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Reactive Species in the Photochemical Hydrogenation of Acridine in Ethanol

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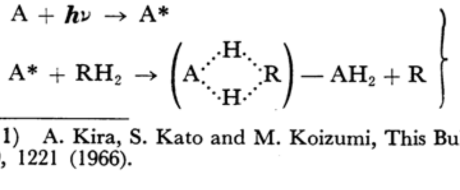
In order to determine the reactive state of acridine when it is photoreduced by ethanol, two types of experiments were undertaken. The first was to study the concentration effect of ethanol on the quantum yield in a benzene solution. These results, however, could not give any unequivocal answer. The second type of experiment was, therefore, made from the standpoint of the triplet energy transfer, using eosine as an energy acceptor for the photoreduction of acridine in an ethanol solution. It was found that, in a deaerated solution, the quantum yield of acridine photoreduction is not affected by the addition of eosine, whereas it was established by the flash technique that, under similar conditions, the energy transfer from the acridine triplet state to eosine occurs at approximately the diffusion-controlled rate. These results lead to the conclusion that the reactive state is not the lowest triplet state.

In a previous paper[1] two paths have been presented for the photochemical reduction of acridine in ethanol. One was:



$$\left.\begin{array}{l} A + h\nu \rightarrow A^* \\ A^* + RH_2 \rightarrow \left(A\overset{\cdot H\cdot}{\underset{\cdot H\cdot}{\quad}}R\right) - AH_2 + R \end{array}\right\} \quad (1)$$

where A* is the singlet excited state of acridine and RH_2 is ethanol. The other was:

$$\left.\begin{array}{lll} & A^* + RH_2 \rightarrow AH + RH & (a) \\ \text{or} & A^T + RH_2 \rightarrow AH + RH & (b) \\ & (2AH \rightarrow A + AH_2) & \end{array}\right\} \quad (2)$$

where A^T is the triplet state of acridine. When oxygen is present, only (1) occurs, since the half hydrogenated acridine produced by (2a) or (2b)

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[1] A. Kira, S. Kato and M. Koizumi, This Bulletin, **39**, 1221 (1966).

reverts to acridine by means of:

$$AH + O_2 \rightarrow A + HO_2$$

The question whether A* or A^T is involved in path 2, however, has not yet been decided. In the present paper attempts will be made to give an unequivocal answer to this question.

Results and Discussion

The Reaction between Acridine and Ethanol in a Benzene Solution.—It is expected that if AH is to be produced by (2a), then a rather high concentration of ethanol would be required for the reaction to occur because the lifetime of A* is 7.2×10^{-10} sec.2) On the other hand, if AH is produced via the triplet state, it is possible that a rather low concentration of ethanol is enough for the reaction rate to become measurable, although it all depends upon the magnitude of the rate constant of $A^T+RH_2 \rightarrow AH+RH$. Since, for the aerated solution, it has already been determined that the reaction really occurs at A*, there is a possibility that the problem can be answered by comparing the concentration effect of ethanol on the rate in aerated and deaerated benzene solutions.

The concentration of acridine was chosen as 5×10^{-5} M, while the concentration of ethanol was varied from 1×10^{-2} M to 17.3 M (pure ethanol). Changes in the absorption spectra in the course of the reaction were quite similar to those in the pure ethanol solution. The $\ln(e^{\alpha cd}-1)$ vs. t plots were satisfactorily linear, and the value of the quantum yield was determined from the slope of the plot. The results are shown in Table I.

It is notable that the ratio of Φ_{dea} to Φ_{aer} is almost constant, independent of the concentration of ethanol. When the reaction occurs at the singlet excited state, the quantum yield, Φ, for the simplest case is given as follows:

$$\Phi = \frac{k_r[RH_2]}{k_d + k_r^s[RH_2]} \qquad (1)^{*1}$$

where k_r, k_r^s and k_d are the rate constants for, respectively, the genuine reaction with ethanol, the total reaction with ethanol (including simple deactivation), and the first-order decay constant in benzene. From Eq. 1 one gets:

$$\frac{\Phi}{1-\Phi}\times\left\{1+\frac{(k_r^s-k_r)}{k_d}[RH_2]\right\}=\frac{k_r}{k_d}[RH_2] \qquad (2)$$

