On the Color-reactions of the Condensed Polycyclic Aromatic Hydrocarbons and their Related Quinones in the Solutions of the Concentrated Sulfuric Acid

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Introduction

The condensed polycyclic aromatic hydrocarbons and their related quinones develop deep beautiful color from yellow to green in the concentrated sulfuric acid. It is understood that these reactions are ascribed to the interaction between the π-electrons of these compounds and the protons in the sulfuric acid, and with the under-standing that these reactions are those of the so-called " between acids and bases " in the sense of Brönsted, the basicity of these compound is evaluated in terms of Hammett's pK_B-values by varying the acidity of the sulfuric acid, and measuring the adsorption-spectrum of these compounds at various concentrations of the acid after the method of L. P. Hammett, with the assumption that the equilibria are obtained between bases and their complexes with protons in the sulfuric acid.

Experimental

The measurement of the absorption-spectra was done with Beckmanntype spectrophotometer, with quartz-cell of which dimensions were $1.0\times 1.0\times 3.0\,\mathrm{cm}^3$, at room temperature. The evaluation of pK-value was done after the method of L. P. Hammett[1], and reasonably the same result was obtained with anthraquinone, of which value was described on the Table V. On this account, this method of measurement is extended to the longer side of the visible region of spectrum, although, owing to the low dispersion of spectrum in this region, the accuracy of the measurement was not so good. The concentrated sulfuric acid used in this measurement was the commercially chemical pure product, not having any traces of peroxides, or nitric acid, or any impurities in the visible region of spectrum in which the measurement had been carried out. The specimens used in this measurement were as follows: perinaphthoindenone (I), benzoanthrone (II), *p*-naphthoquinone (III), anthraquinone (IV), naphthacene-

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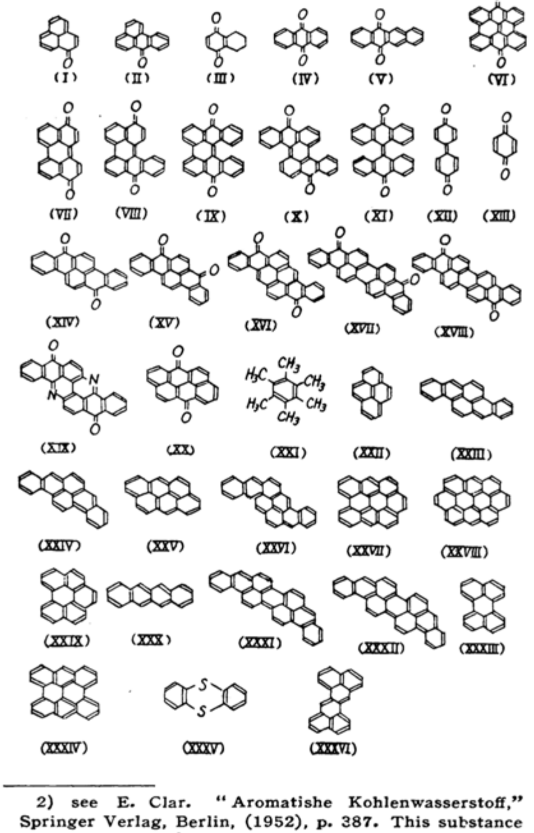
[1] Leo. A. Flexser, Louis P. Hammett and Andrew Dingwall, *J. Am. Chem Soc.*, **57**, 2103 (1935).

