On the Association of Condensed Polycyclic Aromatic Compounds in Concentrated Sulfuric Acid

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Several investigations have been made of the aggregation of dye molecules or ions in aqueous solutions, and it seems clear that some dyes form dimers and polymers under suitable conditions. Qualitative discussions of the factors determining the associations and also of the spectral shifts caused by them have also been made[1-9].

The polycyclic aromatic hydrocarbons and their related quinons in concentrated sulfuric acid possess strong absorptions in the visible region which are ascribed to monomeric proton-complexes. Some of these spectral responses show a blue shift with an increasing concentration of the solute. These phenomena are interpreted as being caused by association of molecules.

These associates are considered, from experimental spectral facts, to be in equilibrium with the monomeric proton-complexes. For instance, dibenzopyrene forms successively, an octamer and the higher polymers in 96 per cent sulfuric acid with an increase in the concentration of the solute. However, it forms a dimer in 86 per cent sulfuric acid and shows no eminent blue spectral shift. Also the case of some of the related quinones such as anthraquinone, which forms a tetramer, *p*-naphthoquinone, and anthanthrone, which forms dimers, no blue shift is observed either. Moreover, tetracene and benzoanthrone form no polymers up to 10^{-2} mol. per liter of the concentration of the solutes.

The object of the present paper is to report these points, with some discussion of the mechanism or of the association of these compounds with reference to the considerations of the above-described investigations[1-9].

Experimental

The measurement of the absorption spectra was carried out with a Beckman DU-type spectrophotometer with quartz-cells, 1.0, 0.1 and 0.05 cm. thick, and with, in the visible region, a thin, transparent glass plate 0.01 cm. thick. The read-off value of the spectral measurement was the mean value of three readings in the concentrated region of solute molecules.

The specimen used in this experiment was prepared and recrystallized from appropriate solvents and was further purified by the repeated sublimation in vacuo of 10^{-3} to 10^{-4} mmHg. The concentrated sulfuric acid used in this experiment was an extra pure grade reagent of the Kanto Chemical Co., Ltd., which was considered to be chemically pure and to be transparent in the visible region of the spectrum. The concentration of the acid was to be ca. 98 per cent.

The solutions of different concentrations used in this experiment were prepared by dilution of the concentrated stock solution, the concentration of which was about 10^{-2} to 10^{-3} mol. per liter and which was freshly prepared before each measurement.

Results and Discussion

Dibenzopyrene (I). — Two strong absorption bands appear in succession in the spectra of the sulfuric acid solution, 10^{-6} mol. per liter,

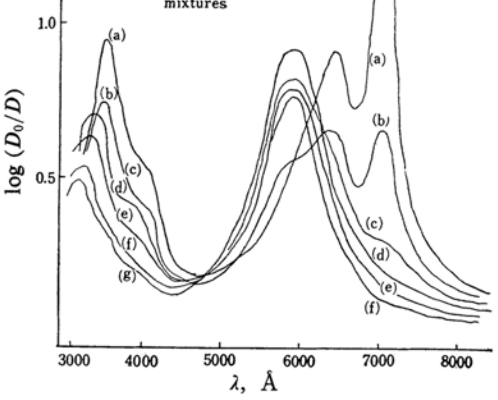

Fig. 1. The absorption spectra of dibenzopyrene in H_2SO_4 of 96% (a), 90% (b), 85% (c), 80% (d), 75% (e) and 70% (f).

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1) E. Rabinowitch and L. F. Epstein, *J. Am. Chem. Soc.*, **63**, 69 (1941).

2) S. E. Sheppard, *Rev. Mod. Phys.*, **14**, 303 (1942).

3) S. E. Sheppard and A. L. Geddes, *J. Am. Chem. Soc.*, **66**, 1955, 2003 (1944).

4) V. L. L. Leoshin, *Acta Physicochim.* U. S. S. R., **1**, 685 (1935).

5) M. Koizumi and N. Mataga, This Bulletin, **27**, 194 (1954).

