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The Absorption Spectra of Dyes. X.[1] Note on the Configuration of the Component Molecules in the Complex State*

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The configuration of the component molecules in the complexes formed between Chrysophenine G (G) and the direct dyes (P), such as Chlorazol Sky Blue FF, has been discussed qualitatively with respect to the relation between the steric structure of the individual P molecules and the enthalpy or the entropy changes in the complex formations. The electrons to be transferred from

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[1] Part IX of this series: T. Hoshi, Y. Tanizaki and N. Ando, This Bulletin, **38**, 725 (1965).

* Presented at the 7th Discussions on Dyeing Chemistry (May, 1965) held by the Chemical Society of Japan and the Society of Fiber Sience and Technology, Japan.

the partner (P) to the G molecule are the π electrons of the functional (hydroxy) groups and are those of the inner-side groups when the respective coupling components of the dye have more than one functional group. The larger the charge density of such an effective functional group becomes, the more the enthalpy change ($-\Delta H$) is increased. It may be said with certainty that there must exist a certain configuration of the component molecules peculiar to the complex formation. Such a configuration may be seen for the combination of G and ND (NW-acid←dianisidine→NW-acid). For other combinations of which the partner of G is more deformed in free than ND state, the shifts of equilibrium to the configuration for the complex state are almost due to an entropy change ($-\Delta S$) which increases in proportion to the magnitude of the deformation.

Hitherto in this series, the complex formation between the disazo direct dyes and Chrysophenine G has been studied.[1-4] According to the conclusion reached on the complex state, the component molecules are arranged side by side when the charge transfer from the partner (to be abbreviated as P) to the G molecule (Chrysophenine G) occurs[1,3]; that is, the π electron on the functional group of the P molecule transfers to the lowest vacant MO (π_G*) of G.[1] Since the charge transfer, as is well known, plays an important role in the intermolecular force, the enthalpy change ($-\Delta H$) for the complex formation should be directly affected by the π electron density of the functional group. Moreover, as the π electron possesses the directional property, there may exist a certain configuration of P and G suitable for a charge transfer. The shifts to such a peculiar configuration of the component molecules must be reflected in the entropy change ($-\Delta S$).

The purpose of the present study is therefore to consider the thermodynamic quantities qualitatively and in connection with the configuration. At the same time, a supplement to the previous discussion will be given, on the basis of the experimental results accumulated so far, regarding the configuration of the complexes formed.

Experimental

The experimental procedure and the treatment of the data obtained were the same as have been described before.[4]

The dyes used here were the symmetric disazo dyes prepared in the usual way from the following diazo and the coupling components, which will hereforth be called by the notations indicated in parentheses; benzidine (B), tolidine (T), dianisidine (D) and 3, 3'-dichlorobenzidine (Cl), and NW-acid (N), J-acid (J), SS-acid (S), H-acid (H) and chromotropic acid (C). A dye, for example, NW-acid←benzidine→NW-acid, will be represented by NB. CT and CCl were excluded because they could not be obtained in a pure enough form to indicate only one spot on the paper chromatograph. The other dyes, when combined with G, showed the spectral change corresponding to the 1 : 1 and 1 : 2 complex formations. However, there were some combinations for which the equilibrium constants for the complex formations could not be estimated for several reasons; some dyes with the first absorption peaks at 530 mμ or at shorter wavelengths were affected by the absorption tail of G at its higher concentrations; others when combined with G did not indicate large enough spectral changes at the isosbestic points for reliable equilibrium constants to be calculated, and so on. The estimated thermodynamic quantities are shown in Table I, in which 1 : 1 means the complex

TABLE I. ΔH kcal./mol. AND ΔS e.u. FOR THE 1:1 (P+G→PG) AND THE 1:2 COMPLEX FORMATIONS (PG+G→GPG)

		B		T		D*		Cl	
		1:1	1:2	1:1	1:2	1:1	1:2	1:1	1:2
N	ΔH	a)		c)		−7.4	−6.7	c)	
	ΔS					1	0		
J	ΔH	a)		c)		−13	−11	a)	
	ΔS					−19	−20		
S	ΔH	b)		g)		−24	−20	f)	−23
	ΔS					−44	−45		−50
H	ΔH	−18	e)	−19	e)	−25	−19	−26	−19
	ΔS	−37		−36		−57	−47	−57	−46
C	ΔH	−15	−11	d)		−27	−19	d)	
	ΔS	−29	−22			−60	−40		

