plot in the upper left-hand corner when the lower donor (benzene) concentration range is used for the measurements. The plot shown in Fig. 2, however, has a much better correlation coefficient (0.9959) for the same data set. For the higher donor concentration range, the formation constants obtained by the two different equations are in excellent agreements within experimental error. For the rest of the systems, the data obtained from two different equations are listed where possible (Table 1). In some of the systems, the data could not be treated by eqn (4).

In order to evaluate the thermodynamic parameters, temperature studies were carried out for the acetone–benzene and acetophenone benzene systems. The temperature dependence of the chemical shifts is shown

Table 1. Formation constants[a]

Systems	Methods of Calculation: Equation (3) K_c^{AD}	Δ_o^{AD}, Hz	Equation (4)	Δ_o^{AD}, Hz
MA-Benzene	0.21 ± 0.07	111.2	0.17 ± 0.06	130.4
TNB-Benzene	0.34 ± 0.09[b]	288.1	0.32 ± 0.08[b]	333.4
	0.28 ± 0.06[c]	288.4	0.28 ± 0.06[c]	287.7
	0.081[d]	282.7	e	
Acetone-Benzene	0.040 ± 0.006	115.4	0.046 ± 0.007	96.7
Acetone-Naphthalene	0.037 ± 0.018	251.8	e	
Acetone-Azulene	0.052 ± 0.039	182.5	e	
Acetophenone-Benzene	0.073 ± 0.017	57.4	0.072 ± 0.014	57.6
Acetophenone-Naphthalene	0.15 ± 0.014	63.6	0.14 ± 0.08	66.1
Acetophenone-Azulene	0.21 ± 0.16	45.8	e	

[a]All K-values listed were obtained in CCl_4, using cyclohexane as an internal reference unless otherwise specified. Unit of K in ℓ mole^{-1}.

[b][TNB] = 0.007604 M with cyclohexane as an internal reference.

[c]Same experimental conditions as in b, but TMS was used as an internal reference. Foster's condition.[23]

[d]Low donor concentration (0.1000 - 0.3500 M with respect to benzene) was used without internal reference.

[e]The data were not treatable by the equation (4).

Table 2. Temperature dependence of association constants[a,b]

Temperature, °K	Systems: Acetone-Benzene	Acetophenone-Benzene
272.2	0.0924	0.173
290.7	0.0488	0.0957
308.2	0.0399	0.0729
328.7	0.0299	0.0406

[a]These experiments were done in CCl_4 with cyclohexane as an internal reference.

[b]Equation (3) was used for the determination of K_{AD}.

Table 3. Thermodynamic properties of acetone-benzene and acetophenone-benzene complexes

Systems	ΔH°, kcal/mole	ΔS°, eu	ΔG°, kcal/mole[a]	Remark
Acetone-Benzene	-3.6 ± 0.7	-18 ± 2	1.8 ± 0.9	b
Acetophenone-Benzene	-3.9 ± 0.2	-18 ± 2	1.5 ± 0.6	b

[a]These were calculated from the relation, $\Delta G^\circ = \Delta H^\circ - T\cdot\Delta S^\circ$.

[b]at 25°C

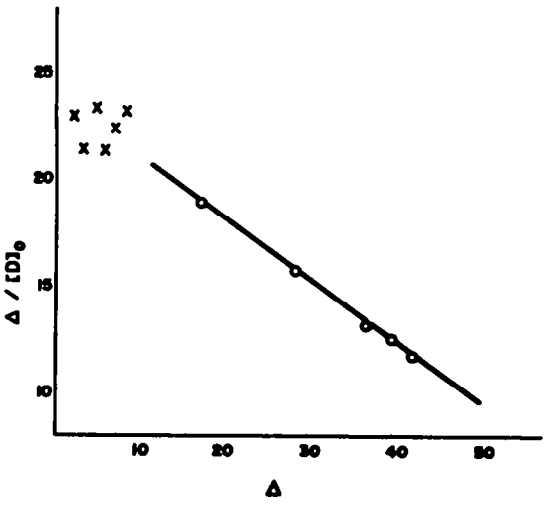

Fig. 1. Plot of eqn (4) for the TNB–benzene system [TNB] = 0.01141 M with (○) tetramethyl silane as an internal reference. The scattered points on the left-hand side corner are for the same system with the donor concentrations low (0.1000–0.3500 M benzene) for the same acceptor concentration. The unit in Δ is Hz (cps).