6) V. Zanker, *Z. physik. Chem.*, **199**, 225 (1955); **200**, 250 (1952).

7) N. Mataga, This Bulletin, **30**, 375 (1957).

8) Y. Mori, Symposium of π-Electronic State, Chem. Soc. Japan, 1955.

9) Th. Förster, "Fluoreszenz Organischer Verbindungen", Vandenhoech und Ruprecht, Göttingen (1951).

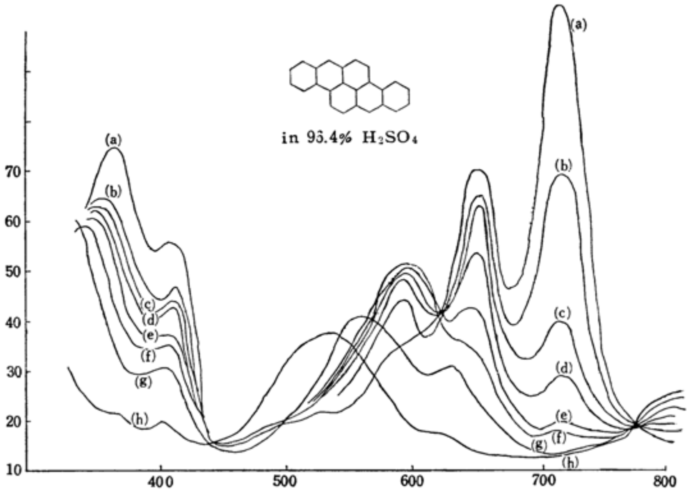
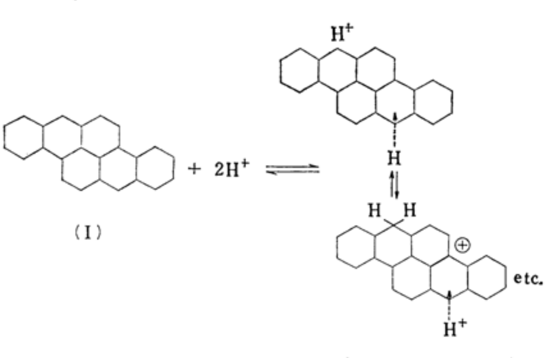


Fig. 2. The absorption spectra of dibenzopyrene with its concentration of $2.7\times10^{-6}\sim5.4\times10^{-5}$ (a), 6.75×10^{-5} (b), 9×10^{-5} (c), 1.35×10^{-4} (d), 2.7×10^{-4} (e), 9×10^{-4} (f), 2.7×10^{-3} (g) and 1.4×10^{-2} mol./l. (h) in 96.4% sulfuric acid.

with the increase in acidity, as is shown in Fig. 1. When this hydrocarbon is dissolved in 86 per cent sulfuric acid, the peak of the absorption band is found in the region of 580 mμ. When 98 per cent sulfuric acid is used, the band shifts to the longer wavelength region, 725 mμ. Both are considered to be in equilibrium with each other and with the protons in the acid. Therefore, the dibenzopyrene molecule is considered to be doubly protonated*. The protons which form a complex with the molecule are believed to be attached to the position of the largest charge-density as follows:



However, a discrepancy from Beer's law occurs with the increase of the concentration of solute up to 10^{-3} mol. per liter in 98 per cent sulfuric acid. New absorption bands appear near 595, 555 and 535 mμ with solute concentrations of 10^{-5}, 10^{-4} and 10^{-3} mol. per liter respectively. They may be interpreted as corresponding to the blue shift of the absorption band at 712 mμ by the influence of association and as being in equilibrium with each other; they have isobestic points near 770, 620, 570, 500, 465, 440 and 350 mμ, as is illustrated in Fig. 2.

Anthrone and Anthraquinone. — No new absorption peaks are found in the wavelength range from 350 to 1000 mμ, and only a decrease in the extinction coefficient at the absorption peak of monomer is observed with an increase in the concentration of the solute.

