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The Primary Process of the Photochemical Dimerization of Carbostyril

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Carbostyril dimerizes photochemically in ethanol to yield its dimer. In order to clarify the primary process of this photochemical dimerization, studies by means of steady-light irradiation and flash spectroscopy and measurements of the absorption spectrum of the intermediate and of the phosphorescence spectrum at 77°K were carried out under various conditions. The transient absorption was observed around 430 mμ, it was identified as being due to a $T-T$ transition of carbostyril. Experiments on both the decay kinetics of the triplet species and the quantum yield of the carbostyril disappearance under various conditions revealed that the photochemical dimerization of carbostyril proceeded through a bimolecular interaction between the triplet and the unexcited molecules.

Recently, a number of interesting photochemical reactions of heterocyclic *N*-oxides have been reported by several workers.[1,2] In the course of our studies of the primary photochemical process of quinoline *N*-oxide and its derivatives, it was necessary to identify the excited state responsible for the photochemical dimerization of carbostyril, for the carbostyril produced photochemically from the quinoline *N*-oxide in ethanol further absorbs ultraviolet light to yield its dimer. Therefore, in order to clarify the primary process of the photochemical dimerization of carbostyril, the present authors carried out investigations by means of steady-light irradiation and flash spectroscopy and measured the absorption spectrum of the intermediate and also the phosphorescence spectrum at 77°K.

Experimental

Materials. The carbostyril used in this experiment was prepared by ultraviolet irradiation for the quinoline *N*-oxide in ethanol, the product was purified by recrystallization several times.[3] Reagent-grade ethanol and dichloromethane were used without further purification. Reagent-grade piperylene was purified by distillation, while isopentane and liquid paraffin were purified by column chromatography (silica gel). Spectro-grade glycerol and methylcyclohexane were also used.

Steady-light Experiment. The light source employed was a Toshiba high-pressure mercury lamp (H-400P), while for 3130 Å irradiation a filter combination of a nickel sulfate solution with a UV-31 Toshiba filter was used. Two kinds of cylindrical quartz reaction cells were used; one was 5 cm in diameter and 1 cm thick, while the other was 5 cm in diameter and 4 cm thick. In order to determine the quantum yield of the carbostyril disappearance, the light intensity was measured with a potassium ferrioxalate actinometer. The absorption spectra were taken with a Hitachi recording spectrophotometer, EPS-3T.

Flash Spectroscopic Experiment. The absorption spectra of the transient species were taken with a flash-photolysis apparatus described in a previous paper.[4] In the case of the decay kinetic studies of the transient species, a xenon flash lamp used for excitation was operated by discharging a bank of condensers of 2 μF charged to 11 kV, 120 joules of energy being dissipated; the half-width of the discharge time was about 10 μsec.

Results and Discussion

Buchardt[3,5] has reported that the carbostyril (I)

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[1] G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).

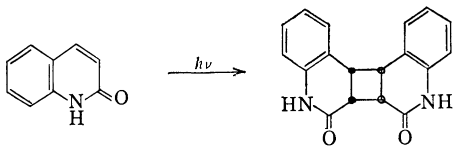
[2] P. Beak and W. R. Messer, "Organic Photochemistry," Vol. 2, ed. by O. L. Chapman, M. Dekker Inc., New York, (1969), p. 117.

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

[4] N. Hata, E. Okutsu, and I. Tanaka, This Bulletin, **41**, 1769 (1968).

[5] O. Buchardt, *Acta Chem. Scand.*, **18**, 1389 (1964).

dimerizes, under irradiation by a 3130 Å light in ethanol under bubbling nitrogen to give the carbostyril dimer (II), which is only slightly soluble in the ethanol used as a solvent.



I II

This photochemical dimerization also proceeded in other solvents, such as water, cyclohexane, and dichloromethane, but it was inhibited by the addition of piperylene or the bubbling in of oxygen. As an example of these experiments, Table 1 shows how the photochemical conversion from carbostyril to its dimer in dichloromethane was influenced by the addition of various amounts of piperylene. It is evident from these results that both oxygen and piperylene act as quenchers for the photochemical dimerization of carbostyril.