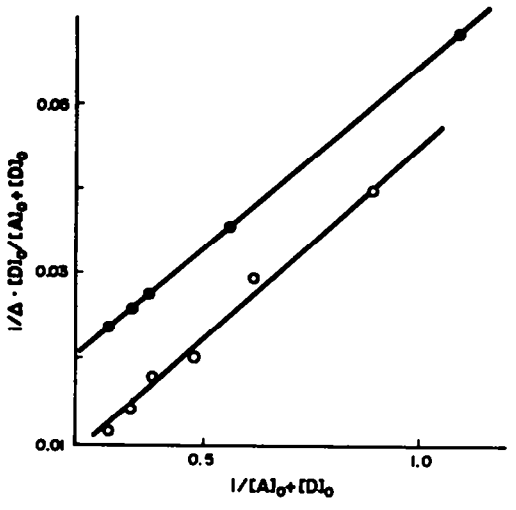

Fig. 2. Plot of eqn (3) for the TNB–benzene system with (⊙) TMS as an internal reference. The lower line (○) is for the low concentrations of the donor (0.1000–0.3500 M benzene) for the same acceptor concentration.

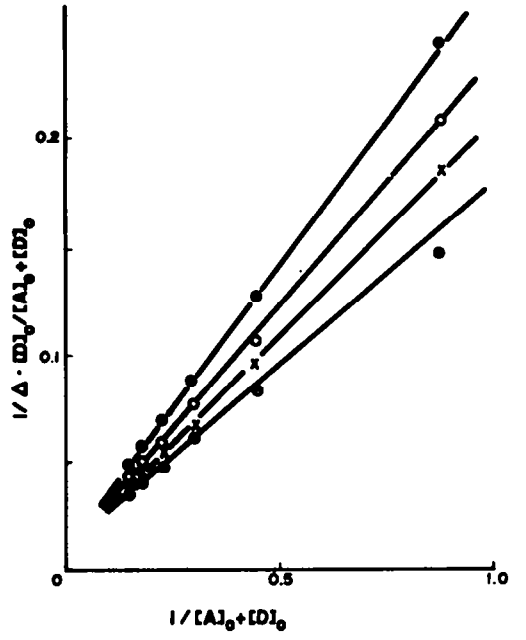

Fig. 3. Temperature dependence of chemical shifts. Plot of eqn (3) for acetone–benzene system at −1.0° (⊙), 17.5° (×), 35.0° (○), and 55.5° (●).

in Fig. 3. The formation constants obtained from plots shown in Fig. 3 were used for the van't Hoff plot,

$$\ln K_c^{AD} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (5)$$

from which the thermodynamic parameters are computed. The results are listed in Tables 2 and 3, and shown in Fig. 4.

The results listed in Table 1 were obtained from the chemical shift measurements employing cyclohexane as an internal reference, since there may exist some association between tetramethylsilane (TMS) and some of the donors or acceptors. It has been suggested that TMS gives rise to an interaction with aromatic solvents.[26] The apparent heats of formation of these complexes are in the order of 1 ~ 2 kcal/mole. The result shown in Table 1, however, indicates that the two constants agree reasonably within experimental error, i.e.

K_c^{AD}, TNB–benzene, with TMS as an internal reference: 0.28;

K_c^{AD}, TNB–benzene, with cyclohexane as an internal reference: 0.34.

