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The Primary Process of the Photochemical Dimerization of Carbostyril (2-Quinolone) in an Aqueous Solution

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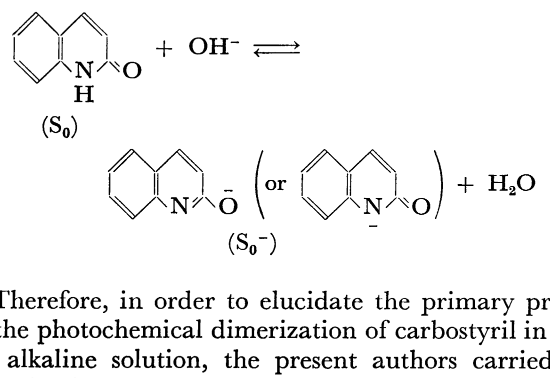
Carbostyril dimerizes photochemically in an aqueous solution, in order to investigate the effect of a hydroxide ion on the primary process of the photochemical dimerization in an aqueous solution, both measurements of the quantum yields and flash spectroscopic experiments were carried out under various conditions. The experiments revealed that the photodimerization reaction proceeded through a bimolecular interaction between the triplet and the unexcited carbostyril molecules, although the triplet carbostyrilate ion was in equilibrium with the triplet carbostyril. The triplet carbostyrilate ion was proved not to be involved in the dimerization process.

As has been described in a previous paper,[1] the photochemical dimerization of carbostyril in deaerated ethanol proceeds through a bimolecular interaction of the triplet carbostyril with the unexcited one. Such a photodimerization has also been reported to take place in an aqueous solution.[2] Meanwhile, the acid-base equilibrium between the carbostyril (S_0) and the carbostyrilate ion (S_0^-) in their ground states has been shown spectrophotometrically in alkaline aqueous solutions as follows:[3]



(1)

Therefore, in order to elucidate the primary process of the photochemical dimerization of carbostyril in such an alkaline solution, the present authors carried out investigations by means of measurements of the quantum yields and by means of flash spectroscopy.

Experimental

The carbostyril used in the experiment was prepared by treating quinoline *N*-oxide with tosyl chloride.[4] The product was purified by recrystallization from methanol several times. Standard specified solutions of sodium hydroxide (Yoneyama Yakuhin Co., Ltd.) were used as the solvents.

The light source employed in the steady-light experiments was a Toshiba high-pressure mercury lamp (H-400 P), while for the 313 nm irradiation a filter combination of a nickel sulfate solution with a UV-31 Toshiba filter was used. The measurements of the quantum yields were carried out by a procedure described previously.[1]

The flash photolysis apparatus was the same as was employed in the previous investigations.[1] The xenon flash lamp used for excitation was operated by discharging a bank of condensers of 1 μF charged to 14.75 kV, 109 joules of energy being dissipated; the duration time of the flash was 5 μsec.

Since the quantum yield of the disappearance of carbostyril was reduced to almost zero in the presence of oxygen in a solution, just as in the case of the ethanol solution,[1] all the experiments—both steady-light and flash spectroscopic—were performed on solutions deaerated by flushing nitrogen at room temperature.

Results

Figure 1 shows the absorption spectra of carbostyril in aqueous solutions containing different amounts of

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[1] T. Yamamuro, I. Tanaka, and N. Hata, This Bulletin, **44**, 667 (1971).

[2] O. Buchardt, *Acta Chem. Scand.*, **17**, 1461 (1963).

[3] G. W. Ewing and E. A. Steck, *J. Amer. Chem. Soc.*, **68**, 2181 (1946).

[4] E. Ochiai and T. Yokogawa, *Yakugaku Zasshi*, **75**, 213 (1955).

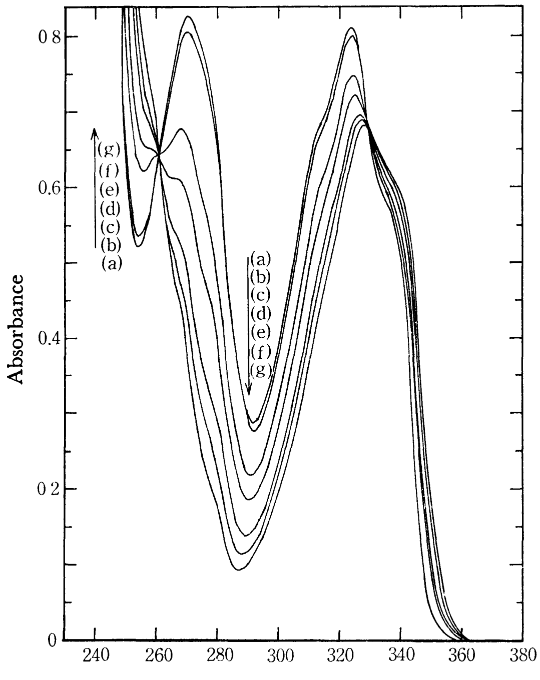


Fig. 1. Absorption spectra of carbostyril in aqueous solution containing different amounts of sodium hydroxide at room temperature (C: 1.23×10^{-4}M).
[OH$^-$]: (a) 0M, (b) 0.001M, (c) 0.01M, (d) 0.02M, (e) 0.05M, (f) 0.10M, (g) 1.0M