buinone (V), mesonaphthodianthrone (VI), 3, 10-perylenequinone (VII), 1, 2-benzoperylene-3, 10-quinone, (VIII), helianthrone (IX), 1, 2, 7, 8-dibenzoperylene-3, 9-quinone (X), dianthrone (XI), diphenoquinone (XII), *p*-benzoquinone (XIII), dibenzopyrenequinone (XIV), isodibenzopyrenequinone (XV), pyranthrone (XVI), violanthrone (XVII), isoviolanthrone (XVIII), flavanthrone (XIX), anthanthrone (XX) hexamethylbenzene (XXI), pyrene (XXII), dibenzopyrenee (XXIII), isodibenzopyrene (XXIV), pyranthrene (XXV), anthanthrene (XXVI), dibenzocoronene (XXVII), ovalene (XXVIII), benzoperylene (XXIX) tetracene (XXX), violanthrene (XXXI), isoviolanthrene (XXXII), perylene (XXXIII), mesonaphthodianthrene (XXXIV), thianthrene (XXXV), zethrene (XXXVI)[2]. The structual formula of these compounds is illustrated on the Table I. These compounds are synthesized after the usual manner described in the literature of this subject. They were recrystallised from preferable sorts of solvents, for instance, 1-methylnaphthalene and were further purified by the repeated sublimation in *vacuo* at 10^{-3}–10^{-4} mm Hg[3]. Each of these compounds was extremely fine, even from the view-point of spectroscopy. The solutions of these compounds used in this measurement were prepared, at first, by dissolving from 4 mg. to 7 mg. of specimens in the concentrated sulfuric acid of which concentration was known, and after that, by diluting the original standard solutions with sulfuric acid of the same quality to the appropriate concentration of both specimens and acidity for the measurement. Beer's law was held for these kinds of specimens and for this method of the preparation of the solutions. It is not necessary to consider the effect of sulfonation at room temperature during the time of measurement after certifying the fact that the filtrate of the diluent of the original solution with aquo., is clear, having no extinction of light in the visible region, and the effect of the influence of peroxides is eliminated with the fact that the evidence for the non-existence of peroxides is certificated by iodometry and the color of the solutions are quite different from those of the corresponding quinones in the cases of hydrocarbons.

TABLE I

STRUCTURAL FORMURA OF SPECIMEN USED IN THIS EXPERIMENT



The state of the existence of these complexes may be considered to be the following form, that, with ketones or quinones each proton (H^+) is attached to the carbonyl group and forms hybride resonance between $(\rangle C=OH)^+$ and $(\rangle\!\!\rangle C-\ddot{O}-H)^+$. It was partially supported by the cryoscopic method to measure the depression of the freezing point of the 100% sulfuric acid by L. P. Hammett and J. Dyrup[4]. It was partially supported by the fact that there exists equilibrium between bases and their complexes in the sulfuric acid, which is shown in Fig. 1 and Fig. 2, and it also exists between complexes and their reduced forms with chromous ion (Cr^{++}). Some of the shapes of the absorption-spectra of the fully reduced forms of the complexes are similar to those of the vatted forms of the original compounds $(\rangle\!\!\rangle C-O-H)$, which are shown in Fig. 3, with flavathrone.

For the state of the existence of the complexes between condensed polynuclear aromatic hydrocarbons and the protons (H^+) in the sulfuric acid, it may be reasonable to consider that there exist equilibria between hydrocarbons (bases) and their complexes. It will be supported empirically from the shapes of the absorption-spectra in various degrees of the acidity of the sulfuric acid, which meet nearly at one definite wavelength with a little correction, considering the solvent effect and which vary regularly showing the so-called existence of equilibria between bases and their complexes, as is shown in the cases of quinones, which are illustrated in Fig. 5 and Fig. 6 and Fig. 7. The absorption-spectra of these compounds in the concentrated sulfuric acid shift towards the longer side of the visible region compared with those of the original ones taken in the non-polar solvents, for instance, 1-methylnaphthalene. For these reasons above mentioned, it may be reasonable to consider the existence of equi-

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[2] see E. Clar. "Aromatishe Kohlenwasserstoff," Springer Verlag, Berlin, (1952), p. 387. This substance was not used in this experiment. It was previously reported in this paper that it was very basic.

[3] Purification of specimens was done by H. Inokuchi in our laboratory, to which the author's sincere thanks are due. H. Inokuchi, This Bulletin, **24**, 222 (1951).