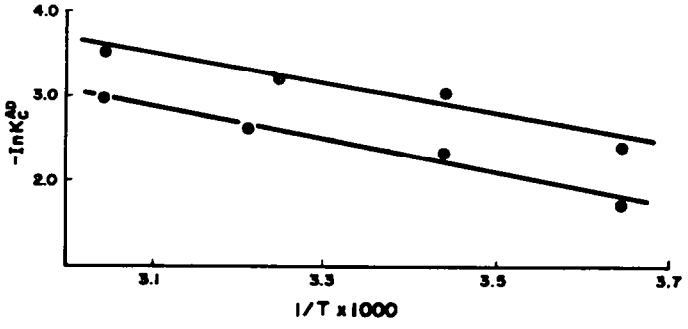

Fig. 4. van't Hoff plot of K's for acetone–benzene system (⊙), and for acetophenone–benzene system (●).

Nevertheless, the variations upon change of the internal reference may not be insignificant, and we decided to use cyclohexane throughout.

Another important point to be noticed from the results in Table 1 is that the association constant of the TNB–benzene system is heavily dependent on the concentration range of the donor molecule. The values are

K_c^{AD}: 0.34 for the range of the benzene concentration of 0.90 ~ 3.6 M

and

K_c^{AD}: 0.081 for the range of the benzene concentration of 0.10 ~ 0.35 M.

The dependence of the association constant on the donor concentration is very significant in this particular case. This concentration dependency of the association constants may be explained by several factors such as the self-association of either or both components, or by an interaction of the solvent with donor molecules (solution nonideality). Our result here is consistent with the model where the solution nonideality is taken into account. As has been pointed out by Hanna *et al.*,[27] there have been many questions as to the solution ideality of carbon tetrachloride with many solutes. Solvent effect on CT complexes have been documented very well in the literature.[28] The question whether or not carbon tetrachloride is really an inert solvent is very important, because carbon tetrachloride is the most frequently used solvent in the studies of molecular complexes by NMR techniques.

To make the problem more explicit, we will discuss the carbon tetrachloride–benzene system. From the facts that benzene has a positive heat of mixing with carbon tetrachloride and that the plot of heat of mixing versus mole fraction of either component is symmetrical, it has been postulated that there exists a 1:1 association complex between the two components.[29,30] The solid–solid equilibrium studies of mixtures of benzene and carbon tetrachloride show the existence of the species $C_6H_6 \cdot 2CCl_4$ in the mixture at very low temperatures.[29,30] Goates *et al.*[3] estimated a heat of dissociation of approximately 3.5 kcal/mole for the $C_6H_6 \cdot CCl_4$ system and suggested that π-bonding between the aromatic ring and the empty 3-d orbital of chlorine may be responsible for this complex. Spectroscopic studies[31,32] showed that there is a characteristic C–T band for the complex, C_6H_6–CCl_4 and the following association constant was obtained[32]

$$K_c^{SD} = 0.076 \pm 0.057.$$

Since benzene forms a complex with carbon tetrachloride, the solvent is therefore a competing reagent for the acceptor, TNB. The correction of the association constant from the observed one was first considered by Merrifield and Phillips.[33] Takahashi *et al.*[34] used a mixed model of interacting and non-interacting solvents and derived an equation

$$K_{c(corr)}^{AD} = \frac{K_{c(obs)}^{AD}}{1 - K_{c(obs)}^{SD}[S]_0} \qquad (6)$$

where $K_{c(corr)}^{AD}$ and $K_{c(obs)}^{AD}$ are the association constants corrected and observed, respectively, K_c^{SD} is the association constant between the solvent and a donor molecule, and $[S]$ is the concentration of the solvent. Taking $K_c^{DS} = 0.076$ and $[S] \cong 10$ M, the $K_{c(corr)}^{AD}$ is estimated to be 0.34, which is in excellent agreement with the one obtained at high donor concentration. The coincidence in this case could be accidental, but the agreement is excellent. It is, therefore, clear that a carbon tetrachloride solution is nonideal.