In the case of anthraquinone, however, a slight increase in the extinction coefficient is found beyond the region of the isobestic point near 460 mμ, in the skirt of the strong absorption peak of the monomer, with an increase in the concentration. This increase may be interpreted as being due to the slight change in the electronic state of monomer as a result of a weak intermolecular hydrogen bond formation between two molecules. As the configuration of the associate, a proton and a $(H_3SO_4)^+$ ion may be supposed to be resonating among a pair of two oxygen atoms of the molecules, which are assumed to take a parallel plane configuration. The structure is centrally symmetrical and possesses many resonating structures in the ground and excited states, unlike the model of the acridine-orange double ion by Zanker⁶⁾, which is anti-symmetric for one axis.

On the other hand, the absorption peak of anthrone in sulfuric acid, where polymerization of the 16th-degree occurs, shows a red-shift,

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* As was reported in a preceding paper (T. Handa, This Bulletin, **28**, 483 (1953)), we were able to obtain the two pK_B values of −5.0 and −7.4.

as is illustrated in Fig. 3, and also a slight increase in the extinction coefficient in the skirt of the main absorption band beyond the isobestic point near 415 mμ with an increase in the solute concentration. The configuration of the associate is supposed not to be coplanar and to be anti-symmetric like the acridine-orange double cation.

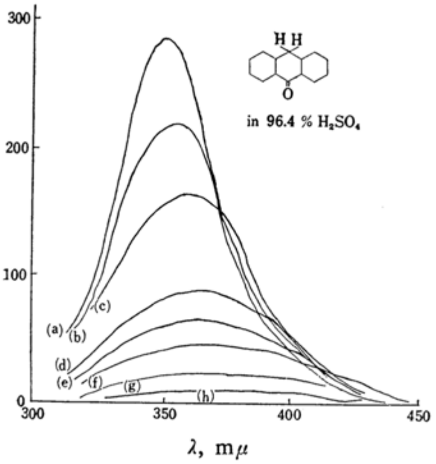

Fig. 3. The spectral response of the absorption spectra of anthrone with its concentration of 5.5×10^{-5} (a), 9.6×10^{-5} (b), 1.45×10^{-4} (c), 2.9×10^{-4} (d), 3.4×10^{-4} (e), 5.6×10^{-4} (f), 1.05×10^{-3} (g), and 5.78×10^{-3} (h) in 96.4% sulfuric acid.

Several quinones, such as *p*-naphthoquinone, anthanthrone and isoviolanthrone in sulfuric acid, whose degrees of polymerization are 2, 4 and 2 respectively, exhibit similar behavior.

Benzanthrone and Benzonaphthenone.—These compounds form no polymers. It is considered that, because of the larger weight of the existence of π-complexes in the ground state which gives the resonating carbonium ion, the potential barrier in the Morse curve in Fig. 5 may be higher than those in other cases because of the electrostatic repulsion of carbonium ions and the fact that they can not ride over this potential barrier to form stable polymers.

From the foregoing experimental facts, the association constant, *k*, and the degree of polymerization have been estimated.

When the equilibrium between monomer and polymer, an associate of *n*-th degree, exists, the association constant, *k*, is expressed as

$$k=\frac{X}{nC_0{}^{n-1}(1-X)^n} \tag{1}$$

where X is the fraction of polymer and C_0 is the concentration of the solute molecule.

The apparent extinction coefficient, ε, at a definite wavelength is expressed as:

$$\varepsilon=\frac{X}{n}\varepsilon_{\mathrm{n}}+(1-X)\varepsilon_{\mathrm{m}} \tag{2}$$

where ε_{n} and ε_{m} are the extinction coefficients of the polymer and the monomer respectively.