sodium hydroxide, where the isosbestic points were observed at 260.5 and 329.5 nm; that is, an acid-base equilibrium was indicated to exist between the carbostyril (S_0) and the carbostyrilate ion (S_0^-), as is represented by Eq. (1). In the present experiments, therefore, the concentrations of S_0 and S_0^- at equilibrium were evaluated by the following equations, respectively:

$$\begin{aligned}[S_0] &= C/(1+K_G[\mathrm{OH}^-])\\ [S_0^-] &= CK_G[\mathrm{OH}^-]/(1+K_G[\mathrm{OH}^-])\end{aligned} \tag{2}$$

where K_G represents the equilibrium constant, and C, the sum of $[S_0]$ and $[S_0^-]$. The equilibrium constant (K_G) was calculated by means of Eq. (3), where ε_λ or ε'_λ is the molar extinction coefficient of S_0 or S_0^- at the λ wavelength and where D_λ is the absorbance of a solution containing S_0 and S_0^-. Thus, the slope of the straight-line obtained by:

$$\frac{(\varepsilon_\lambda-\varepsilon_\lambda')C}{D_\lambda-\varepsilon_\lambda'C} = 1 + K_G[\mathrm{OH}^-] \tag{3}$$

plotting $(\varepsilon_\lambda-\varepsilon'_\lambda)C/(D_\lambda-\varepsilon'_\lambda C)$ against [OH$^-$], gave the value of K_G as 62.3M^{-1}.

Steady-light Experiments. The quantum yields (Φ) of the carbostyril disappearance were determined as a function of the concentration of a hydroxide ion in an aqueous solution ($C=1.23\times10^{-4}$M) at room temperature. Figure 2 shows the results thus obtained where the plot of Φ against [OH$^-$] was replaced by that of Φ *vs.* $[S_0]$. As may be seen from Fig. 2, the quantum yield increased very rapidly with an increase in the concentration of S_0 expect at very low concentrations of S_0, but at higher concentrations the quantum yield gradually approached about 0.2. Because of such a characteristic dependence of Φ on $[S_0]$, it is convenient for the subsequent discussion to divide the concentration range of S_0 into three regions, I, II, and III, as is indicated in Fig. 2. On the other hand, the quantum yield in water was 0.21, regardless of the concentration of S_0 ($\approx C$).

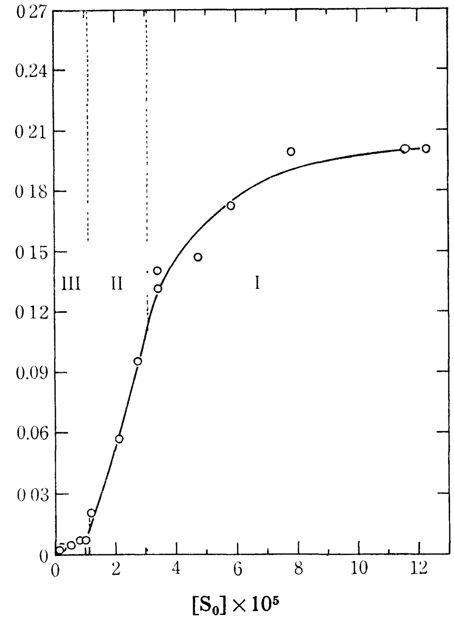


Fig. 2. Quantum yield of carbostyril disappearance *vs.* $[S_0]$ in alkaline aqueous solution at room temperature ($C=1.23\times10^{-4}$M).

