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Kinetic Studies of Association and Dissociation Reactions of Congo Red by the Temperature-Jump Method

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The association of dye in an aqueous solution has been widely studied through the application of the polarograghic[1] or spectroscopical methods.[2-7] However, there is little information available concerning the kinetics of the association and dissociation reactions of dye.[8] The present study was undertaken in order to obtain kinetic and thermodynamic information concerning the association and dissociation of congo red by the use of the temperature-jump method.

Experimental

The techniques and apparatus used were fully described in a previous paper.[9] The temperature-jump, of about 4°C, was caused by discharging a 0.1 μF capacitor, charged to approximately 20 kV, through the solution. The wavelength of observation was 500 mμ. The congo red was kindly provided in an extremely pure form by Professor Suzawa.* The inoic strength of the solution was adjusted to $\mu=0.1$ by the addition of NaCl. All the solutions were prepared using distilled, air-free water in order to prevent the formation of air bubbles upon the discharge of the capacitor. The reciprocal relaxation time, τ^{-1}, was calculated from the plots of $-\log \Delta C$ *vs.* the time, where ΔC is the deviation of the concentration from its equilibrium value. The method of least-squares was employed to calculate the most probable values of the rate constants.

Results and Discussion

Table 1 shows the mean reciprocal relaxation times obtained from this study in the concentration range of 10^{-6} to 10^{-5}M at various temperatures. The dependence of the relaxation time on pH was not observed. This means that the observed relaxation phenomena are not associated with the hydrogen ion. Now, let us assume the following association-dissociation equilibrium at a low concentration of the dye:

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_2 \qquad (1)$$

Table 1. THE RECIPROCAL RELAXATION TIME AT VARIOUS TEMPERATURES

$C_0\times10^6$	$(1/\tau)_{av}$, sec^{-1}		
	13°C	17°C	22°C
1	—	93	—
2	62	118	—
3	69	142	182
4	66	133	183
5	67	162	213
6	62	153	231
7	68	141	244
8	67	174	259
9	73	171	253
10	89	196	—

where A and A_2 are the monomer and the dimer of the dye, and where k_1 and k_2 are the forward and backward rate constants respectively. The rate of association for this system is, then, given by:

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2] \qquad (2)$$

The reciprocal relaxation time is related to the rate constants and the monomer concentration at equilibrium, $[A]_0$, as follows:

$$\tau^{-1} = 4k_1[A]_0 + k_2 \qquad (3)$$

Equation (3) can be rewritten in terms of the total concentration, C_0, by the use of the $C_0=[A]_0+2[A_2]_0$ and $k_2/k_1=[A]_0^2/[A_2]_0=K$ relationships. Therefore,

$$\tau^{-2} = 8k_1k_2C_0 + k_2^2 \qquad (4)$$

where K is the equilibrium constant. Figure 1 shows plots of τ^{-2} *vs.* C_0. The rate constants were calculated from the intercepts and slopes using the least-squares method. These values are listed in Table 2.

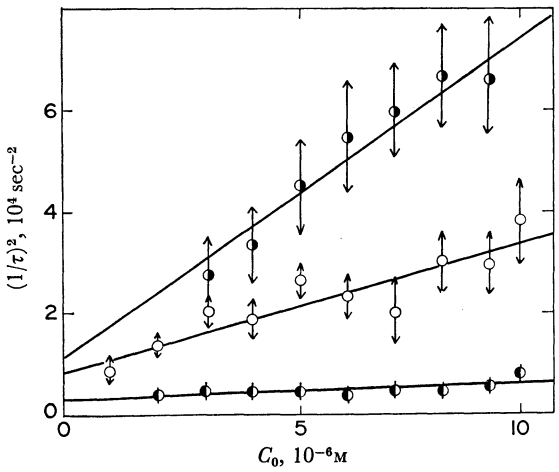

Fig. 1. The plots of $(1/\tau)^2$ *vs.* C_0 at various temperatures: ◐, 13°C; ○, 17°C; ◑, 22°C.