This idea about solution nonideality and complexation with donor molecules has recently been examined for other systems.[35,36] The effect of self-complexation on the association constants has been considered by Tanner and Bruice[39] and the following equation was derived to correct the observed association constant when there is n-merization in donor species in the solution.

$$K = K'(1 - nK_n[D]^{n-1})$$

where K' is an apparent equilibrium constant and K is a true one. Inspection of this equation indicates that the higher the n-merization is, the lower the true association constant will be. This effect, therefore, is opposite to the one we have observed in our system. We can conclude therefore, at least for our system, that the effect of the solvent participation plays the dominant role on the K's concentration dependency rather than self-association of one component, and that the higher the donor concentration is, the closer the apparent association constant will be to the real value.

The result of temperature studies shown in Tables 2 and 3 indicates that the measured $\Delta H°$, $\Delta S°$ and $\Delta G°$ values are well in the range of the thermodynamic functions reported previously for other weakly interacting complexes.[4]

In conclusion, the CT complex formation constants of several photochemically interesting organic systems have been obtained under concentration conditions different from those usually used in the investigation of CT complexes. The interaction shown by the association constants appears to be small enough to suggest that ground state interactions may not be significant in photochemical processes. Systems containing acetophenone appear to be more associated than those involving acetone. This could be due to the fact that the net dipole of acetophenone is greater than that of acetone, or to the increased polarizability of the π-system of acetophenone.

EXPERIMENTAL

Materials. Reagent grade 1,3,5-trinitrobenzene (Eastman Organic = E.O.; TNB), maleic anhydride (E.O.; MA), benzophenone (E.O.), acetophenone (Columbia Organic = C.O.), azulene (C.O.), and naphthalene (C.O.) were used after appropriate purifications such as repeated crystallizations, sublimations, and/or distillations. Carbon tetrachloride (Fischer Cestified = F.C.), cyclohexane (F.C.), acetone (F.C.), and benzene (Malinkrodt Analytical) were used without further purification.

Measurements. Solns of MA, acetone, acetophenone, benzophenone and azulene were prepared by adding weighed amounts of the materials into the volumetric flask, followed by dilution with CCl_4 to the mark. The TNB soln was prepared by saturating TNB in CCl_4 at room temp. and the concentration was determined by gravimetric analysis. The naphthalene soln was prepared by saturating naphthalene in CCl_4 at room temp., and the concentration was determined by measuring the density of the saturated soln at 18°. The formula used for the calculation was[37]

$$d_4^{18} = 1.59605 - 0.008375 \text{ (weight of naphthalene)} \qquad (7)$$

where d_4^{18} is the density of naphthalene–CCl_4 binary soln at 18°, based on the density at 4°.

After mixing prepared donor and acceptor solns with appropriate proportions, they were equilibrated for about 1 hr at room temp. and the NMRs were taken at the NMR probe temp. (37–38°). Before taking spectra, each sample was maintained at 37–38° in a water bath for about 30 min. NMR spectra were taken at the narrowest possible sweep width for the particular complexed hydrogen and the acceptor hydrogen to secure the most accurate measurements. Sweep time was always controlled at 1 Hz per sec. Cyclohexane was used as an internal reference unless otherwise mentioned. For the systems containing acetone and acetophenone, chemical shifts of Me protons of these molecules were measured, whereas the chemical shifts of the proton on the double bond (MA) and aromatic protons (TNB) were employed for Δ measurements for other systems.

The temp. study was done with a Varian Associates V-6040 variable temp. controller. The probe temp. could be maintained within an error of ±1°. Low probe temp. was measured by using the Varian Associates' 943346-06 MeOH standard sample and high temp. was measured by the Varian Associates' 943346-05 ethylene glycol standard sample. Each sample was equilibrated for at least 1 hr at the same temp. before the chemical shift was measured in the NMR probe. After about 15 min of stabilization with Varian Associates' V-6040 temp. controller using liquid N_2 in the case of low temps and N_2 gas in the case of high temps, the chemical shifts of the equilibrated samples were measured. Temp. measurements were made before and after each experiment and the experimental value was discarded whenever the temp. variation was more than ±1° from the designated temp.

Acknowledgement—We gratefully acknowledge the support of the Robert A. Welch Foundation, Houston, Texas, in this research.

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