[4] L. P. Hammett and J. Dyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932); ibid., **55**, 1900 (1933).

libria between these compounds and their complexes with protons in the sulfuric acid, and estimate the basicity as the function of pK_B from the absorption curves after L. P. Hammett, putting that;

$$C = C_B + C_{BH^+} \qquad (1)$$

$$\varepsilon = \log I_0/I/dc \qquad (2)$$

$$C_{BH^+}/C_B = \frac{\varepsilon_{BH^+} - \varepsilon}{\varepsilon - \varepsilon_B} \qquad (3)$$

$$pK_B = -\log \frac{a_{H^+} a_B}{a_{BH^+}} \qquad (4)$$

$$H_0 = -\log (a_{H^+}) \qquad (5)$$

$$H_0 = pK_B - \log C_{BH^+}/C_B \qquad (6)$$

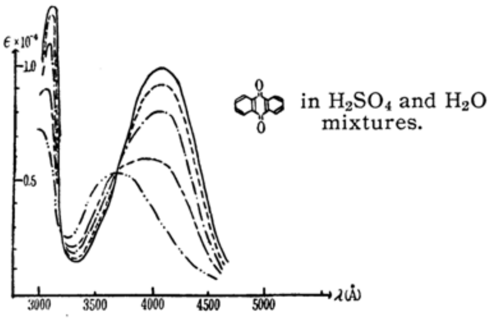
C; Molar concentration of specimen, suffix B means unprotonated base, BH^+ means protonated base.

ε; Molar extinction-coefficient of specimen.

a; Molar activity coefficient of each component.

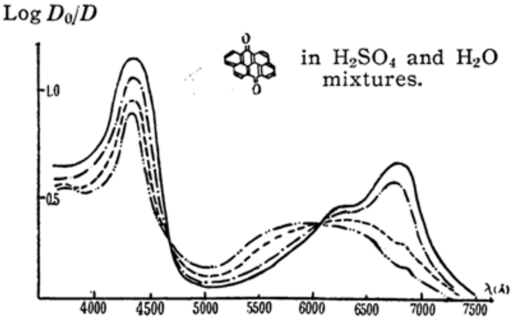
H_0; Logarithm of the activity of the hydrogen ion.

H_0 being the Kolthoff's acidity-function which really means the value of $\log a_{H^+}$. Equation (2) means that Beer's law is held. K is the dissociation constant of the ionized base. So from the equation from (1) to (6), the base-strength pK_B is defined. The pK_B of each of these compounds have been estimated in this manner. Among the results obtained, for instance, the result for anthraquinone was in good agreement with that of L. P. Hammett. The former value is -7.5, the latter is -8.0. In this case the absorption curves are corrected approximately against the influence of the solvent-effect by the lateral shift of spectrograph with the isobestic-point or the sharp peak of the absorption-curve as standards after L. P. Hammet. The small difference of pK_B to that of L. P. Hammett was found, when the Kolthoff's table was used unlike in the case of him, who had used his own table. In this sense the result obtained agreed well with that of L. P. Hammett. The absorption-spectra of anthraquinone in various acidity of sulfuric acid is illustrated in Fig. 1.



——— 100% H_2SO_4 – – – – – – 89% H_2SO_4
– – – – – – 96% H_2SO_4 —·—··— 86% H_2SO_4
—·—·— 93% H_2SO_4

Fig. 1. The absorption spectrum of anthraquinone in H_2SO_4 and H_2O mixtures (corrected by the lateral schift).



——— 100% H_2SO_4 – – – – – – 92% H_2SO_4
—·—·— 96% H_2SO_4 —··—·· 85% H_2SO_4

Fig. 2. The absorption spectrum of anthanthrene in H_2SO_4 and H_2O mixtures (corrected by the lateral schift).

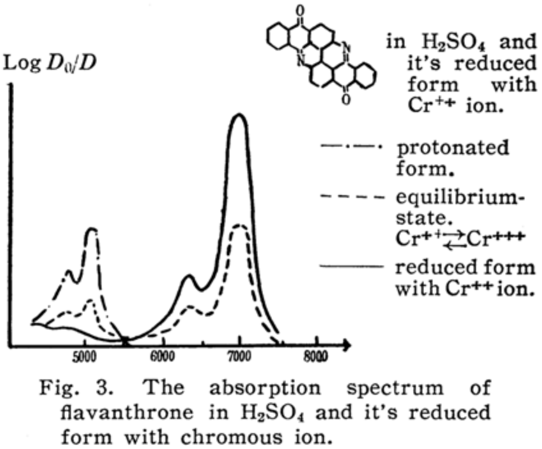


Fig. 3. The absorption spectrum of flavanthrone in H_2SO_4 and it's reduced form with chromous ion.