On the other hand, when the triplet state is a reactive species:

$$\Phi = \varphi_{S-T}^{A}\frac{k_r'[RH_2]}{k_d'+k_r^{s}{}'[RH_2]} \qquad (3)$$

where φ_{S-T}^{A} is the probability of the intersystem crossing3) and where k_r', $k_r^s{}'$ and k_d' are the analogous rate constants for the triplet state, just as k_r, k_r^s and k_d are for A*. From Eq. 3:

$$\frac{\Phi}{\varphi_{S-T}^{A}-\Phi}\times\left\{1+\frac{(k_r^s{}'-k_r')[RH_2]}{k_d}\right\}=\frac{k_r'}{k_d'}[RH_2] \qquad (4)$$

As may be expected from Eq. 2, the plot of log-$[\Phi_{aer}/(1-\Phi_{aer})]$ against log$[RH_2]$ for the aerated solution does not give the slope of unity; rather, it gives approximately 0.8. In the same way, when both log$[\Delta\Phi/(1-\Delta\Phi)]$ and log$[\Delta\Phi/(\varphi_{S-T}^{A}-\Delta\Phi)]$ $(\Delta\Phi=\Phi_{dea}-\Phi_{aer})$ are plotted against log-$[RH_2]$ for the dearated solution, the slopes of the curves also have similar values. This deviation from unity might be due partly to the dependence of k_r's and k_d's on the composition of the solution, but it is more plausible to attribute this deviation mainly to the assumption that $k_r^s=k_r$, especially in the lower concentration region of ethanol. If one takes proper $(k_r^s-k_r)/k_d$ values, which are ca.

TABLE I. QUANTUM YIELDS* OF THE PHOTOREDUCTION OF ACRIDINE BY ETHANOL IN BENZENE
[acridine]: 5×10^{-6} M, Temperature: 25°C

Concn. of ethanol M	Φ_{dea}**	Φ_{aer}**	$\Delta\Phi(=\Phi_{dea}-\Phi_{aer})$	$\frac{\Phi_{dea}}{\Phi_{aer}}$
0	$3.0_6\times10^{-4}$	$4.4_6\times10^{-5}$		(6.9)
1×10^{-2}	8.2×10^{-4}	2.0×10^{-4}	6.2×10^{-4}	4.1
5×10^{-2}	$2.5_3\times10^{-3}$	$6.9_6\times10^{-4}$	$1.8_3\times10^{-3}$	3.6
1×10^{-1}	$6.1_3\times10^{-3}$	$1.6_4\times10^{-3}$	$4.4_9\times10^{-3}$	3.7
5×10^{-1}	$1.7_7\times10^{-2}$	$4.5_3\times10^{-3}$	$1.3_2\times10^{-2}$	3.9
1	$3.2_9\times10^{-2}$	$7.4_4\times10^{-3}$	$2.5_5\times10^{-2}$	4.4
				av. 4.0
8.6 (50% Vol.)	$9.0_0\times10^{-2}$	$1.9_7\times10^{-2}$	$7.0_2\times10^{-2}$	4.6
17.3 (100%)	$1.2_3\times10^{-1}$	$4.3_8\times10^{-2}$	$7.9_7\times10^{-2}$	2.8

* Correction is made for the quantum yield in pure benzene.

** Φ_{dea} and Φ_{aer} are respectively the quantum yield for the deaerated and aerated solutions.

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2) H. Kokubum, Symposium of Photochemistry, Sendai, 1963.

*1 In general a factor depending on the succeeding steps should be multiplied.

3) According to our unpublished findings, the value of φ_{S-T}^{A} in a benzene solution is about 0.24.

1 in all cases, then the plot of the logarithm of the left side of Eqs. 2 and 4 against $\log[RH_2]$ can be made to have a slope of 1. The results are shown in Fig. 1.

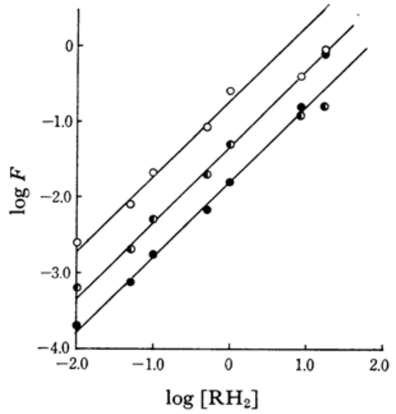

Fig. 1. Plots of $\log F$ vs. $\log[RH_2]$.

$F = \Delta\Phi \cdot K/(\varphi^{A}_{\mathrm{ST}} - \Delta\Phi)$ for ○,
$\Delta\Phi \cdot K/(1-\Delta\Phi)$ for ◐ and
$\Phi_{aer} \cdot K/(1-\Phi_{aer})$ for ●,
where $K = \left\{1 + \dfrac{(k_r^s - k_r)}{k_d}[RH_2]\right\}$ etc.
and where the coefficients of $[RH_2]$ are put unity.