Flash Spectroscopic Experiments. Figure 3 shows the T–T absorption of carbostyril in aqueous solutions con-

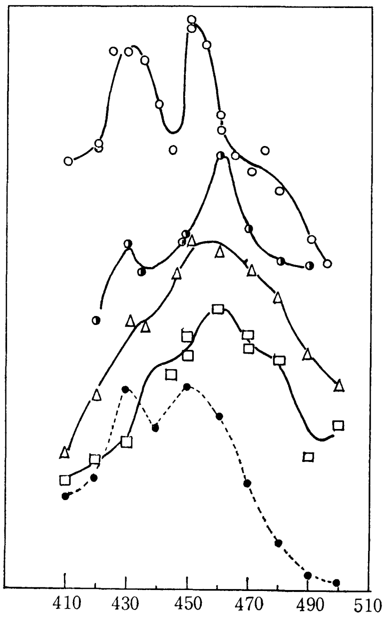


Fig. 3. Transient absorption of carbostyril at room temperature.
○: in water (C: 0.16×10^{-4}M)
◑: in 0.1M NaOH aqueous solution (C: 1.08×10^{-4}M)
△: in 0.5M NaOH aqueous solution (C: 1.13×10^{-4}M)
□: in 1.0M NaOH aqueous solution (C: 1.13×10^{-4}M)
●: in 70% ethanol aqueous solution (C: 0.30×10^{-4}M)

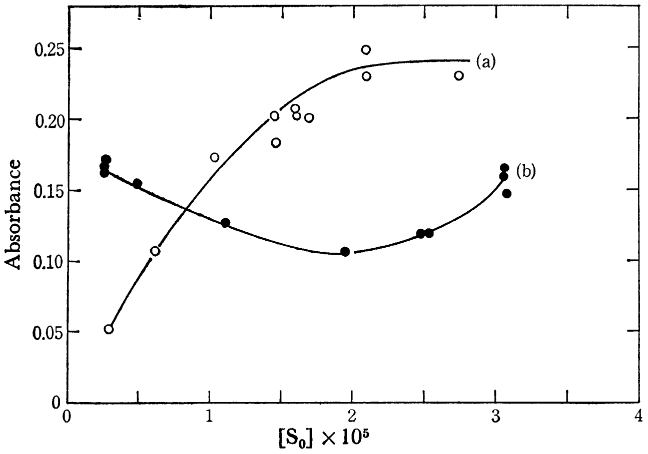


Fig. 4. Absorbance of transient absorption at 450 nm *vs.* $[\mathrm{S}_0]$ at room temperature.
(a), ○: in water
(b), ●: in NaOH solution (C: 1.0×10^{-4}M)

taining different amounts of sodium hydroxide, and also in a 70% ethanol aqueous solution at room temperature. As can be seen from Fig. 3, the transient absorption was altered significantly when the solvent was changed from water to alkaline solutions. Figure 4 shows the plot of the absorbance of the transient absorption at 450 nm against $[\mathrm{S}_0]$ in water (a) or a NaOH solution (b). It is clear from these figures that the transients observed in alkaline solutions consist of two kinds of species, the carbostyril (T_1) around 420—470 nm and the carbostyrilate ion (T_1^-) at about 440—490 nm, in their lowest triplet states. In addition, the transient absorption was confirmed to decay by means of first-order kinetics.

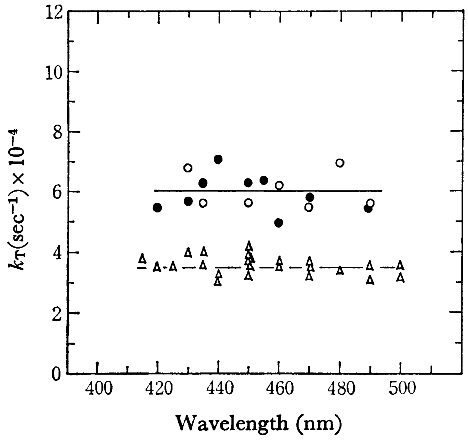


Fig. 5. Decay rate constant (k_T) of transient at various wavelengths at room temperature.
●: in water (C: 0.16×10^{-4}M)
○: in 0.1M NaOH aqueous solution (C: 1.08×10^{-4}M)
△: in 1.0M NaOH aqueous solution (C: 1.13×10^{-4}M)

Figure 5 shows first-order decay rate constants (k_T) determined at different wavelengths; the data indicate that the decay constant of the triplet carbostyril is nearly equal to that of the triplet carbostyrilate ion.

Next, the effect of the concentration of a hydroxide ion on the decay constant of the transients at 450 nm was examined at room temperature (Fig. 6). The (a) curve in Fig. 6 shows the plot of k_T against $[\mathrm{S}_0]$ in the place of $[\mathrm{OH}^-]$. The (b) curve illustrates the plot of k_T *vs.* $[\mathrm{S}_0]$ in water, while the (c) curve is the plot of k_T *vs.* $[\mathrm{S}_0]$ when $[\mathrm{S}_0^-]$ was kept to 1.0×10^{-4}M. The slope ($3.18\times10^9\ \mathrm{sec}^{-1}\mathrm{M}^{-1}$) of the (a) curve in Region I was in good agreement with that ($3.12\times10^9\ \mathrm{sec}^{-1}\mathrm{M}^{-1}$) of the (b) curve, whereas the (a) curve in Region III coincided in slope with the (c) curve. It is obvious from these results that the dependence of $[\mathrm{S}_0]$ of k_T is quite similar to that of the quantum yield shown in Fig. 2.