Another example in the longer side of the visible region is illustrated with anthanthrone of which pK_B is estimated on the Table II, and of which absorption-curves are shown in Fig. 2. The state of existence of equilibrium between the complex and it's reduced form with chromous ion (Cr^{++}), which suggests the nature of this type of complex, is shown in Fig. 3, with flavanthrone in which protons (H^+) may be assumed to be attached to both the carbonyl group and nitrogen atoms. In Fig. 3, curve (I) shows that of the completely reduced form, curve (II) shows that of the complex-form which may be called the oxidized form, With other complexes of quinones, they may be said to be similar to those of the vatted states, which are shown in Fig. 4. With mere hydrocarbons in this series, the same may be said as those of quinones. However, in these cases, it will be necessary to consider how many numbers of protons are attached to the hydrocarbon molecule and to what positions in the molecule they are attached. In this report, we have as-

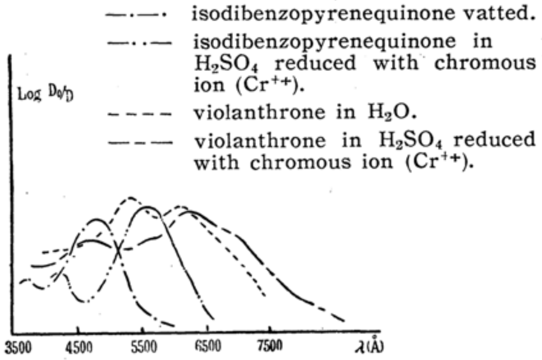


Fig. 4. The absorption spectra of isodibenzoquinone and violanthrone vatted in H_2O, and reduced with chromous ion (Cr^{++}) in H_2SO_4.

TABLE II
pK_B VALUES FOR ANTHANTHRONE BY ISOBESTIC-POINT METHOD

Wave-lenghth (Å)	Optical density in H_2SO_4 and H_2O mixtures 100%	96%	92%	85%	pK_B*	pK_B**
6500	0.50	0.45	0.36	0.31	−7.6	−7.5
6600	0.56	0.51	0.34	0.25	−7.5	−7.7
6700	0.63	0.55	0.30	0.20	−7.7	−8.0
6800	0.66	0.55	0.26	0.15	−7.8	−8.1
6900	0.58	0.44	0.22	0.12	−8.0	−8.1
7000	0.38	0.28	0.17	0.09	−8.1	−8.0
				average	−7.8	−7.9
		Total average			−7.8	

* means the pK_B values from the absorption-curves observed in 96% H_2SO_4 and 100% H_2SO_4. It is assumed that in 100% H_2SO_4 the specimen is completely protonated.

** means the pK_B values from the absorption-curves observed in 92% H_2SO_4 and 100% H_2SO_4.

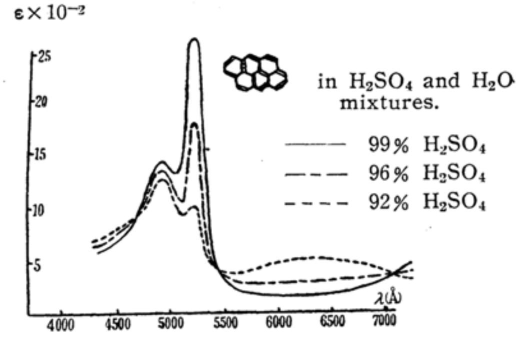


Fig. 5. The absorption spectrum of anthanthrene in H_2SO_4 and H_2O mixtures (corrected by the lateral schift).

