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Some Notes on Molecular Complexes between Iodine and Polynuclear Aromatic Hydrocarbons

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It has been observed that when iodine concentration is high in a mixture of iodine and polynuclear aromatic hydrocarbon in carbon tetrachloride, the spectral data may be interpreted on the assumption of 2:1 molecular complex formation between iodine and aromatic hydrocarbon. The equilibrium constants for 2:1 complexes were, however, found to be much higher than those of the corresponding 1:1 complexes and they were further found to be independent of the nature of the hydrocarbon. Interpretation of the experimental data based on contact charge transfer appears to be much more reasonable in the present case.

IN a previous communication¹ using high hydrocarbon but low iodine concentration in carbon tetrachloride solution, it has been shown by Bhattacharya and Basu that there is formation of 1:1 molecular complexes of charge transfer type in these systems. The equilibrium constant for complex forming reaction was found to increase with the lowering of the ionization potential of the aromatic hydrocarbons. If, however, the iodine concentration is increased much above that of the hydrocarbon concentration, two different types of interaction may take place. Since the hydrocarbons are undoubtedly π donors, the possibility of one hydrocarbon molecule complexing with two iodine molecules, in which iodine occupies two equivalent positions above and below the plane of the hydrocarbon molecule, exists. On the other hand, if there is any contact charge transfer effect present in iodine-hydrocarbon system, then this effect may become predominant at higher iodine concentration. In order to see if this could be settled experimentally, the spectrophotometric investigations were repeated with high iodine but low aromatic hydrocarbon concentration, the results of which are reported herein.

In order to estimate the equilibrium constant from the measurement of optical densities of mixtures of iodine and aromatic hydrocarbons, Benesi-Hildebrand type of relations² may be deduced for 1:1 and 2:1 complexes as follows. Let us assume that the equilibrium may be represented as



and



In these equations A and I_2 represent aromatic hydrocarbon and iodine, respectively. The optical density of a solution containing the molecular species (1) and (2) is given by

$$\text{O.D.} = l\bar{\epsilon}[A]_0 = l[\epsilon_0[A] + \epsilon_1[AI_2] + \epsilon_2[A(I_2)_2]], \quad (3)$$

¹ Bhattacharya and Basu, *Trans. Faraday Soc.* **54**, 1286 (1958).

² Benesi and Hildebrand, *J. Am. Chem. Soc.* **71**, 2703 (1949).

provided the absorption due to iodine is negligible at the wavelength where O.D. measurements are made. The ϵ_i 's are the appropriate molar extinction coefficients. Combining (1)-(3) with the equation representing the conservation of hydrocarbon,

$$[A]_0 = [A]\{1 + K_1[I_2] + K_2[I_2]^2\}, \quad (4)$$

one obtains

$$[I_2]/(\bar{\epsilon} - \epsilon_0) = \frac{1 + K_1[I_2] + K_2[I_2]^2}{(\epsilon_1 - \epsilon_0)K_1 + (\epsilon_2 - \epsilon_0)K_2[I_2]} \quad (5)$$

if $[I_2] \gg [A]$. In these expressions $\bar{\epsilon}$ is the formal extinction coefficient of a solution containing an initial concentration of hydrocarbon $[A]_0$ moles/liter = O.D./ $[A]_0 l$, ϵ_0 = molar extinction coefficient of the hydrocarbon at the same wavelength and ϵ_1 and ϵ_2 are the molar extinction coefficients of 1:1 and 2:1 complex, respectively. If there is only 1:1 complex formation, then the relation (5) shows that a plot of $(\bar{\epsilon} - \epsilon_0)^{-1}$ against $1/[I_2]$ should be linear, from the slope and intercept of which the equilibrium constant K_1 and molar extinction coefficient ϵ_1 can be calculated. On the other hand, for 2:1 complex a plot of $(\bar{\epsilon} - \epsilon_0)^{-1}$ against $1/[I_2]^2$ should be linear, the slope and the intercept of which will similarly give K_2 and ϵ_2 . It may be observed that for 1:1 complex the relation (5) reduces effectively to Benesi-Hildebrand equation. On the other hand, if the interaction be predominantly of contact type, then Benesi-Hildebrand plot will give a straight line of zero intercept.