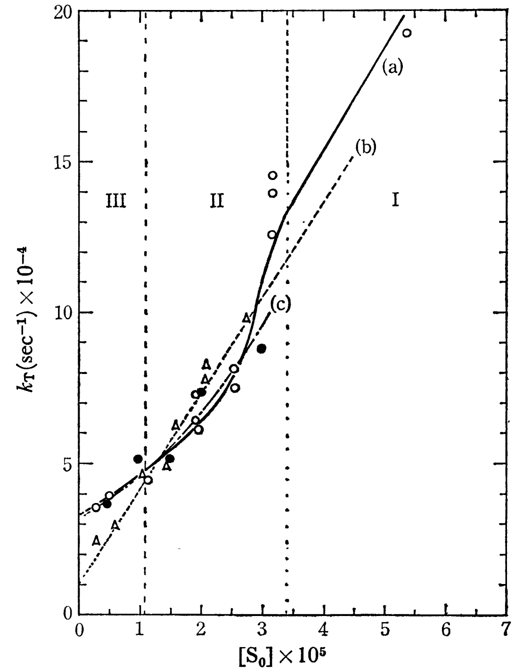


Fig. 6. Decay rate constant (k_T) of transients at 450 nm *vs.* $[\mathrm{S}_0]$ at room temperature.
curve (a), ○: in alkaline aqueous solution (C: 1.13×10^{-4}M)
curve (b), △: in water
curve (c), ●: in alkaline aqueous solution ($[\mathrm{S}_0^-]$: 1.0×10^{-4}M)

The decay constants of the transients at 450 nm were also measured as a function of the concentration of S_0^-, while the concentration of S_0 was kept constant at 0.15×10^{-4}M (Fig. 7). As a result, it was found to remain constant at $5.5\times10^4\ \mathrm{sec}^{-1}$, regardless of the concentration of S_0^-. Therefore, it seems reasonable to

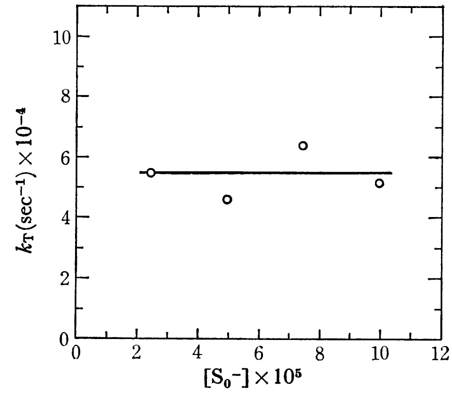
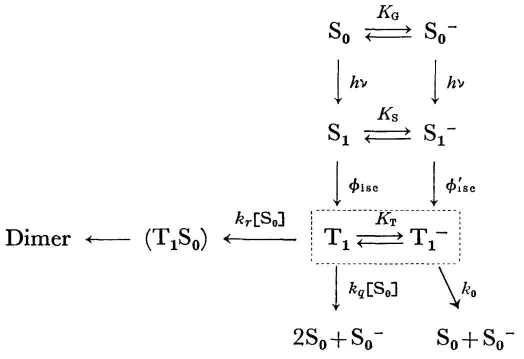


Fig. 7. Decay rate constant (k_T) of transients at 450 nm *vs.* $[\mathrm{S}_0^-]$ in alkaline aqueous solution at room temperature ($[\mathrm{S}_0]$: 0.15×10^{-4}M)

conclude that the decay rate constant is dependent on the concentration of only S_0, not S_0^-.

Discussion

The experimental results described in the preceding section suggest that the photochemical dimerization of carbostyril in an alkaline solution proceeds through a bimolecular interaction between the triplet and the ground-state carbostyrils, although the triplet carbostyrilate ion is considered to be in equilibrium with the triplet carbostyril. When we also assume an acid-base equilibrium between the carbostyril (S_1) and the carbostyrilate ion (S_1^-) in their excited singlet states, the following scheme, Scheme 1, can be generally postulated for the primary process of the photodimerization in an alkaline aqueous solution:



Scheme 1.

where K_G, K_S, and K_T represent the equilibrium constant in the ground, the excited singlet, and the lowest triplet states, and where ϕ_{isc} and ϕ'_{isc} are the efficiencies of the $S_1 \rightarrow T_1$ and, $S_1^- \rightarrow T_1^-$ intersystem crossing.[5]