Table 1. Effect of piperylene on the photochemical conversion from carbostyril to its dimer[a)]

Piperylene (M)	0	0.5×10^{-4}	1.0×10^{-4}	1.8×10^{-4}	7.0×10^{-4}	3.5×10^{-3}
Conversion (%)[b)]	47	38	32	30	25	11

a) Solvent: dichloromethane (under bubbling nitrogen)
Concentration of carbostyril: 3.52×10^{-3} M (60 cc)
Irradition time: 75 min.

b) Conversion refers to the percentage of carbostyril converted to its dimer.

Figure 1 shows the progressive spectral change of carbostyril on 3130 Å irradiation in ethanol, where it was observed that the absorption of carbostyril decreased progressively with the irradiation time and that a new absorption band appeared around 255 mμ as the irradiation time increased, with isosbestic points at 265 mμ, 283 mμ, and 298 mμ. On the basis of a comparison with the absorption spectrum of the carbostyril dimer in ethanol (Fig. 2), the new absorption band which appeared around 255 mμ on 3130 Å irradiation is considered to be due to a carbostyril dimer.

The phosphorescence spectrum from EPA, ethanol, or methylcyclohexane glass containing approximately 1.0×10^{-4}M carbostyril was measured at 77°K; the spectrum thus obtained is shown in Fig. 3. It was estimated, from the first maximum of the phosphorescence spectrum (434 mμ), that the lowest triplet state of carbostyril has an excitation energy of about 66 kcal·mol^{-1}. Consequently, the addition of piperylene (E_T=57 kcal·mol^{-1}) to the carbostyril in amounts much greater than the molar equivalence led to the complete disappearance of the phosphorescence (Fig. 3). From this result, the radius of the active sphere with the piperylene molecule at its center, where triplet carbostyril molecules outside this sphere were assumed not to be quenched, was estimated to be about 15 Å. The phosphorescence lifetime (τ_p) of carbostyril in EPA at 77°K was also determined to be 0.88 sec (Fig. 9).

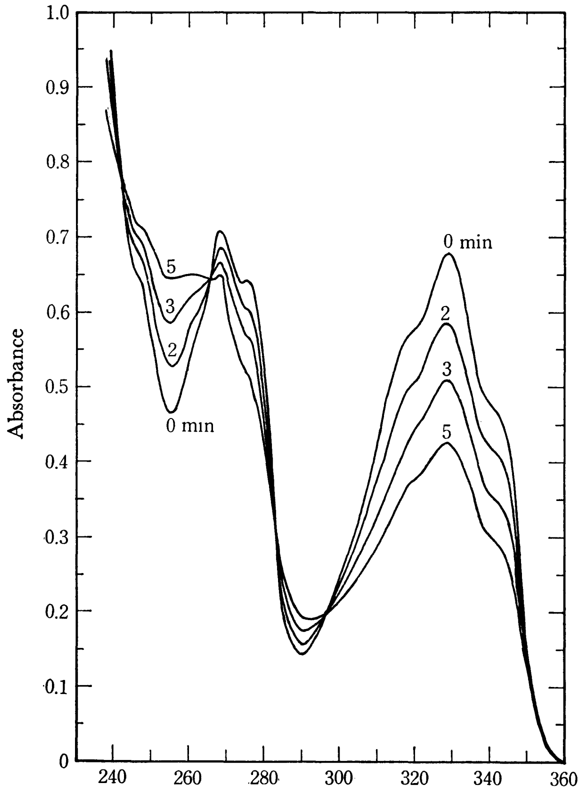


Fig. 1. Spectral change of carbostyril on 3130 Å irradiation in deaerated ethanol (initial concentration of carbostyril: 1.05×10^{-4}M).