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Table 2. The kinetic values for the association and dissociation reaction of congo red at various temperatures

	13°C	17°C	22°C
k_1, 10^6 sec^{-1} M^{-1}	0.70±0.16	3.5 ±0.8	6.7 ±1.5
k_2, 10^2 sec^{-1}	0.55±0.05	0.92±0.10	1.2 ±0.2
K, 10^{-4} M	0.79±0.26	0.26±0.09	0.17±0.05

According to Eyring's rate theory, the rate constant, k_i, is related to the activation energy, the activation enthalpy and the activation entropy as is the next equation:

$$k_i = PT\exp\left(-\frac{\Delta F_i^*}{RT}\right) = PT\exp\left(-\frac{\Delta H_i^* - T\Delta S_i^*}{RT}\right) \quad (5)$$

where P is the constant, R is the gas constant, T is the absolute temperature, ΔF_i^* is the activation energy, ΔH_i^* is the activation enthalpy, and ΔS_i^* is the activation entropy. Figure 2 shows the plots of $\ln(k_i/T)$ *vs.* $1/T$. The activation enthalpies were obtained from the slopes, while the enthalpy change was calculated from

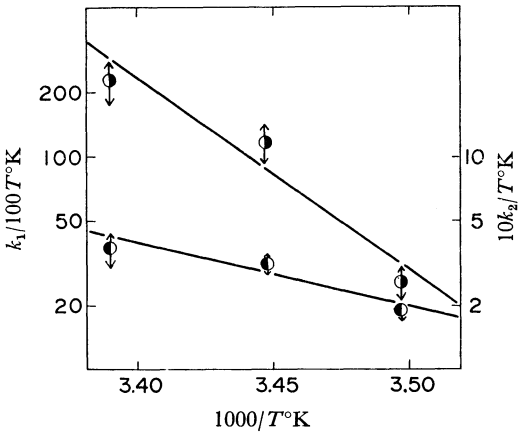

Fig. 2. Temperature dependence of rate constants in the association and dissociation reaction of congo red: ◑, k_1; ◐, k_2.

the difference between the activation enthalpies in the two states. Furthermore, the changes in the free energy and the entropy were calculated by the use of the $\Delta F = -RT\ln K$ and $\Delta F = \Delta H - T\Delta S$ relationships. These values are $\Delta H_1^* = 41$ kcal/mol, $\Delta H_2^* = 15$ kcal/mol, $\Delta H = \Delta H_1^* - \Delta H_2^* = 26$ kcal/mol, $\Delta F = \Delta F_1^* - \Delta F_2^* = -5.4$ kcal/mol at 13°C, -6.1 kcal/mol at 17°C, -6.5 kcal/mol at 22°C, and $\Delta S \cong 110$ cal/mol·deg.

The single relaxation phenomena and the linearity of the plots of τ^{-2} *vs.* C_0 show that the relaxation phenomena obtained in this study are attributable to the disturbance of the monomer-dimer equilibrium of congo red in the concentration range of 10^{-6} to 10^{-5}M. This proves that only the monomer and dimer of congo red exist in this concentration range at $\mu = 0.1$. In general, it has been reported that the polymerization of dyestuffs does not stop at the dimeric state, but often proceeds to trimers and higher polymers. Though even in the more concentrated solutions the relaxation spectra could be observed, they were not characterized by a single relaxation time. This shows that the higher polymers exist in the solutions of more than 10^{-5}M.

Only a few reports have been published containing thermodynamic information about the association of dyes.[4,7] It is, however, noteworthy that the changes in enthalpy and entropy obtained for the monomer-dimer equilibrium of congo red are large when compared with those obtained for other dyes.[4,7] The large change in entropy shows that the association and dissociation reactions of congo red are entropy-controled. The positive entropy change for dimer formation must be a consequence of the decreased structuring of the solvent about the dimers, and consequently the dimeric state must be stabilized with an increase in the temperature. As the congo red molecule, however, has a very complex structure, it is difficult to determine how dyes aggregate structurally. Further studies of analogous systems by relaxation methods will lead to a clarification of the aggregation mechanism of congo red.