Assuming photostationary state conditions, the quantum yield (Φ) of the carbostyril disappearance can be given by the following equation:

$$\Phi = \frac{k_r[S_0]}{k_T} \frac{\phi_{isc}+K_S[OH^-]\phi'_{isc}}{1+K_S[OH^-]} \tag{4}$$

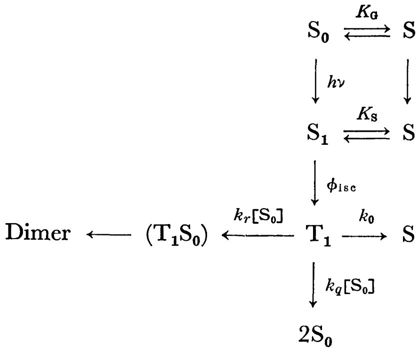
where: $$k_T = (k_r+k_q)[S_0] + k_0 \tag{4'}$$

and where k_r represents the apparent rate constant for the formation of the transient complex (T_1S_0), and k_q and k_0, the apparent quenching rate constants by S_0 or the apparent first-order decay rate constant of the transient species ($T_1+T_1^-$). We can then obtain Eq. (5) by substituting $[OH^-]=[S_0^-]/K_G[S_0]$ into Eq. (4):

$$\Phi = \frac{k_r[S_0]}{k_T} \frac{K_G[S_0]\phi_{isc}+K_S[S_0^-]\phi'_{isc}}{K_G[S_0]+K_S[S_0^-]} \tag{5}$$

On the basis of Eq. (5), a subsequent discussion of the primary process of the photochemical dimerization of carbostyril in an alkaline solution will be made in the concentration ranges of S_0 and OH^-, each divided into three regions, I, II, and III, as has been described before.

Region I ($[S_0] \gtrsim 3.40\times10^{-5}$M or $[OH^-] \lesssim 0.052$M).
In view of the results shown in Fig. 6 that the slope of the (a) curve in Region I is substantially equal to that of the (b) curve, the transient absorption observed may be regarded as being due mostly to the triplet carbostyril; hence, the triplet carbostyrilate ion is assumed not to exist appreciably in this region (Scheme 2).



Scheme 2.

According to Scheme 2, Eq. (5) could be approximately expressed by Eq. (6).

$$\Phi = \frac{k_r[S_0]}{k_T} \frac{K_G[S_0]\phi_{isc}}{K_G[S_0]+K_S[S_0^-]} \tag{6}$$

On the other hand, k_r+k_q and k_0 were evaluated from the (b) curve in Fig. 6 to be 3.12×10^9 sec^{-1}M^{-1} and 1.12×10^4 sec^{-1} respectively, indicating that (k_r+k_q)-$[S_0]/k_0$ is greater than 9.5. Consequently, Eq. (6) can be simplified to Eq. (7), if we assume that k_0 can be neglected compared with $(k_r+k_q)[S_0]$:

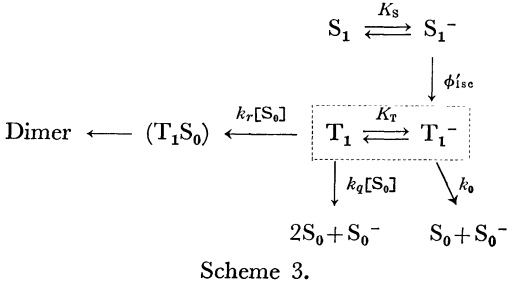
$$\Phi = \frac{k_r}{k_r+k_q} \frac{K_G[S_0]\phi_{isc}}{K_G[S_0]+K_S[S_0^-]} \tag{7}$$

By substituting for $[S_0^-]$ its equivalent, $C-[S_0]$, we obtain Eq. (8):

$$\frac{1}{\Phi} = \frac{1}{\phi_{isc}}\left(1+\frac{k_q}{k_r}\right)\left(\frac{K_SC}{K_G}\frac{1}{[S_0]}+\frac{K_G-K_S}{K_G}\right) \tag{8}$$

That is, $1/\Phi$ in Region I is expected to increase in proportion to $1/[S_0]$. It is shown in Fig. 8 that the plot of $1/\Phi$ against $1/[S_0]$ gives a straight-line relation; this is consistent with Eq. (8). From the slope (1.24×10^{-4}M) and the intercept (3.83) of the straight line, ϕ_{isc} and K_S were evaluated to be $0.21(1+k_q/k_r)$ and 13.0M^{-1} respectively.

Region III ($[S_0] \lesssim 1.11\times10^{-5}$ or $[OH^-] \gtrsim 0.23$M).
In Region III the concentration of carbostyril is extremely low compared with that of the carbostyrilate ion; thus, the latter is considered to be mainly concerned with a light absorption (Scheme 3).