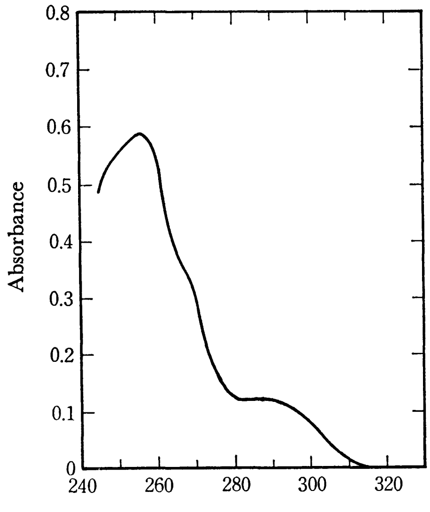


Fig. 2. Absorption spectrum of carbostyil dimer in ethanol.

The quantum yields of the carbostyril disappearance in deaerated ethanol were measured under various conditions. Figure 4 shows the effect of the light intensity on the quantum yield of the carbostyril disappearance, the results indicate that the quantum yield was independent of the light intensity. The quantum yield of the carbostyril disappearance as a function of the concentration was also determined; the results are shown in Fig. 5. As may be seen from Fig. 5, the quantum yield increased with an increase in the con-

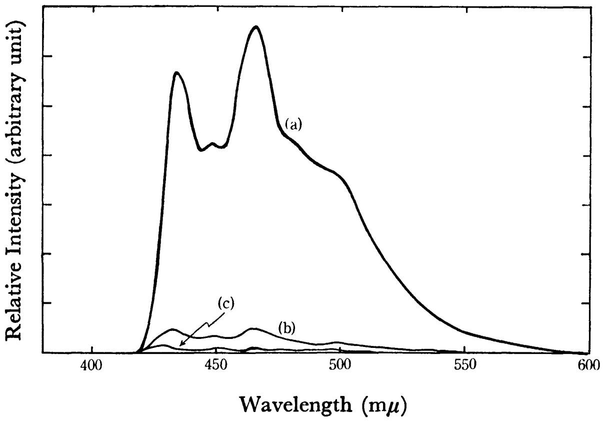


Fig. 3. Phosphorescence spectrum of carbostyril in methylcyclohexane at 77°K (concentration of carbostyril: 1.0×10^{-4}M).
(a) [Piperylene]: 0 M
(b) [Piperylene]: 1.0×10^{-1}M
(c) [Piperylene]: 2.0×10^{-1}M

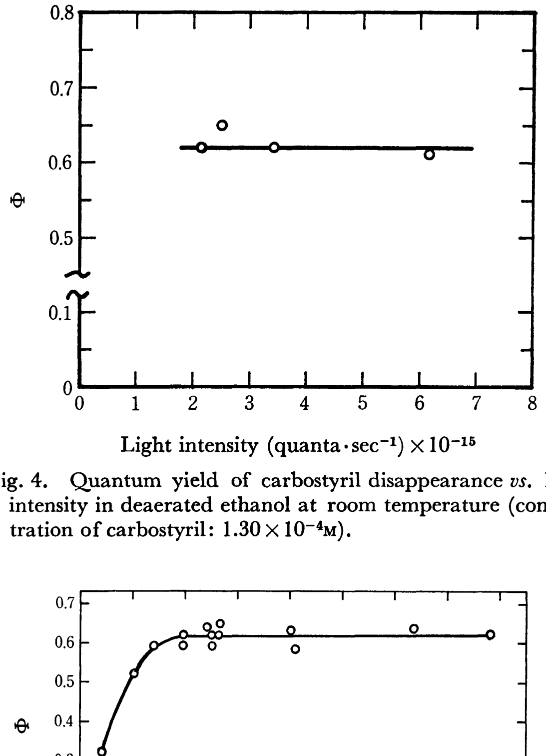


Fig. 4. Quantum yield of carbostyril disappearance *vs.* light intensity in deaerated ethanol at room temperature (concentration of carbostyril: 1.30×10^{-4}M).