The values of k_r/k_d's are evaluted from the point at $\log[RH_2]=0$. For the deaerated solution, the values of k_r and k_r^s are:

$$\begin{cases} k_r' = 2.0\times 10^{-1}k_d' \\ k_r^{s}{}' = 1.2k_d' \end{cases} \qquad \begin{cases} k_r = 4.6\times 10^{-2}k_d \\ k_r^s = 1.05k_d \end{cases}$$

and for the aerated solution:

$$\begin{cases} k_r = 1.6\times 10^{-2}k_d \\ k_r^s = 1.02k_d \end{cases}$$

If one assumes $k_d \simeq 10^{10}\ \mathrm{sec}^{-1}$ and $k_d' \approx 2\times 10^{3}\ \mathrm{sec}^{-1}$,[4] then for the reaction 2a:

$$k_r = 4.6\times 10^{8}\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1},\quad k_r^s = 10^{10}\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$

and for (2b):

$$k_r' = 4\times 10^{2}\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1},\quad k_r^{s}{}' = 2.4\times 10^{3}\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}.$$

Thus, the above values of the rate constants can make both the reactions, 2a and 2b, consistent with the experimental results, and so no definite answer can be given. However, the results in Table I, particularly the constancy of Φ_{dea}/Φ_{aer}, seem to favor the view that a reactive state is S* and not T. Even if A^T reacts with ethanol, there is no doubt that its reactivity is exceedingly small.

The Effect of the Addition of Eosine on the Photoreduction of Acridine in Ethanol.— In principle, the present problem can be solved if an effective quencher of A^T is added and if its effect on the rate of photoreduction is examined. Thus, if a reactive species is triplet acridine, then the rate may be expected to decrease to about one-third of the original value, whereas the rate should be scarcely affected if the reactive species is A*. However, we do not know what substance is a suitable triplet quencher. We have tried eosine as a test substance, since this dye has a triplet level definitely lower than that of acridine[5] and since its absorbance at 365 mμ is very small. It was found that the addition of eosine (5×10^{-6} M or 1×10^{-5} M) did not affect the rate beyond the limits of experimental error, and yet the optical density of eosine was found to decrease beyond the limit of experimental error, though to a small extent. The results are shown in Table II, where ΔD is the difference in the optical density of eosine before and after 5 minutes' irradition.

It should be noted that, according to our preliminary experiments, eosine is rapidly photoreduced by a 365 mμ light in the presence of 10^{-4} M acridan. In spite of this fact, it is believed that the ΔD value in Table II is not due to the produced acridan, though the bad reproducibility of the data might partially be due to it.

From the above results, there is scarcely any doubt that the addition of eosine does not affect the rate of the photoreduction of acridine. However, there still seems to be some doubt as to whether eosine is really acting as an efficient quencher under the present experimental conditions, since the decrease in the optical density of eosine is quite small. The order of the magnitude of ΔD to be expected can be estimated in the following way. If the above results are to be explained by the following scheme:

$$A + h\nu \rightarrow A^*$$
$$A^* + RH_2 \rightarrow AH_2 + R \qquad (1)$$
$$\llcorner\!\longrightarrow AH + RH \qquad (2a)$$
$$A^* \rightarrow A^T \qquad (3)$$
$$A^T + E \rightarrow A + E^T \qquad (4)$$
$$E^T + RH_2 \rightarrow (EH + RH) \rightarrow EH_2 + R \qquad (5)$$

where E is eosine, then the decrease in the eosine concentration, $-d[E]$, should be given by:

$$-d[E] = I^{A}_{ab}\cdot\varphi^{A}_{S-T}\cdot\alpha\cdot\beta\,dt$$

where I^{A}_{ab} is the quantity of light absorbed by acridine, where φ^{A}_{S-T} is the probability of the intersystem crossing of acridine, and where α and β are, respectively, a parameter for the efficiency of the energy transfer (process 4) and the probability that the triplet eosine reacts with ethanol.

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[4] To be published.

[5] According to G. N. Lewis and M. Kasha (*J. Am. Chem. Soc.*, **66**, 2100 (1944)), the triplet level of eosine is 14900 cm^{-1}, while D. F. Evans (*J. Chem. Soc.*, **1957**, 1351) reported that the triplet level of acridine is 15840 cm^{-1}. See also Hammond et. al., *J. Am. Chem. Soc.*, **86**, 3197 (1964).