EXPERIMENTAL

The method of purification of the hydrocarbons has been described in greater detail in the previous communication.¹ As iodine concentrations used in the present study were several hundred times those used in the previous communication, the solvent was carefully purified in order to eliminate the formation of I_3^- ion as much as possible. O.D. measurements were made in Beckman spectrophotometer model DU using 1-cm silica cells. In the range of 340 m μ to 430 m μ the absorption due to iodine was low compared to hydrocarbons and the complexes. The small amount of ab-

TABLE I. Spectral data for I₂-hydrocarbon mixtures.

Hydrocarbons	Concentration of hydrocarbon (moles/liter)	1/[I ₂]	1/[I ₂] ²	1/($\bar{\epsilon}-\epsilon_0$)	ϵ_2	$K_2 \times 10^{-2}$
Naphthalene $\lambda_{\text{max}} = 363 \text{ m}\mu$	0.001806	17.1	292	0.00972	181	3.82
		19.6	384	0.01095		
		22.8	521	0.01369		
		27.4	751	0.01632		
Anthracene $\lambda_{\text{max}} = 430 \text{ m}\mu$	0.001000	12.5	156	0.00579	227	4.10
		14.4	204	0.00651		
		16.7	279	0.00738		
		20.0	400	0.00816		
		25.0	625	0.01132		
Pyrene $\lambda_{\text{max}} = 425 \text{ m}\mu$	0.001695	13.2	173	0.00663	200	4.00
		14.8	219	0.00764		
		18.9	359	0.00957		
		19.8	392	0.01004		
		26.3	694	0.01344		
Phenanthrene $\lambda_{\text{max}} = 367 \text{ m}\mu$	0.002517	14.7	215	0.00769	175	5.43
		18.9	357	0.00952		
		22.1	487	0.01077		
		26.4	699	0.01281		
Chrysene $\lambda_{\text{max}} = 388 \text{ m}\mu$	0.000639	14.1	200	0.00486	185	4.00
		16.2	262	0.00586		
		18.9	357	0.00667		
		22.6	511	0.00779		
Stilbene $\lambda_{\text{max}} = 372 \text{ m}\mu$	0.001097	14.7	215	0.00599	238	4.70
		18.9	357	0.00738		
		22.1	488	0.00835		
		26.4	699	0.01027		

sorption due to iodine was eliminated by balancing the mixture against a solution of iodine having the same concentration as the mixture.

RESULTS

The first step in the execution of the proposed scheme of work was to locate the characteristic absorption band of the complex for each hydrocarbon. It was observed that when the iodine concentration was high and the hydrocarbon concentration was a tenth (or less) of the iodine concentration, the characteristic absorption maximum came out at about the same position as that previously reported with high hydrocarbon and low iodine concentration. The characteristic λ_{max} are recorded in the Table I. The O.D. values of a number of mixtures of constant but low hydrocarbon and different but high iodine concentrations were measured at the characteristic λ_{max} . The relevant data are summarized in Table I and $1/(\bar{\epsilon}-\epsilon_0)$ vs $1/[I_2]$ and $1/[I_2]^2$ plots are given in Figs. 1 and 2.

DISCUSSION

It may be observed from the Figs. 1 and 2 that a plot of $(\bar{\epsilon}-\epsilon_0)^{-1}$ against $1/[I_2]$ as well as against $1/[I_2]^2$ is linear, but the first plot gives a straight line having zero intercept, in almost all cases, on the $(\bar{\epsilon}-\epsilon_0)^{-1}$ axis, which is a physically impossible result on the basis of complex formation—stable or otherwise.

The equilibrium (1) is therefore of negligible importance in these systems. The second plot, however, gives a straight line with a positive slope and a positive intercept, from which the equilibrium constant for 2:1 complex formation was calculated by the relation (5) and is listed in the Table I. It appears that the equilibrium constant is independent of the nature of the hydrocarbon and is practically constant. Further the absolute value of the equilibrium constant is much larger for 2:1 than for 1:1 molecular complexes.