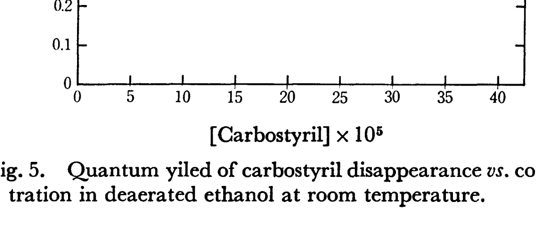


Fig. 5. Quantum yiled of carbostyril disappearance *vs.* concentration in deaerated ethanol at room temperature.

centration, approaching a constant value at concentrations of more than 1.0×10^{-4}M.

Next, in order to characterize the excited state responsible for the photochemical dimerization, the effect of piperylene on the quantum yield of the carbostyril disappearance was investigated, with the piperylene being chosen as the triplet quencher. Figure 6 shows plots of Φ/Φ_Q against the concentration of piperylene

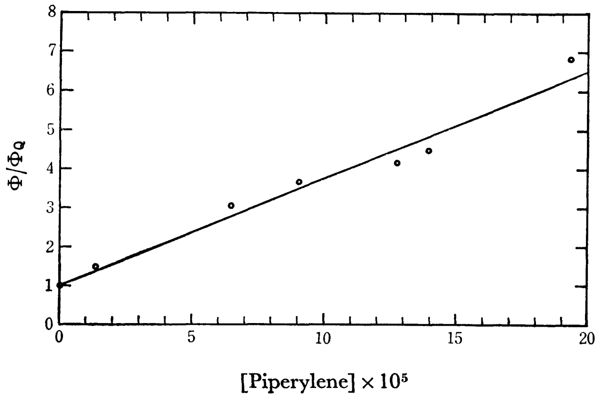


Fig. 6. Stern-Volmer plot for carbostyril dissapearance by piperylene in deaerated ethanol at 20°C (concentration of carbostyril: 1.20×10^{-4}M).

([Q]), where Φ and Φ_Q represent the quantum yield of the carbostyril disappearance in the absence and in the presence of piperylene respectively. It is apparent from Fig. 6 that the simple Stern-Volmer relationship (1):

$$\Phi/\Phi_Q = 1 + K_Q[Q] \tag{1}$$

is followed in this reaction. The quenching constant, K_Q, at $[S_0]=1.20\times10^{-4}$M, $[S_0]$ being the initial concentration of carbostyril, was estimated, from the slope of the curve in Fig. 6, to be $2.76\times10^4\ l\cdot\text{mole}^{-1}$. The quenching constant in this photochemical dimerization is represented by Eq. (2):

$$K_Q = \frac{k_8}{k_2 + k_3 + (k_4+k_5)[S_0]} \tag{2}$$

from a consideration of the following reaction scheme, (i)—(viii), to be given below. The observed value of K_Q will be compared with that estimated from a flash-spectroscopic experiment later.

The dependence of the quantum yield on the concentration of carbostyril and the quenching experiment seem to be explained by the following mechanism:

$$\begin{array}{lll}
S_0 + h\nu \longrightarrow S_1 \longrightarrow T_1 & I_a\phi_{isc} & \text{(i)} \\
T_1 \longrightarrow S_0 & k_2 & \text{(ii)} \\
T_1 \longrightarrow \text{Decomposition} & k_3 & \text{(iii)} \\
T_1 + S_0 \longrightarrow S_0 + S_0 & k_4[S_0] & \text{(iv)} \\
T_1 + S_0 \longrightarrow (T_1S_0) & k_5[S_0] & \text{(v)} \\
(T_1S_0) \longrightarrow \text{Dimer} & k_6 & \text{(vi)} \\
(T_1S_0) \longrightarrow S_0 + S_0 & k_7 & \text{(vii)} \\
T_1 + Q \longrightarrow S_0 + Q & k_8[Q] & \text{(viii)}
\end{array}$$