TABLE II. THE EFFECT OF ADDITION OF EOSINE ON THE QUANTUM YIELD OF PHOTOREDUCTION OF ACRIDINE
Temperature 25°C

Concn. of acridine M	Concn. of eosine M	Φ	ΔD
Deaerated solution			
5×10^{-5}	0	$1.2_5\times10^{-1}$	—
5×10^{-5}	0	$1.2_3\times10^{-1}$	—
5×10^{-5}	5×10^{-6}	$1.1_8\times10^{-1}$	0.015
5×10^{-5}	1×10^{-5}	$1.1_9\times10^{-1}$	0.22
1×10^{-4}	0	$1.2_9\times10^{-1}$	—
1×10^{-4}	5×10^{-6}	$1.1_8\times10^{-1}$	0.08
1×10^{-4}	7.5×10^{-6}	$1.2_1\times10^{-1}$	0.02
1×10^{-4}	7.5×10^{-6}	$1.2_3\times10^{-1}$	0.01
1×10^{-4}	9×10^{-6}	$1.2_5\times10^{-1}$	0.56
1×10^{-4}	1×10^{-5}	$1.2_0\times10^{-1}$	0.31
1×10^{-4}	1×10^{-5}	$1.2_7\times10^{-1}$	0.02 (after 3 min.) 0.04
Aerated solution			
5×10^{-5}	0	$4.3_8\times10^{-2}$	
5×10^{-5}	5×10^{-6}	$4.3_8\times10^{-2}$	−0.03 (after 10 min.)
1×10^{-4}	0	$4.3_5\times10^{-2}$	—
1×10^{-4}	1×10^{-5}	$4.6_5\times10^{-2}$	0
Controle (deaerated)			
0	1×10^{-5}		0.005 (after 3 min.) 0.08 (after 30 min.)
0	1×10^{-5}		0.025 (after 3 min.) 0.04 (after 30 min.)

Since

$$-\mathrm{d}[\mathrm{A}] = I^{\mathrm{A}}_{ab}\cdot\Phi^{\mathrm{A}}_{dea}\,\mathrm{d}t$$

one gets:

$$-\mathrm{d}[\mathrm{E}] = -\mathrm{d}[\mathrm{A}]\times\frac{\varphi^{\mathrm{A}}_{\mathrm{S-T}}\cdot\alpha\cdot\beta}{\Phi^{\mathrm{A}}_{dea}}$$

Integration gives:

$$\Delta[\mathrm{E}] = \Delta[\mathrm{A}]\times\frac{\varphi^{\mathrm{A}}_{\mathrm{S-T}}\cdot\alpha\cdot\beta}{\Phi^{\mathrm{A}}_{dea}}$$

Φ^{A}_{dea} is $\simeq0.1$; if one tentatively puts $\varphi^{\mathrm{A}}_{\mathrm{S-T}}\approx0.1$,³⁾ $\alpha\approx1$, and $\beta\approx0.01$,⁶⁾ then:

$$\Delta[\mathrm{E}] = \Delta[\mathrm{A}]\times\frac{1}{100}$$

When the concentration of acridine is 5×10^{-5} M and 1×10^{-4} M, the ΔD values should be 0.05 and 0.10 respectively after 5 minutes' illumination, by which time acridine disappears almost quantitatively. These values are perhaps the upper limit which can be expected, and the experimental values are quite reasonable, at least in the order of magnitude.

Thus, it seems quite plausible that the reactive species of acridine is the singlet excited state and not the triplet state. It is worthwhile to add here that the above results obviate any appreciable occurence of such a process as $\mathrm{AH}+\mathrm{E}\rightarrow\mathrm{A}+\mathrm{EH}$, i. e., the transfer of the hydrogen atom from semi reduced acridine to eosine. If this reaction were to occur, then the reduction of the acridine concentration should be caused by the addition of eosine.

Direct Proof of the $\mathrm{A^T}+\mathrm{E}\rightarrow\mathrm{A}+\mathrm{E^T}$ Process by Flash Photolytic Experiments. — In order to establish the $\mathrm{A^T}+\mathrm{E}\rightarrow\mathrm{A}+\mathrm{E^T}$ process more conclusively, flash photolytic studies were made of a solution of acridine and eosine in ethanol. The experimental conditions, such as the concentration of acridine, the flash intensity, and the filter system, are similar to those used for the acridine solution in ethanol.¹⁾ The concentration of eosine was changed from 3×10^{-6} to 2×10^{-5} M. The filter transmits only the light in the absorption region of acridine.