sumed the numbers of protons attached or dispatched from the hydrocarbon molecule reversibly, empirically from the shapes of the absorption-curves of the complexes in the acid, as is shown in Fig. 5 and Fig. 6 and Fig. 7, which are considered to be in equilibria with the original hydrocarbons. These are usually one, and in several cases two protons which contribute to pK or basicity. The problem, to what positions in the molecule the protons are attached can not be discussed in this method of measurement. Even, it may be inferred from the whole result of this report as follows; they may be attached to the positions in the molecule where the π-electrons are localized. In Fig. 5 which is the case of anthanthrene molecule, it is shown from it's shapes of absorption-curves as in the case of quinones, that there exist equilibrium between hydrocarbon and its complex. There exist three isobestic-points above 4000Å which support the existence of equilibrium-state and in this case in one definite range of wave-length between the isobestic-points, there is only mere increase or decrease of extinction of light with the elevation of the concentration of the acid. In this case, it is assumed that there is only one proton which takes parts in the complex-formation, or in other words, there is only one phase of substance or complex. In Fig. 6 which is the case of dibenzopyrene (XXIII), there are also isobestic-points, but in this case in one definite range of wavelength from 5000 to 6000 Å, there are both increase and decrease of extinction of light with the elevation of the degrees of acidity. In this case, it is assumed that there exist two final states of complexes (one-proton-complex, and two-proton-complex in the sense mentioned above.). The complex-formation proceeds by two steps in this case. On the Table III, the evaluation of pK is shown with violanthrene. In every case, when we add very small amounts of chromous ion (Cr^{++}), the shape of the absorption-curve changes, there stands another peak towards the shorter side of the spectrum, which seems to be in equilibrium with the former one, and the solution be comes to possess fluorescence. But, it is not studied quantitatively here. In this report, the color-change of a specimen is described, when Cr^{++} ion is added, on the Table IV. This color-change is reversible, when hydrogenperoxide or free radical is added.

TABLE III
pK_B VALUES FOR VIOLANTHRENE BY ISOVESTIC-POINT METHOD

Wave-lenghth (Å)	Extinction-coefficient in H_2SO_4 and H_2O mixtures ($\varepsilon\times10^{-4}$) 99.5%	96%	92%	85%	pK_B
6500	27.5	26.5	25.5	18.0	
6600	27.0	26.0	25.0	18.0	
6700	26.3	25.5	24.5	17.6	−7.0
6800	33.0	30.0	26.0	16.3	−7.4
6900	44.0	40.0	34.0	18.0	−7.4
7000	62.0	56.0	45.0	21.0	−7.4
7100	74.0	66.0	56.0	23.0	−7.4
7200	60.0	52.0	41.0	21.0	−7.3
7300	32.0	30.0	26.0	16.0	−7.1
7400	21.0	20.0	18.0	13.0	−7.0
				average	−7.2

TABLE IV

THE COLOR-REACTIONS OF CONDENSED POLYNUCLEAR AROMATIC HYDROCARBONS AND THEIR RELATED QUINONES IN THE CONCENTRATED SULFURIC ACID

Index No. of structural formula of specimen	Name of specimens	Color-change in H_2SO_4 $(+H_2O_2)$	$\rightleftarrows$ (Cr^{++})
XX	anthanthrene	green	red brown
VI	mesonaphthodianthrene	red viollet	colorless
XIV	dibenzopyrenequinone	viollet	pale brown
IX	helianthrone	orange	greenish yellow
XVIII	violanthrone	red viollet	green
XVIII	isoviolanthrone	green	blue
XVI	pyranthrone	blue	orange-red
XV	isodibenzopyrenequinone	dark orange	red-viollet
XIX	flavanthrone	orange	green
	indanthrone	dark brown	pale brown
	perylene-tetracerboxylic acid	scarlet	green
XXXI	violanthrene	blue green	sky blue
XXXIII	perylene	green red viollet	blue green
XXVIII	ovalene	green	red viollet
XXVII	dibenzocoronene	dark green	red viollet
XXXV	thianthrene	red	colorless
XXIII	dibenzopyrene	blue-green	red violet
II	benzanthrone	red	red (No Change)

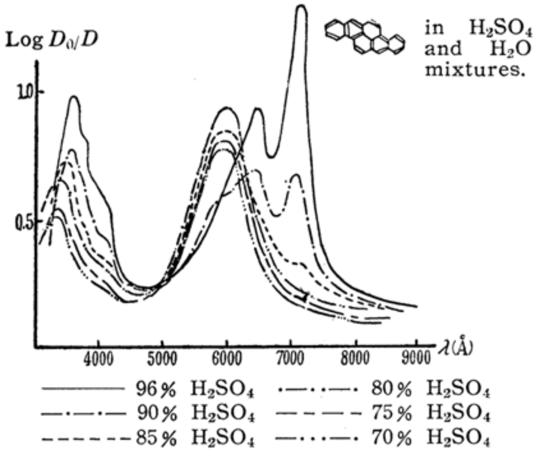


Fig. 6. The absorption spectrum of dibenzopyrene in H_2SO_4 and H_2O mixtures.