Assuming the photostationary state conditions, the quantum yield of the carbostyril disappearance in the absence of a quencher could be given by the following equation:

$$\Phi = A\left(1 - \frac{C}{1 + B[S_0]}\right) \tag{3}$$

where:

$$A = \frac{k_5 k_6 \phi_{isc}}{(k_4+k_5)(k_6+k_7)}$$

$$B = \frac{k_4 + k_5}{k_2 + k_3}$$

$$C = 1 - \frac{(1+k_4/k_5)(1+k_7/k_6)}{(1+k_2/k_3)}$$

and where ϕ_{isc} represents the efficiency of the S_1—T_1 intersystem crossing. Equation (3) accounts qualitatively for the concentration dependency of the quantum yield.

As has been described above, the photochemical dimerization of carbostyril is considered to proceed through a bimolecular interaction between the triplet and the unexcited molecules. However, another mechanism is also considered to be possible for this reaction. That is, the dimerization might occur from an interaction of the unexcited molecule (S_0) with the intermediate (M) which may be produced from the triplet state of carbostyril as follows:

$$T_1 \longrightarrow M \qquad \text{(ix)}$$

$$M + S_0 \longrightarrow (MS_0) \qquad \text{(x)}$$

$$(MS_0) \longrightarrow \text{Dimer} \qquad \text{(xi)}$$

Therefore, it is necessary to determine which mechanism is most reasonable in accounting for this reaction. If the dimerization proceeds through the processes (v) and (vi), the *T–T* absorption of carbostyril can possibly be observed. On the other hand, if the processes (ix)—(xi) are involved in the dimerization, the absorption spectrum of the intermediate (M) or, simultaneously, a *T–T* absorption of carbostyril will probably be obtained. That is, the detection and identification of triplet species and the examination of their kinetic behavior could be important in determining the mechanism of the photochemical dimerization of carbostyril.

Figure 7 shows the absorption spectrum of the transient species produced by a flash excitation of the carbostyril in such solvents as glycerol (room temperature), liquid paraffin (268°K), and EPA (77°K).[6] In each case, the transient absorption was observed in the region between 380 mμ and 500 mμ.

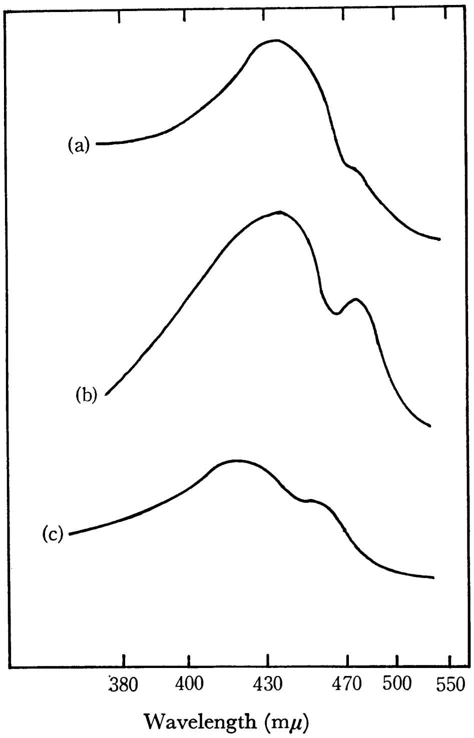


Fig. 7. Transient absorption of carbostyril.
(a) in glycerol (room temperature)
(b) in liquid paraffin (268°K)
(c) in EPA (77°K)

The decay constant of the transient absorption (k_T) was determined at several wavelengths in deaerated ethanol (room temperature), liquid paraffin (268°K), glycerol (room temperature), and EPA (77°K); the results are shown in Figs. 8 and 9. As may be seen from Figs. 8 and 9, the decay obeyed the first-order law and the decay constant was independent of the wavelength. The decay lifetime ($\tau_T = 1/k_T$) in EPA at 77°K was 0.96 sec, very close to the phosphorescence lifetime ($\tau_p =$ 0.88 sec) described before. These results suggest that