From Eqs. 1 and 2, we can obtain the following relation:

$$\log C_0(1-\varepsilon/\varepsilon_{\mathrm{m}}) =\log(Ck)+n\log C_0\left(\frac{\varepsilon}{\varepsilon_{\mathrm{m}}}-\frac{\varepsilon_{\mathrm{n}}}{n\varepsilon_{\mathrm{m}}}\right) \tag{3}$$

where

$$C=n^n\left(n-\frac{\varepsilon_{\mathrm{n}}}{\varepsilon_{\mathrm{m}}}\right)^{1-n}$$

As a rough approximation, we can neglect $\varepsilon_{\mathrm{n}}/\varepsilon_{\mathrm{m}}$ as compared with $\varepsilon/\varepsilon_{\mathrm{m}}$; therefore

$$\log C_0\left(1-\frac{\varepsilon}{\varepsilon_{\mathrm{m}}}\right) =\log(Ck)+n\log C_0\left(\frac{\varepsilon}{\varepsilon_{\mathrm{m}}}\right) \tag{4}$$

When we apply Eq. 4 to determine the *n* for the dibenzopyrene molecule in 96 per cent concentrated sulfuric acid this degree is 8, as is shown in Fig. 4. Further, the new absorption band at the wavelength of 985 mμ may correspond to that of the octamer of the dibenzopyrene diprotonium cation, while the equilibrium constant, *k*, at 20°C is estimated to be approximately 3×10^{28}. We may expect the qualitative dimerization of the octamer of the dibenzopyrene diprotonium cation from the new absorption band near 555 mμ. The high degree polymerization proceeds in successive steps with the increase in the concentration of the dibenzopyrene molecule in such a manner as 8, 16, 32, and so on.

With the elevation of the temperature of the solution from 20 to 70°C, the intensity of the

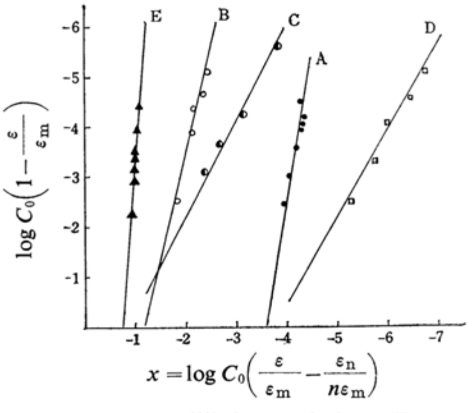

Fig. 4. The equilibrium relation (Eq. 3) between the monomer and the polymer of dibenzopyrene (A), anthraquinone (B), isoviolanthrone (C), anthanthrone (D) and anthrone (E) in sulfuric acid.

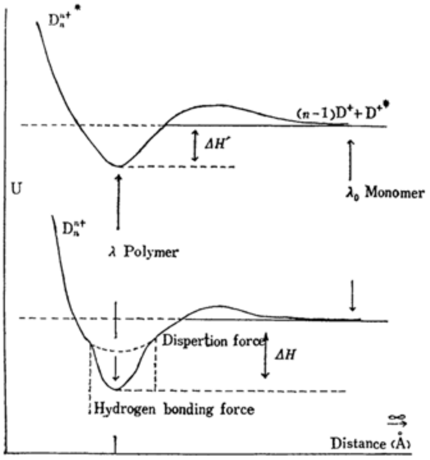

Fig. 5. The assumed Morse-curve of the polymers of the mono-protonium cations of a condensed aromatic compound in concentrated sulfuric acid.

absorption band at 580 mμ, which corresponds to the optical absorption of the octamer, decreases, while that at 710 mμ, corresponding to the monomer, increases. This may be understood as being due to the thermal decomposition of the polymers. The values of $\log k$ at temperature of 20, 45 and 70°C are 28.5, 25.4 and 22.3 respectively. From the above temperature dependency of the equilibrium constant, the heat of the association of the octamer of dibenzopyrene in concentrated sulfuric acid is estimated to be 54 kcal./mol. from the following equation (Eq. 3):

$$\Delta H = \frac{\boldsymbol{R} T_1 T_2 \ln k_2/k_1}{T_2 - T_1} \tag{5}$$

where k_1 and k_2 are association constants at temperatures of T_1 and T_2 respectively. The value of the entropy may be estimated, for the association of the dibenzopyrene octamer, as 47 cal./mol. deg.