* Taken from Ref. 4.

a) The isosbestic points due to the influence of the tail of G did not appear because the first absorption peaks of P's were at too short wavelengths (530 mμ).

b) The equilibrium constants could not be calculated because the spectral change corresponding to the 1 : 2 complex formation did not retain well-defined isosbestic points.

c) In spite of the indication of the well-defined isosbestic points due to the complex formations, the spectral changes corresponding to the 1 : 1 and the 1 : 2 complex formations at the 1 : 2 and the 1 : 1 isosbestic points respectively were too small for the equilibrium constants to be calculated.

d) The sample could not be purified so as to provide only one spot on the paper chromatograph as the other samples could.

e) The spectral change due to the 1 : 2 complex formation at the 1 : 1 isosbestic point was too small for K_2 to be calculated.

f) The spectral change due to the 1 : 1 complex formation at the 1 : 2 isosbestic point was too small for K_1 to be calculated.

g) The values obtained were extensively dispersed; for example, the $-\Delta H$ values were dispersed from −18 to −23.

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[2] T. Kobayashi, Y. Tanizaki and N. Ando, This Bulletin, **33**, 661 (1960).

[3] T. Kobayashi, K. Saito, Y. Tanizaki and N. Ando, ibid., **35**, 935 (1962).

[4] Y. Tanizaki, T. Hoshi and N. Ando, ibid., **38**, 264 (1965).

formation of the P+G→PG type, and 1 : 2, that of the PG+G→GPG type.

Results and Discussion

The thermodynamic quantities for the complex formations of 1 : 1 (P+G→PG) and 1 : 2 (P+2G →GPG) are summarized in Tables II and III for the D and the H series respectively. There can be discussed by means of the data in Table II the effect of the structural differences for the coupling components, and, by means of the data in Table III, that for the diazo components.

TABLE II. THE ENTHALPY AND ENTROPY CHANGES FOR THE D SERIES; ΔH_1, ΔS_1 FOR P+G→PG, AND ΔH_2, ΔS_2 FOR P+2G→GPG.

P	ND	JD	SD	HD	CD
ΔH_1, kcal./mol.	−7.4	−13	−24	−25	−27
ΔH_2, kcal./mol.	−14	−24	−44	−44	−46
ΔS_1, e. u.	1	−19	−44	−57	−60
ΔS_2, e. u.	1	−39	−89	−104	−100

TABLE III. THE ENTHALPY AND ENTROPY CHANGES FOR THE H SERIES; ΔH_1, ΔS_1 FOR P+G→PG, AND ΔH_2, ΔS_2 FOR P+2G→GPG.

P	HB	HT	HD	HCl
ΔH_1, kcal./mol.	−18	−19	−25	−26
ΔH_2, kcal./mol.	—	—	−44	−45
ΔS_1, e. u.	−37	−36	−57	−57
ΔS_2, e. u.	—	—	−104	−103

The Enthalpy Change.—It has been clarified that the lone pair electrons on the amino group of SS-acid (S) cannot conjugate to the naphthalene link due to the intramolecular hydrogen bond formation of the N···H–O type, as is shown in Fig. 1.[5] The π electrons of the hydroxyl groups must, therefore, be alone responsible for the SD→G charge transfer, provided the SD molecule allows of the above-mentioned situation for S. On the other hand, all the amino and/or the hydroxyl groups of H and C have π type lone pair electrons, because of the hydrogen bond formation in the N–H···O or O–H···O form respectively (Fig. 1).[5] That is, the HD and the CD molecule have twice as many functional groups with π type lone pair electrons as the SD molecule. According to Table II, however, the ΔH's of SD, HS and CD are nearly in the same order. This suggests strongly that only the π electrons of the internal functional groups (the hydroxyl groups) of P are responsible for the charge transfer. The reason why the π electrons on the end functional groups attached to the outside ring of naphthalene are ineffective could not be found. At any rate, the internal hydroxyl groups will be discussed with the above facts in mind.

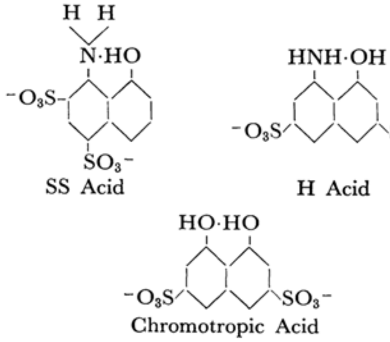

Fig. 1. The type of the hydrogen bonding of SS acid, H acid and chromotropic acid.