We are thus faced with a number of problems. First, why does the characteristic absorption band for 2:1 complex appears at about the same position as that of the 1:1 complex? Secondly, why is the equilibrium constant for 2:1 complex so much larger than that for 1:1 complex, and why is it independent of the nature of the hydrocarbon?

No satisfactory answer can be given to any of these questions, which makes the very existence of 2:1 molecular complexes in these systems rather doubtful. The fact that $(\bar{\epsilon}-\epsilon_0)^{-1}$ is linear with respect to $1/[I_2]$ and $1/[I_2]^2$, suggests that the system probably is concentration-dependent in a more complicated way, and the two types of equilibrium cannot be distinguished, with the experimental data in the concentration range over which the measurement was extended.

If, however, we assume that the charge transfer is of a contact type, then the linear $(\bar{\epsilon}-\epsilon_0)^{-1}$ vs $1/[I_2]$ plot with zero intercept is understandable from the con-

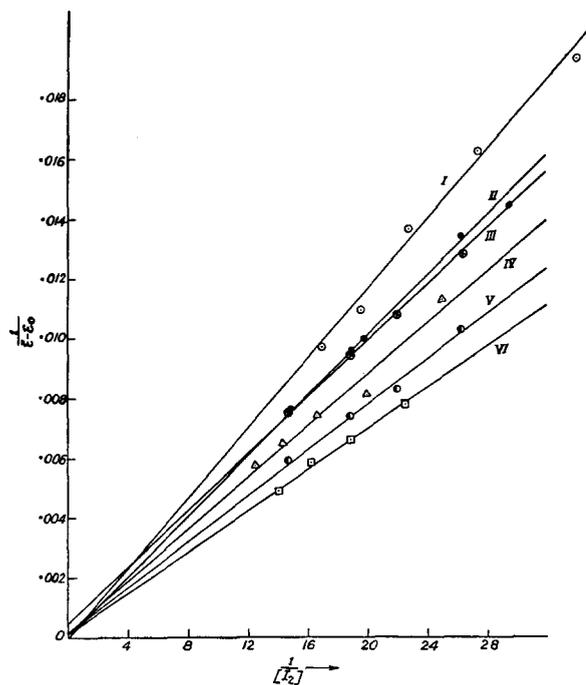


FIG. 1. Plot for 1:1 complexes. Curve I, naphthalene; II, pyrene; III, phenanthrene; IV, anthracene; V, stilbene; VI, chrysene.

sideration of Orgel and Mulliken's analysis.³ We may suggest that in hydrocarbons- I_2 systems the charge transfer is due both to 1:1 complex formation and to molecular contact. At low iodine concentration the absorption due to 1:1 complex is more important,

³ Orgel and Mulliken, J. Am. Chem. Soc. **79**, 4839 (1957).

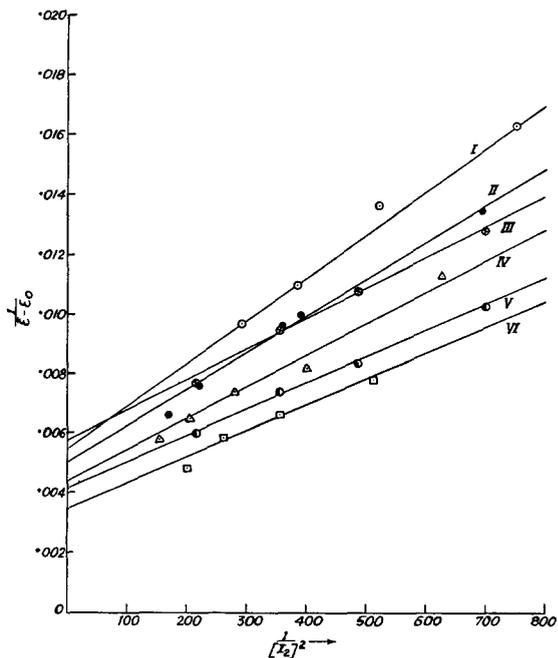


FIG. 2. Plot for 2:1 complex formation. Curve I, naphthalene, II, pyrene; III, phenanthrene; IV, anthracene; V, stilbene; VI, chrysene.

while at high iodine concentration, as each hydrocarbon molecule makes many more contacts with iodine, the contact charge transfer becomes predominant.

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