An example of the transient absorption spectra is shown in Fig. 2.

The concentration of acridine in this case is 1×10^{-5} M. At 93 μ sec. after the flash, the absorption spectra are quite similar to those of the acridine triplet state.¹⁾ At 360 μ sec., the shape of the spectra becomes quite different and resembles rather those of eosine intermediates,⁷⁾ although it is not exactly identical.

Judging from the decay of the triplet acridine,

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6) According to M. Imamura and M. Koizumi (This Bulletin, **29**, 899 (1956)), the quantum yield of the photoreduction of eosine in ethanol is $\sim5\times10^{-4}$. The value of $\varphi^{\mathrm{E}}_{\mathrm{S-T}}$ is 0.023 according to C. A. Parker (*Trans. Faraday Soc.*, **57**, 1894 (1961)), while in our unpublished results it is >0.05. The molar extinction coefficient of eosine in ethanol is $\sim10^5$.

7) A. Kira and S. Kato, *Science Rep. Tohoku Univ., Ser. 1*, **48**, 232 (1965).

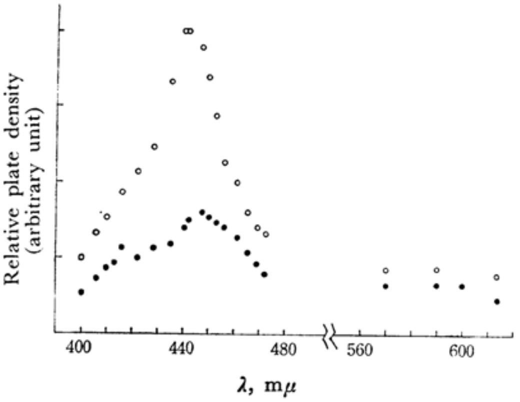

Fig. 2. Transient spectra of acridine in degassed ethanol solution containing eosine.
Acridine 1×10^{-4} M Eosine 1×10^{-5} M
○ 93 μ sec. and ● 360 μ sec. after the flash irradiation

its quantity at this stage is expected to be practically nil, so that there is no doubt that the absorption spectra at this stage are due to the transient intermediates originating from eosine. However, since the lifetime of the singlet excited state of acridine A* is of the order of 10^{-10} sec., there is no possibility for 10^{-5} M of eosine to react with A*. Besides, when a degassed solution of eosine in ethanol is irradiated under conditions similar to those above, no transient absorption is observable at 440 mμ. Therefore, it can be colculded that the transient species in question is produced by the reaction of the triplet state acridine, A^T, and eosine.

The decay curves of the optical density at 440 mμ for several eosine concentrations are shown in Fig. 3. The following features are to be noted; 1) The later stage of the decay curves, after ~300 μ sec., is exponential and has the same rate constant, $k=2\times10^3$ sec^{-1}, irrespective of the eosine concentration. 2) The first stage decays much faster, but the effect of the eosine concentration on the decay rate is not appreciable. 3) At the initial stage, the optical density becomes smaller with the increase in the eosine concentration, whereas 4) in the later stage, it becomes higher with the increase in the eosine concentration.

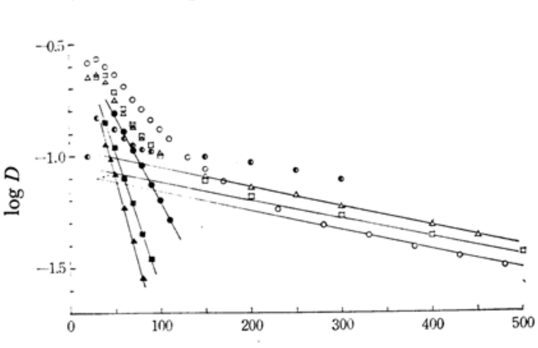

Fig. 3. Decay curves of the absorption at 440 mμ. White symbols refer to observed data and black symbols, to the decay of the triplet state evaluted from them.
Acridine 3×10^{-5} M
Eosine concentrations: ○ and ● 3×10^{-6} M, □ and ■ 6×10^{-6} M, △ and ▲ 8×10^{-6} M and ◐ 2×10^{-5} M

Findings 1 and 4 lead to the view that the later stage involves a certain intermediate produced from eosine. Furthermore, the value of k and the spectral feature support the view that this is mainly the triplet state of eosine, E^T. Findings 2 and 3 can then be interpreted in terms of the superposition of the decay of A^T and the rise in E^T.