The effective functional groups of the P dyes used here are, therefore, just the hydroxyl groups. According to the findings described above, it ought to be possible to explain the relative magnitude of $-\Delta H$ in connection with the π electron densities of such hydroxyl groups. The relative π electron density will be comparable with that of the total charge density in the usual sense. It can be said that the larger the charge density of the hydroxyl group, the more the difficulty of the proton dissociation of the group. The order of the starting pH value for the dissociation of the hydroxyl groups has been found to be C(4.2) < J(5.6) < N(6.2) < S(8.0) ≑ H(8.4), where the figures in parentheses indicate the approximate pH values.[5] As the solvent water used here had a pH value of 6, nearly a half of C and also a small amount of J could be dissociated in the solution. Accordingly, the plausible order of the charge density is N < J ≑ S < H < C in the solution. If it is assumed that the condition of the hydroxyl groups is preserved because of the same coupling positions of the components,* the charge densities of the hydroxyl groups of the P dyes in the D series may plausibly be arranged in the same order as that of the coupling components, i. e., (ND) < JD < SD ≑ HD ≑ CD. Indeed, the order just mentioned corresponds well—including ND—with that of the magnitude of the $-\Delta H$'s in Table II.

In the H series, the coupling component, H-acid, is the common ingredient; therefore, the kinds of substituents at the 3,3′ positions of the biphenyl skeleton must be correlated with the charge density on the hydroxyl groups. The resonance effect of the substituent will hinder the electron of the hydroxyl group from migrating to the inner conjugate system. If this is the case, the π electron density of the hydroxyl group

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[5] Y. Tanizaki, H. Inoué and N. Ando, This Bulletin, **38**, 1419 (1965).

* This assumption is adequate except in the case of ND, because, as will be shown in the following section, all of the dyes in the D series but ND are affected by some steric effects and, consequently, the relative situation of the charge densities of the hydroxyl groups could not be altered. At present, however, no reason can be found for arranging ND on the left side as above.

will be larger in the case of HD and HCl than in that of HB and HT. Consequently, the transition probability of P→G in the former case will become larger than in the latter. In fact, the order of the magnitude of $-\Delta H$'s in Table III comes up to this expectation.

The above consideration can equally be applied to both the PG (1 : 1) and the GPG (1 : 2) complexes.

In the 1 : 2 complex state, the two G molecules have been considered to be equivalent to one another.[1,2] This is not inconsistent with the magnitude of the ΔH values obtained here, because, for all cases, the $-2\Delta H_1 > -\Delta H_2$ relation is always maintained.

Entropy Change.—First of all, concerning the ΔS value, it is interesting to notice the following relations which appear in Table II;

for the ND–G system: $\Delta S_1 \doteqdot \Delta S_2 \doteqdot 0$ (1)

for the JD–G and SD–G systems: $2\Delta S_1 \doteqdot \Delta S_2$ (2)

for the HD–G and CD–G systems: $-2\Delta S_1 < -\Delta S_2$ (3)

and for both ΔS_1 and ΔS_2 :

$$0 \doteqdot -\Delta S(\mathrm{ND}) < -\Delta S(\mathrm{JD}) < -\Delta S(\mathrm{SD}) < -\Delta S(\mathrm{HD}) \doteqdot -\Delta S(\mathrm{CD}) \quad (4)$$

Relation 1 implies that ND and G have not been suffered from any structural restriction by the complex formation; Relation 2, that the amount of deformation is equally distributed to the first (P+G →PG) and the second process (PG+G→GPG), and Relation 3, that the deformation is larger in the first process than in the second.

In order to enable the charge transfer to take place, the π_P orbital of the hydroxyl groups of P and the $\pi_G{}^*$ orbital of G must overlap with each other. Besides, the π_P orbital originally has a directional property, as has been described above. For that reason, both of the component molecules are required to change the configuration into that suitable for the above conditions.