Scheme 3.

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[5] Although there exists quenching from the excited singlet states (S_1, S_1^-) to the ground states (S_0, S_0^-), there are not written in Scheme 1.

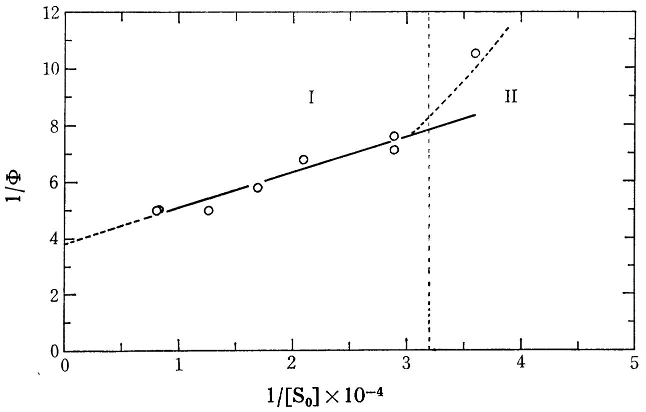


Fig. 8. $1/\Phi$ *vs.* $1/[S_0]$ in Regions I.

According to Scheme 3, Eq. (5) can be simplified as follows:

$$\frac{1}{\Phi}=\frac{1}{\phi'_{\rm isc}}\left(1+\frac{k_{\rm q}}{k_{\rm r}}\right)\left\{\left(1+\frac{k_0}{k_{\rm r}+k_{\rm q}}\frac{1}{[S_0^-]}\frac{K_G}{K_S}+\frac{k_0}{k_{\rm r}+k_{\rm q}}\frac{1}{[S_0]}\right)+\frac{K_G[S_0]}{K_S[S_0^-]}\right\} \tag{9}$$

On the other hand, the values of $k_{\rm r}+k_{\rm q}$ and k_0 were evaluated from the (a) curve in Fig. 6 to be $1.15\times 10^9\ \mathrm{sec^{-1}M^{-1}}$ and $3.40\times 10^4\ \mathrm{sec^{-1}}$ respectively. In addition, the concentration of S_0^- in this region is around 11.8×10^{-5}M; hence:

$$1+\frac{k_0}{k_{\rm r}+k_{\rm q}}\frac{1}{[S_0^-]}\frac{K_G}{K_S}+\frac{k_0}{k_{\rm r}+k_{\rm q}}\frac{1}{[S_0]}\gtrsim 4.0$$

and $K_G[S_0]/K_S[S_0^-]\lesssim 0.48$; that is, $K_G[S_0]/K_S[S_0^-]$ is considered to be negligible compared with the other terms in Eq. (9). For this reason, we can further simplify Eqs. (9) to (10):

$$\frac{1}{\Phi}=\frac{1}{\phi'_{\rm isc}}\left(1+\frac{k_{\rm q}}{k_{\rm r}}\right)\left(1+\frac{k_0}{k_{\rm r}+k_{\rm q}}\frac{1}{[S_0^-]}\frac{K_G}{K_S}+\frac{k_0}{k_{\rm r}+k_{\rm q}}\frac{1}{[S_0]}\right) \tag{10}$$

Accordingly, $1/\Phi$ in Region III is expected to vary linearly with $1/[S_0]$. In fact, it is shown in Fig. 9 that the plot of $1/\Phi$ against $1/[S_0]$ gives a linear relationship in accordance with Eq. (10); $\phi'_{\rm isc}$ was estimated from the slope (9.91×10^{-4}M) of the straight line to be $3.0\times 10^{-2}(1+k_{\rm q}/k_{\rm r})$.

Region II ($1.11\times 10^{-5}\mathrm{M}\lesssim [S_0]\lesssim 3.40\times 10^{-5}$M or $0.23\mathrm{M}\gtrsim[\mathrm{OH^-}]\gtrsim 0.052$M). As can be seen from Fig. 6, both $k_{\rm r}+k_{\rm q}$ and k_0 in Region II depend on the concentration of S_0. In Eq. (5) the ratio of $K_G[S_0]\phi_{\rm isc}/(K_G[S_0]+K_S[S_0^-])$ to $K_S[S_0^-]\phi'_{\rm isc}/(K_G[S_0]+K_S[S_0^-])$ corresponds to $[T_1]/[T_1^-]$, where T_1 and T_1^- are the triplet species produced by the intersystem crossing from S_1 and S_1^- respectively. Assuming that the triplet carbostyrilate ion is not quenched by S_0, $k_{\rm q}/k_{\rm r}$ should be independent of $[S_0]$ and $[\mathrm{OH^-}]$; thus, there could be $3.32\lesssim[T_1]/[T_1^-]\lesssim 12.8$. Under these circumstances, the triplet carbostyrilate ion can be inferred to be mainly produced by the $S_1\rightarrow T_1\rightarrow T_1^-$ process, but not from S_1^- (Scheme 4).