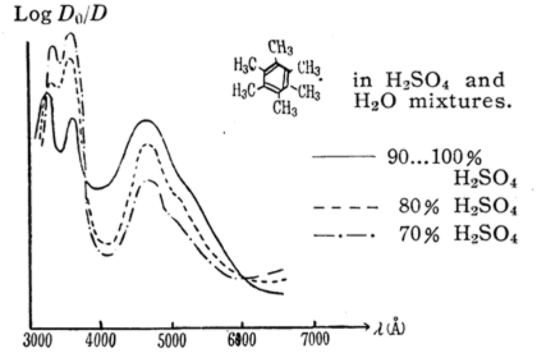


Fig. 7. The absorptionspectrum of hexamethylbenzene in H_2SO_4 and H_2O mixtures (corrected by the lateral schift).

Results and Discussions

The estimated pK_B with various condensed polynuclear aromatic hydrocarbons and their related quinones are shown on the Table V. It seems from that table that pK_B becomes smaller as the molecular-weight becomes larger. However, as in the case of dibenzopyrene, there exist two values of pK_B which means that two protons actually take parts in the complex-formation. The smaller value is −7.4, which is comparatively equivalent to that of anthanthrene, ovalene, dibenzocoronene, etc. The relatively larger value is −5.1, which is equivalent to hexamethylbenzene, pyrene, tetracene. To explain the contradiction between the experimental results, and the general understanding which suggests that the basicity or freee energy of complex-formation becomes larger as the molecular weight increases, it may be reasonable to think that the smaller value of anthanthrene, ovalen, dibenzocoronene, which are found in the experiment is the smaller one of the two pK_B values, the larger one not being able to be found in this measurement, perpaps owing to the low solubility or unstability of these compounds in the sulfuric acid. In the case of smaller molecules such as hexamethylbenzen, or tetracene, it may be considered that one proton takes part in the complex-formation. In the case of larger molecules such as anthanthrene,

TABLE V

pK_B VALUES FOR CONDENSED POLYNUCLEAR AROMATIC HYDROCARBONS AND THEIR RELATED QUINONES BY ISOBESTIC-POINT METHOD

Index No. of structural formura of specimens	Name of speciment	pK_B
I	peri-naphthoindanone	−0.4
II	benzanthrone	−3.2
III	*p*-naphthoquinone	−7.2
IV	anthraquinone	−7.5
V	naphthacenequinone	−8.4
VI	mesonaphthodianthrone	−6.0
VII	perylenequinone	−5.5
VIII	1.2-benzoperylene-3.10-quinone	−4.7
IX	helianthrone	−5.2
X	1.2.7.8.-dibenzo-3.9.-quinone	−5.1
XI	dianthrone	*
XII	diphenoquinone	**
XIII	*p*-benzoquinone	***
XIV	dibenzopyrenequinone	−7.4
XVI	pyranthrone	−6.0
XVII	violanthrone	−7.6
XX	anthanthrone	−7.9
XXI	hexamethylbenzene	−5.0
XII	pyrene	−4.7
XXIII	dibenzopyrene	−5.1 −7.4
XXV	anthantrene	−7.4
XXVI	pyranthrene	−8.2
XXVII	dibenzocoronene	−8.7
XXVIII	ovalene	−8.9
XXX	tetracene	−6.6
XXIX	benzoperylene	−8.3
XXXI	violanthrene	−7.3
XXXIII	perylene	−5.2****
XXXIV	mesonaphthodianthrene	−6.0*****

*, **, ***. It is not yet possible to measure the value owing to the destruction of specimens in the concentrated sulfuric acid.