From these experimental results, the equilibrium constants of isoviolanthrone at temperatures 20, 45 and 70°C are determined to be 3.4, 3.0 and 2.7 respectively. Therefore, the heat of association for this molecule is roughly estimated as 6.4 kcal./mol.

Discussion

The foregoing results suggest that the formation of the associates of complexes among sulfuric acid and the condensed polycyclic aromatic hydrocarbons and their related quinones are divided into three types. The first type exhibits a blue-shift of the absorption-peaks of the spectra of the associates and forms the higher associates in successive steps with the increase in the concentration of the solute. A typical example is the case of doubly protonated dibenzopyrene in 96 per cent sulfuric acid.

The second type does not exhibit any blue-shift of the absorption-peaks of the spectra of the associates but forms one kind of associate with a definite degree of association and does not form the higher associate with the increase of the concentration of the solute. Examples are singly protonated dibenzopyrene in 86 per cent sulfuric acid and singly protonated anthraquinone in 96 per cent sulfuric acid. The third type forms no associate. An example of this is benzoanthrone in 96 per cent sulfuric acid.

Concerning the cause of association, we may imagine, firstly, the London-type dispersion force and, secondly, a hydrogen bonding-like force among proton and oxygen atoms. It is very uncertain whether or not such forces are exerted on monomers in a strongly polarized solvent. Rabinowitch and Epstein have ascribed the cause of the dimerisation of thionine molecules in water and ethanol to the London-type dispersion force and have estimated the stable intermolecular distance, r_0, by assuming that the minimum potential energy, U_0, in the Morse curve is approximately equal to the heat of association.

When we ascribe the cause of the association in the case of doubly protonated dibenzopyrene with the association degree of 8, to the London-type dispersion force, we can estimate the mean intermolecular distance, r_0, as do Rabinowitch et al.*, on the assumption that the heat of association per pair of the octamer or $\Delta H/7$ is equal to the minimum potential energy, U_0, in this case. The estimated value of r_0 is approximately 3.2 Å when we put the experimental oscillation-strength, f, as equal to 0.53 and λ as equal to 6825 Å, which figures are estimated from the absorption spectrum, and the refractive index of the solvent, n as 1.44.

This is a reasonable value compared with the one estimated in the case of the dimerization of thionic molecules studied by Rabinowitch et al. and compared with the van der Waals radii of the aromatic molecule in the solid state.

When we assume the experimental heat of association to consist of only the dispersion energy in the case of the singly protonated dibenzopyrene (where no blue-shift is observed dimerization), the intermolecular distance, r_0, is estimated to be ca. 2.6 Å, which is considered to be unreasonably small. This is also the

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$$\partial U/\partial r = 0 \tag{1}$$

$$U_0 = -1.74\times10^{-7} f^2 \lambda_O{}^3/r^6 - 3.287\times10^{-10} f^3 \lambda_O{}^4/r^8 - 5.825\times10^{-13} f^4 \lambda_O{}^5/r^{10} + 330/D_r + x/r^{12} \tag{2}$$

$$f \risingdotseq 4.32\times10^{-9}\times n\int \varepsilon\, d(1/\lambda) \tag{3}$$

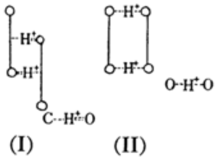
TABLE I

Name of substance	pK	Degree of polymerization	log K*1	f*2	λ_0 Å	H*3 kcals./mol.
p-Naphthoquinone	−7.5	1.7	1.9	0.21	4100	
Anthraquiaone	−7.5	4.1	12.3	0.39	4100	ca. 23
Anthanthrone	−7.4	1.9	2.5	0.24	6360	
Isoviolanthrone	−6.8	1.85	3.2	0.27	7170	6.4
Anthron	−6.5	16	60	0.59	3500	ca. 114
Dibenzopyrene (I)	−5.0	2.0	3.3	0.34	5800	
Dibenzopyrene (II)	−7.4	7.8	28.5	0.30	7100	54.5

*1 log K: The equilibrium-constant at 20°C.
*2 f: The empirical oscillator-strength obtained from the graphs.
*3 H: The experimental heat of the association.