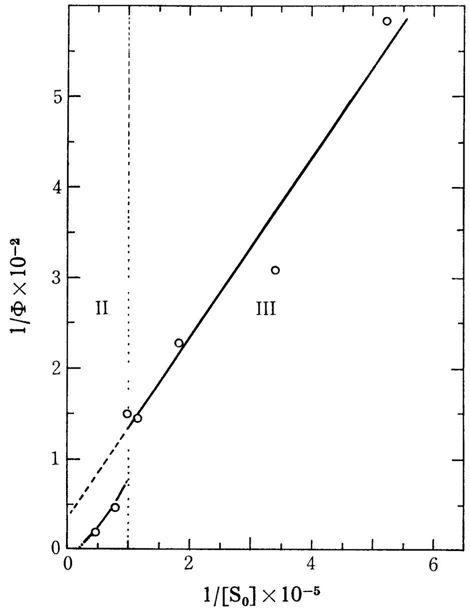
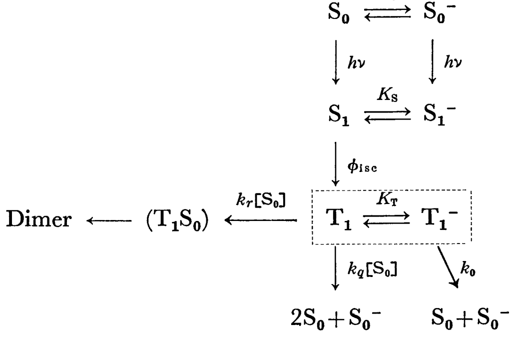


Fig. 9. $1/\Phi$ *vs.* $1/[S_0]$ in Region III.



Scheme 4.

According to Scheme 4, Eq. (5) can be approximated as follows:

$$\frac{1}{\Phi}=\frac{1}{\phi_{\rm isc}}\left(1+\frac{k_{\rm q}}{k_{\rm r}}\right)\left(\frac{k_0}{k_{\rm r}+k_{\rm q}}\frac{1}{[S_0]}+1\right)\times\left(\frac{K_SC}{K_G}\frac{1}{[S_0]}+\frac{K_G-K_S}{K_G}\right) \tag{11}$$

Figure 10 shows the plot of $1/\Phi$ against $1/[S_0]$, where a clear-cut straight-line relation was not observed in Region II as has been expected from Eq. (11). The decay rate (R) of the transient species ($T_1+T_1^-$) at equilibrium is given by the following equation:

$$R=\{(k_{\rm r}+k_{\rm q})[S_0]+k_0\}[T_1+T_1^-]$$

Based on the fact that the photochemical dimerization proceeds through an interaction between T_1 (not T_1^-) and S_0, the decay rate (R) could also be given by the following relation:

$$R=(k_{\rm ro}+k_{\rm qo})[S_0][T_1]+k_0[T_1+T_1^-]$$

where $k_{\rm ro}$ and $k_{\rm qo}$ correspond to $k_{\rm r}$ and $k_{\rm q}$ respectively in water. Accordingly, Eq. (12) is obtained by a combination of the equations described above:

$$\frac{k_{\rm ro}+k_{\rm qo}}{k_{\rm r}+k_{\rm q}}=1+\frac{[T_1^-]}{[T_1]} \tag{12}$$

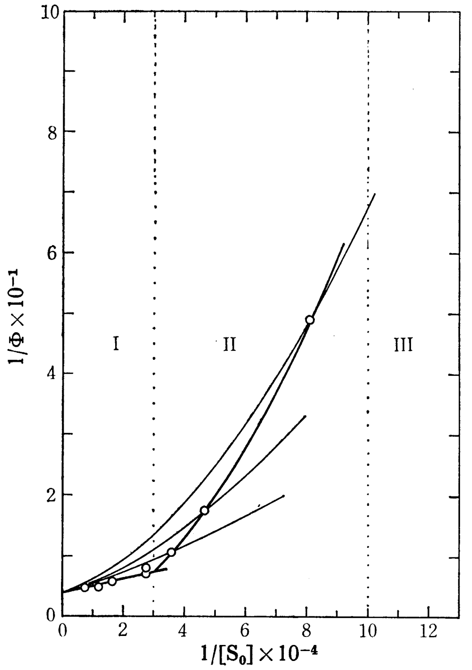


Fig. 10. $1/\Phi$ *vs.* $1/[S_0]$ in Regions I and II.