The above interpretation is further supported by the finding that the solution of acridine and eosine in ethanol ([A]: 5×10^{-5} M, [E]: 8×10^{-6} M), when irradiated by the light absorbed only by eosine, displays the transient absorption spectra the decay constant of which is $k=2.4\times10^3$ sec^{-7}, i. e., just the same as that above. This value also agrees with the decay constant of E^T in ethanol.7)

Thus, the present results naturally lead to the following scheme:

$$A^T \xrightarrow{k_d^A} A \qquad A^T + E \xrightarrow{k_4} A + E^T$$

$$E^T \xrightarrow{k^E} E^X \text{ or } E \text{ (the yield of } E^X \text{ being } \beta)$$

where E^X is a secondary intermediate of eosine (probably semiquinone) but with a longer life. Since the initial concentration of A^T is 10^{-6} M at most, the following equations can easily be derived on the basis of the above scheme:

$$\left\{\begin{aligned} &[A^T] = [A^T]_0 e^{-(k_d^A + k_4[E]_0)t} = [A^T]_0 e^{-\kappa t} \\ &[E^T] = \frac{k_4[E]_0[A^T]_0}{\kappa - E}(-e^{-\kappa t} + e^{-k^E t}) \\ &\frac{1}{\beta}[E^X] = \frac{k_4[E]_0[A^T]_0}{\kappa} + \frac{k^E k_4[E]_0[A^T]_0}{\kappa - k^E} \\ &\qquad \times\left(\frac{1}{\kappa}e^{-\kappa t} - \frac{1}{k^E}e^{-k^E t}\right) \end{aligned}\right.$$

However, since β is very small, as has been estimated above, the optical density at 440 mμ is given by:

$$D = (\varepsilon[A^T] + \varepsilon'[E^T])d \tag{5}$$

with a good approximation, where ε and ε' are, respectively, the molar extinction coefficients of A^T and E^T.

The decay at the later stage is then given by:

$$\frac{k_4[E]_0[A^T]_0 d\varepsilon'}{\kappa - k^E} e^{-k^E t} \tag{6}$$

This interprets quantitatively the increase in the optical density with the eosine concentration. In the initial stage, two terms containing $e^{-\kappa t}$ and $e^{-k^E t}$ superpose, and the contribution of the second term increases with $[E]_0$, this is the reason why the apparent decay is not so much affected by the eosine concentration.

In order to evaluate κ, one has to subtract Eq. 6 from Eq. 5 and has to plot the logarithm of the residue against the time. The results are shown in Fig. 3 with black symbols. The observed κ-values thus obtained are plotted against the eosine concentrations in Fig. 4.

The value of k_4 obtained is $3.4\times10^9\ \text{M}^{-1}\text{sec}^{-1}$. Although the above analysis is approximate in nature on account of the neglect of the second-order decay of A^T, yet it seems quite satisfactory, even quantitatively. Thus it may be concluded that the $A^T+E\rightarrow A+E^T$ process can occur very quickly, perhaps with a diffusion-controlled rate constant.

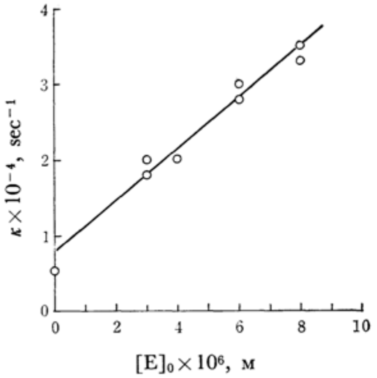

Fig. 4. The relation between the observed first order rate constant of triplet acridine and the eosine concentration.

Conclusion

The present study has shown that: 1) The energy transfer between the acridine triplet state and the ground state eosine occurs very efficiently, and that 2) in spite of this triplet energy transfer, the photoreduction of acridine is scarcely affected at all by the presence of eosine.

It may, therefore, be concluded that the reactive state of acridine is not the triplet state. As Kellmann and Dubois have proposed,[8] however, there is a possiblity of the $n-\pi^*$ T state being the reactive one. This state, according to them, has a lifetime of the order of 10^{-8} sec., so the presence of 10^{-5} M of eosine will scarcely affect this state. It is a problem for the future to decide how much of the reaction occurs at the S* and at the $n-\pi^*$ T states and, further, to decide the fraction of molecular and radical mechanisms in each reactive state.

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8) A. Kellmann and J. T. Dubois, *J. Chem. Phys.*, **42**, 2518 (1965).