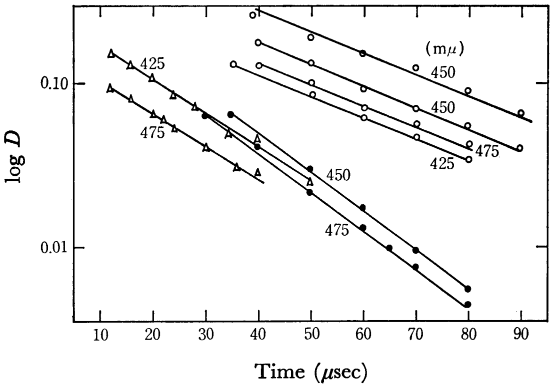


Fig. 8. Decay analysis for the transient species at several wavelengths in various solvents at room temperature.
○ in glycerol ● in liquid paraffin △ in ethanol

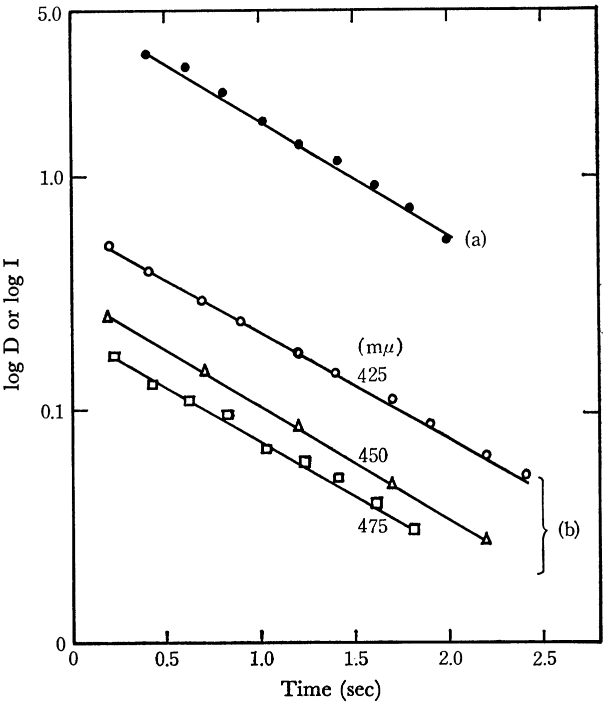


Fig. 9. Decay analysis for the phosphorescence (a) and for the transient species (b) at several wavelength in EPA (1:1:3) at 77°K (concentration of carbostyril: 1.0×10^{-4}M).

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[6] The absorption spectrum of the transient species in EPA at 77°K was taken by means of a steady-light crossed illumination.

the transient absorption around 430 mμ is due to a T–T transition of carbostyril.

The next problem is to clarify whether or not the triplet species observed is responsible for the photochemical dimerization of carbostyril. If the dimerization proceeds through a bimolecular interaction of the unexcited molecule with the triplet molecule, the decay rate of the triplet species may be given by the following equation:

$$k_T = k_2 + k_3 + (k_4+k_5)[S_0] \qquad (4)$$

That is, the decay rate may be expected to vary linearly with the initial concentration of carbostyril. When the piperylene is added to a solution of carbostyril, the decay rate is probably given by the following equation:

$$k_T = k_2 + k_3 + (k_4+k_5)[S_0] + k_8[Q] \qquad (5)$$

That is, when $[S_0]$=constant, the rate is considered to increase in proportion to the concentration of the quencher. Therefore, the effects of both the concentration of carbostyril and that of piperylene on the decay rate were examined in deaerated ethanol at room temperature. As is shown in Fig. 10, it was seen that the decay rate of the triplet species was directly proportional to the initial concentration of carbostyril; this was consistent with Eq. (4). k_4+k_5 was evaluated from the slope of the curve, while k_2+k_3 was estimated by extrapolating the concentration of carbostyril to zero. In this manner, the following values were obtained:

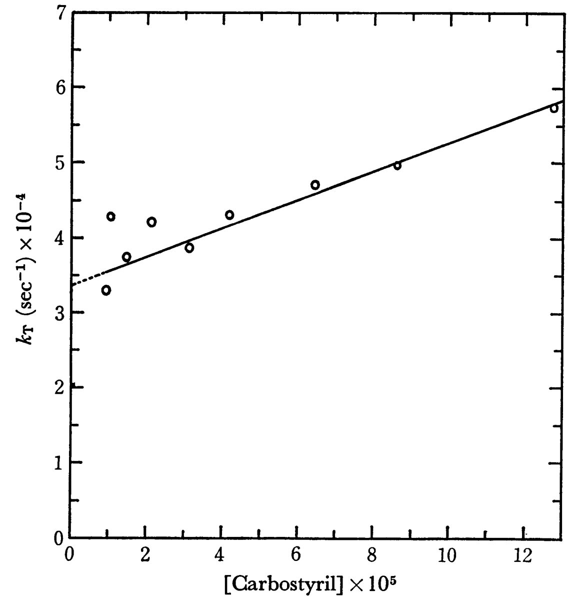

Fig. 10. Decay constant of the triplet species *vs.* concentration in deaerated ethanol at 34°C.

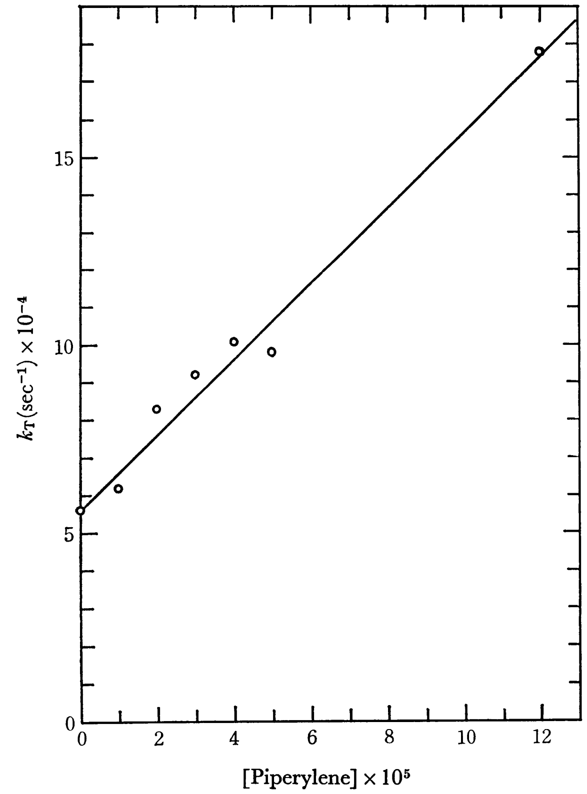

Fig. 11. Quenching of the triplet species by various amounts of piperylene in deaerated ethanol at 35°C (concentration of carbostyril: 1.16 × 10^{-4}M).

$k_2+k_3=3.36\times10^4\ \text{sec}^{-1}$ and $k_4+k_5=1.92\times10^8\ l\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$

The effect of the concentration of the quencher on the decay rate of the triplet species at $[S_0]=1.16\times10^{-4}$M is shown in Fig. 11. As was expected from Eq. (5), a linear relationship between k_T and [Q] was found and the k_8 obtained from the slope was 1.01×10^9 mol^{-1} l sec^{-1}. By substituting the observed values of k_8, k_2+k_3, and k_4+k_5 and $[S_0]=1.20\times10^{-4}$M into Eq. (2), K_Q was obtained as $1.78\times10^4\ l\cdot\text{mol}^{-1}$; this value agreed closely with that obtained by the steady-light experiment. These facts support the idea that the photochemical dimerization of carbostyril proceeds through a bimolecular interaction between the triplet and the unexcited molecules.

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