Since $[T_1^-]/[T_1] = K_T[OH^-]$, Eq. (12) can then be converted into Eq. (13).

$$\frac{k_{ro}+k_{qo}}{k_r+k_q} = 1 + K_T[OH^-] \tag{13}$$

That is, if the assumptions that an acid-base equilibrium exists between the triplet carbostyril and the triplet carbostyrilate ion, and that the dimerization process involves only the triplet carbostyril, not the carbostyrilate ion, are reasonable, a linear relationship could be obtained between $(k_{ro}+k_{qo})/(k_r+k_q)$ and $[OH^-]$.

On the other hand, the values of $k_0/(k_r+k_q)$ at several concentrations of S_0, such as 2.77×10^{-5}M, 2.13×10^{-5}M, and 1.23×10^{-5}M, were calculated, by substituting the observed values of Φ (0.095, 0.057, and 0.021) respectively at these concentrations of S_0 into Eq. (11), to be 0.78×10^{-5}M, 1.79×10^{-5}M, and 3.21×10^{-5}M, respectively (Fig. 10). The value of $k_0/(k_r+k_q)$ in Region I or III was also estimated from the results in Fig. 6 to be 0.359×10^{-5}M or 2.96×10^{-5}M. From such estimations, $k_0/(k_r+k_q)$ in Region II was shown to exist between those in Regions I and III obtained from the flash experimental data; this is parallel to an increase in the concentration of the triplet carbostyrilate ion with a decrease in the S_0 value or an increase in the OH^- value.

The decay constant (k_T) of the transient species $(T_1+T_1^-)$ is derived from Eqs. (2) and (4′) as follows:

$$k_T = (k_r+k_q)\left(\frac{C}{1+K_G[OH^-]} + \frac{k_0}{k_r+k_q}\right) \tag{14}$$

Therefore, k_r+k_q and k_0 at various concentrations of OH^-, or S_0, were estimated by substituting the observed values of k_T into Eq. (14); the results are listed in Table 1. Both k_r+k_q and k_0 in Region II were observed to exist between the corresponding values in Regions I and III.

TABLE 1. VALUES OF (k_r+k_q) AND k_0 IN REGIONS I, II, AND III

Region	$[OH^-]$	$(k_r+k_q)\times10^{-9}(\text{sec}^{-1}\text{M}^{-1})$	$k_0\times10^{-4}(\text{sec}^{-1}\text{M}^{-1})$
I	0.0	3.12	1.12
	0.01	3.12	1.12
	0.02	3.12	1.12
	0.05	3.12	1.12
II	0.07	2.34	1.82
	0.1	1.68	3.01
	0.2	1.33	3.53
III	0.25	1.15	3.40
	0.3	1.15	3.40
	0.5	1.15	3.40
	1.0	1.15	3.40
	1.5	1.15	3.40

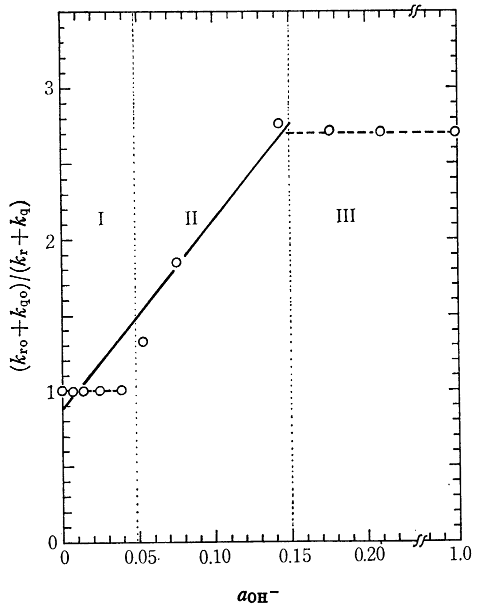


Fig. 11. $(k_{ro}+k_{qo})/(k_r+k_q)$ *vs.* a_{OH^-} in Regions I, II, and III.[6]

As can readily be seen from Fig. 11 using the values in Table 1, the plot between them gave a linear relationship, consistent with Eq. (13); the equilibrium constant (K_T) was then estimated from the slope to be 12.5M^{-1}.

These facts also support the present idea about the primary process of photochemical dimerization in an alkaline aqueous solution.

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[6] The activities (a_{OH^-}) were estimated from the values of mean activity coefficients described in the following literatures; H. S. Harned and J. C. Heckel, *J. Amer. Chem. Soc.*, **55**, 4838 (1933) and G. Akerlof and G. Kegels, *ibid.*, **62**, 620 (1940).