****, *****. New trials are being attempted with other appropriate solvents and at low temperature.

ovalene, violanthrene, dibenzopyrene, it may be considered that two protones take part in the complex-formation. It may be thought that there is a relatively small difference of pK_B value with the shape of the molecule in such smaller molecules as hexamethylbenzene, tetracene etc., as in the cases of aza-aromatic hydrocarbons such as pyridine, quinoline, and acridine. When one proton is added to the molecule, the aromaticity for the rest of the molecule is reasonably destroyed and so the basicity corresponding to the next proton becomes much smaller than that corresponding to the first one, as in the case of diazine such as pyrimidine, pyrazine, cinnoline etc[5]. It may be possible, on the same way of consideration, to explain the difference of pK_B value, or the basicity between the monoketones such as perinaphhtoindenone, benzoanthrone, and quinones such as anthraquinone, violanthrone etc. In the cases of quinones, it seems unreasonable to consider that there exist two values of pK_B from the cryoscopic data of L. P. Hammett and J. Dyrup, who had determined the number of protons attached to the anthraquinone molecule from the depression of the freezingpoint of the sulfuric acid. However, in the present measurement, one value (−7.5) is found, which seems to be considerably smaller compared with that of benzoanthrone of which pK_B value is −3.2. To explain the considerably large difference, it may be considered that in the present measurement it is unable to find the larger one of two pK owing to the stability of one-proton-complex, or the low-solubility of that in the sulfuric acid. The relatively small difference between the pK values of various quinones may be ascribed to the molecular structure of each molecule. The relatively larger pK_B observed in violanthrene, mesonaphthodianthrene molecule compared with that observed in ovalene, anthanthrene molecule, suggests that the proton is easily attached to the molecule which is more or less easily excited, or which seems to have localized π-electron. Such sorts of molecules are known to have more or less localized π-electron from the magnetic study by H. Akamatu and Y. Matunaga in our laboratory[6]. It is reported by E. Clar that zethrene is easily soluble in the glacial acetic acid to be protonated by it, which means its pK_B is relatively very large, or it is relatively very basic compared with other hydrocarbons of this sort. It is explained that zethrene possesses localized π-electron from the standpoint of organic chemistry and may be a little para-magnetic, if measured. From this standpoint pentacene, and hexacene may be more basic than tetra-

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5) A. Albert, R. Goldacre and J. Phillips., *J. Chem. Soc.*, **1948**, 2240.

6) H. Akamatu and Y. Matsunaga, This Bulletin **26**, 364 (1953).

cene, if they are measured. In addition, the molecular extinction-coefficient of violanthrene in the sulfuric acid is about twenty times larger than that taken in non-polar solvent.

Summary

The basicity of the condensed polynuclear aromatic hydrocarbons and their related quinones with higher molecular weight have been measured after the method of L. P. Hammett and J. Dyrup, and it is approximately estimated in terms of pK_B. In dibenzopyrene molecule two values of pK_B have been found. The larger seems to correspond to that of the smaller molecules such as hexamethylbenzene, tetracene. The smaller one seems to be equivalent to that of ovalene, anthanthrene etc. approximately, with which molecules the larger pK_B value seems to be unable to be found, owing to the unstability or the low-solubility of them in the sulfuric acid in the present method of measurement. The relatively large difference of pK_B between monoketones and quinones seems to be explained on the same considerations as above. The relatively small difference of pK_B seems to be dependent on the molecular structure as in the case of azaaromatic hydrocarbons such as pyridine, quinoline and acridine. From the results of such series of molecules as violanthrene, mesonaphhtodianthrene, zethrene, compared with the series of circulartype of molecules such as ovalene, anthanthrene, it is suggested that the proton is more easily attached to the molecule which seems to have localized π-electron in some sense.

The author expresses his hearty thanks to Prof. H. Akamatu, who has directed him throughout this study and to Dr. Inokuchi and M. Kobayashi and to Mr. Matsunaga for their collaboration and advice in this study. The cost of this study was defrayed from the grant of the Ministry of Education, to which the author's thanks are due.

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