Though all of the P dyes take similar chemical structures, some differences may be seen in the three-dimensional structures between them, i. e., the differences in the torsional angles about the bonds shown in Fig. 2, as R_0, R_1 and R_2 are dependent on the sort of coupling components, though R_0 and R_1 may be almost independent. In the case of ND (see Fig. 2), the hydrogen bond formation is possible ($R_2=0°$), while in HD the electrostatic repulsion between the negative charge on the sulfonic group and the lone-pair electrons of the azo group exceeds the sum of the hydrogen bonding force and the resonance force of the C–N bond, $R_2=50$—$60°$.[6] That to is say, the $R_2(\mathrm{ND}) \ll R_2(\mathrm{HD})$ relation can well be correlated to the $-\Delta S(\mathrm{ND}) \ll -\Delta S(\mathrm{HD})$ relation. Therefore, it may be expected that a parallelism exists between the order of the tortional angle, R_2, in the free state and that of the entropy change.

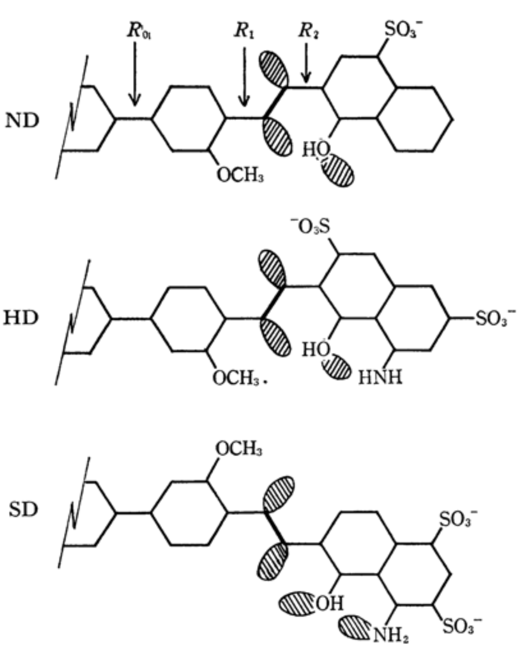

Fig. 2. Steric structures of ND, HD and SD; shadings indicate the σ type lone pair electrons.

Let us assume here that the ND molecule keeps the ideal conformation for the complex formation, because it can form the complexes without any entropy change. According to this assumption, the other P dyes have to become somewhat deformed in order to approach such an ideal conformation.

JD and CD have previously been considered to have nearly the same order of R_2 as HD.[6] However, JD has amino groups at the end β positions of the naphthalene links, while HD has these at the end α positions. The resonance effect of the amino group of J slightly increases the charge density at the opposite β position to be coupled with the diazo component, while that of the amino group of H cannot do that.[7] In the case of JD, therefore, the amino group could increase the resonance force of the C–N bond (R_2) and could also increase the charge density of the azo-nitrogen atom adjacent to biphenyl. For that reason, the R_2 angle of JD may become smaller than that of HD. The order of the torsion angles is considered to be as follows (R_2(SD) will not be considered here):

$$0° \doteqdot R_2(\mathrm{ND}) < R_2(\mathrm{JD}) < R_2(\mathrm{HD}) \doteqdot R_2(\mathrm{CD}) \quad (5)$$

Relation 5 coincides with Relation 4 except for

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[6] T. Kobayashi, Y. Tanizaki and N. Ando, ibid., **33**, 913 (1960).

[7] H. Baba and S. Suzuki, ibid., **34**, 82 (1961).

SD. If Relations 4 and 5 are parallel, it must be said that R_2(SD) can be positioned between R_2(JD) and R_2(HD), indicating that the R_2 of SD is also fairly large. This, together with the drawing of SD in Fig. 2, implies the existence of some repulsive force acting between the σ type lone-pair electrons of the hydroxyl group and those of the azo-nitrogen atom. The fact of the steric structure of SD just mentioned must be emphasized, because the conventional image of the SD molecule has been one in which an intramolecular hydrogen bond is formed like the ND molecule shown in Fig. 2, that, i. e., the R_2 angle of SD is zero.6)

In the H series, since R_0 and R_2 can be assumed to be invariant because of the common coupling components, the difference in the entropy change of Table III may be attributed to the difference in R_1 values. As may be seen from the drawing of HD in Fig. 2, the torsion of R_1 is mainly due to the electrostatic repulsion or the steric hindrance of the methoxy group in relation to the σ type lone-pair electrons of the azo-nitrogen atom. Also, in the case of HCl, a similar situation involving the chlorine atom can be taken into consideration. Such substituent effects may be larger for HD and HCl than for HB and perhaps for HT as well. The corresponding torsion angles R_1 for the former class will, therefore, become larger than those for the latter. Thus, the entropy change difference appearing in the two classes, (HB, HT) and (HD, HCl), can reasonably be explained.

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