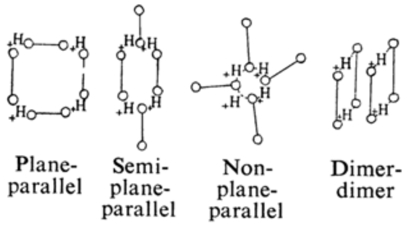
case for isoviolanthrone in 96 per cent sulfuric acid. In this case, the r_0 is estimated to be ca. 2 Å, as it is in the cases of anthraquinone, anthanthrone, p-naphthoquinone and anthrones.

These intermolecular distances are considered to be unreasonably small. In these compounds, we can not observe the blue-shift of the absorption-peak of the monomers.



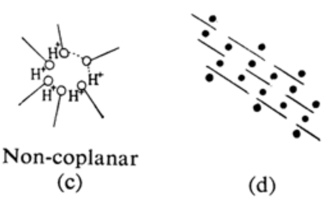
(a)

Isoviolanthrone (I)
Anthanthrone (II)
Mono-protonium cation dimer



(b)

Various configuration of tetramer of anthraquinone-mono-protonium cation.



(c) (d)

Fig. 6. The assumed configuration of several polymers of polycyclic aromatics: Mono-protonium cation dimer of isoviolanthrone and anthanthrone (a), tetramer of anthraquinone-mono-protonium cation (b), 16th-mer of anthrone mono-protonium cation (c) and octamer of dibenzopyrene diprotonium cation (d).

○ Oxygen atom ● $H_3^+SO_4$ ion
—— Dibenzopyrene (d)

Therefore, it may be necessary to assume some force like the intermolecular hydrogen-bonding which such combinations as O···H$^+$···O, C···H$^+$···O and C···H$^+$···C exert within a certain range of the intermolecular distance in the Morse curve, in addition to the dispersion force as illustrated in Fig. 5, in the strongly polarized environment with both positive and negative charges. The experimental heat of association may be put approximately as the sum of the potential energy, U', of the dispersion force and the heat of the formation of the weak intermolecular hydrogen-bonding, U''.

In the case of the related quinones, the effect of the intermolecular hydrogen-bonding, O···H$^+$···O and O$^+$···H···O, may be considered to play an important role in the association compared with the effect of the dispersion force. The amount of the hydrogen-bonding may be estimated as 2∼4 kcal./mol., assuming the state of the existence of polymer to be as is illustrated in Fig. 6.

In the case of benzoanthrone, the term from the electrostatic repulsive energy among those positive charges in the carbon skelton which are caused by the larger basicity of the molecule might play an important role in the above considerations.

Summary

The effect of the concentration on the absorption spectra of condensed polycyclic aromatic hydrocarbons and their related carbonyl derivatives in concentrated surfuric acid was studied in the concentration range from 10^{-6} to 10^{-3} mol. per liter. The free energies and heats of formation of these associates were also measured.

In the case of the dibenzopyrene molecule in 96 per cent sulfuric acid, it is observed that various kinds of association, such as 8, 16 etc., were obtained in successive steps with the

increase in the concentration of the solute, while in the case of carbonyl derivatives, only one kind of associate was observed, the number of degree of association of which was observed to be 2, 4 and 16.

In the case of dibenzopyrene in 96 per cent sulfuric acid, where it is believed to be doubly protonated, the cause of association might be explained by the dispersion effect, while the blue-shift of the absorption peak of the monomer is clearly observed in successive steps succession with the increase in the concentration of the solute.

However in the case of carbonyl derivatives and dibenzopyrene in 86 per cent sulfuric acid, where they are singly protonated, it is observed that they do not show any blue-shift of their absorption peaks but a lowering of the extinction coefficient.

As is illustrated in Table I, their experimental heat of association may possibly not be explained by the dispersion effect alone. It may be necessary to take into consideration some kind of hydrogen-bonding between the carbonyl oxygen atoms and the proton.

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