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Photochemical Reaction between Acridine and Acridan in the Presence and in the Absence of Oxygen. I. Studies by the Steady Light Illumination

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Photochemical reactions between acridine and acridan in benzene solution have been studied. The product is diacridan in the absence of oxygen, while in the presence of oxygen, it is acridine. The reactive excited state in both cases is, most likely, the lowest π-π^* triplet state. Contrary to the expectation, the kinetics in the degassed solution is difficult to interpret. The rate of acridine production in the presence of oxygen, gives a sharp maximum near $\sim 10^{-4}$ M of oxygen at fixed acridan concentrations. Its quantum yield is reproduced by $\Phi = 0.25 \times \beta[AH_2]/(\alpha[O_2] + \beta[AH_2])$ with $\alpha/\beta = 3.3$ (1). Two schemes consistent with (1) have been tentatively presented in which one involves the mere deactivation of the triplet acridine by oxygen, and the other assumes the formation of an excited oxygen (or the like), which oxidizes acridan but is partially deactivated by a certain substance.

In previous papers,[1] we have established that the photoreduction of acridine in the alcoholic solution proceeds *via* dual mechanisms, radical and molecular, of which the former involves the formation of semi-reduced acridine while the latter consists of a single elementary reaction. Furthermore, the reactive state of acridine was decided to be either the excited singlet state or the n-π^* triplet state, the lowest π-π^* triplet state being entirely unreactive.[1,2]

Now it is interesting to study whether more stronger reducing agents may react with the π-π^* triplet state of acridine. This paper reports that in the benzene solution the lowest triplet acridine, which is perhaps π-π^* state, reacts with acridan both in the presence and in the absence of oxygen, yielding in the former case acridine and in the latter case mainly diacridan. One reason that we have chosen acridan as a reducing agent is that the reaction is expected to be simple since no other intermediates than semi-reduced acridine may be involved.[3] The kinetics, however, has proved to be not so simple as we expected beforehand.

Experimental

Material. Acridine was recrystallized twice from an aqueous ethanol solution and then sublimed two times. Acridan was prepared by reducing acridine with sodium amalgam, then recrystallized from ethanol and finally sublimed.

Procedure. An apparatus is almost the same as the one used in a previous paper.[4] Light source is a super-high pressure mercury lamp. Light shorter than 350 mμ was completely removed to prevent the excitation of acridan. The light quantity was measured by a ferric potassium oxalate actinometer. All the measurements were made at 25°C. The concentration of oxygen was determined from the pressure of oxygen (or air) with the use of Bunsen's coefficient of oxygen at 25°C, 0.205.[6]

Results and Discussion

Degassed Solution

As Fig. 1 shows, the irradiation causes the decline in the absorption peak of acridine at 358 mμ and the elevation in the region around 290 mμ with an isosbestic point at 329 mμ. Such behavior is seen under all the present experimental conditions at least in the initial stage of the reaction. It was checked that the addition of a small amount of water scarcely affects the reaction.

Identification of the Reaction Product. White precipitate obtained from the irradiated solution containing 6.6×10^{-3} M acridine and 6.6×10^{-3} M acridan, was identified as diacridan

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[1] A. Kira, S. Kato and M. Koizumi, This Bulletin, **39**, 1221 (1966); A. Kira, Y. Ikeda and M. Koizumi, *ibid.*, **39**, 1673 (1966).

[2] *Cf.* A. Kellmann, *J. Chim. Phys.*, **63**, 936 (1966); A. Kellmann and J. T. Dubois, *J. Chem. Phys.*, **42**, 2518 (1965).

[3] M. Giurgea, G. Mihai, V. Topa and M. Musa, *J. Chim. Phys.*, **61**, 619 (1964).

[4] S. Kato, S. Minagawa and M. Koizumi, This Bulltin, **34**, 1026 (1961); S. Niizuma and M. Koizumi, *ibid.*, **36**, 1629 (1963).

[5] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

[6] "Kagaku Binran (Handbook of Chemistry)," Chem. Soc. Japan, (ed.), Maruzen, Tokyo (1966), p. 621.

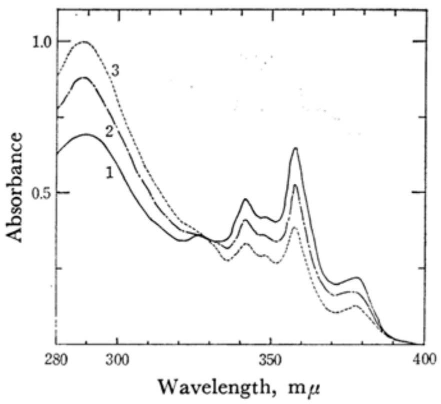

Fig. 1. Change of absorption spectra by irradiation (degassed benzene solution).
$[A]=5\times10^{-5}$ M
$[AH_2]=5\times10^{-5}$ M
1) before illumination
2) 5 min after illumination
3) 30 min after illumination

by means of an IR measurement.[7] The photoproduct in the degassed benzene solution gradually turned into acridine and acridan even in the dark; in the aerated solution it changed to acridine. When the solution which had been submitted to the reaction, was aerated and then illuminated again, acridine was recovered with a high quantum yield. Figure 2 shows an example. In the figure, Curve a represents the decrease of acridine when the degassed solution of acridine and acridan was irradiated, and Curve b shows the recovery of acridine when the solution thus obtained was aerated and reilluminated. It is evident that the production of acridine proceeds in two steps; the first rapid reaction may be ascribed to the oxidation of diacridan while the second is due to the oxidation of acridan (see below). This was confirmed by the finding that the original quantity of acridine was recovered near the end of the first stage. All the above results confirm that the photoproduct is diacridan.

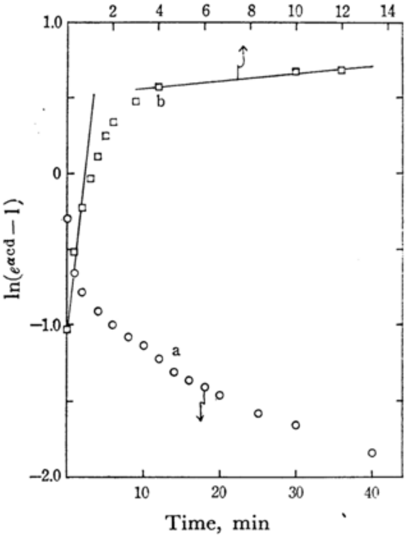

Fig. 2. $\ln(e^{\alpha cd}-1)$ *vs.* t plot.
$[A]=5\times10^{-5}$ M
$[AH_2]=1\times10^{-4}$ M
a. Degassed solution, when irradiated.
b. Air was introduced to an irradiated solution, a, and then irradiated again.

General Feature of the Kinetics. Since the reaction occurs at a rather low concentration of acridan, it is plausible to consider that a reactive state of acridine is the lowest triplet state with a long life. If the reaction proceeds according to the following scheme,

$$\begin{aligned} &A \xrightarrow{h\nu} A^* \\ &A^* \longrightarrow A^T \\ &A^T + AH_2 \rightarrow 2AH && [1] \\ &2AH \longrightarrow (AH)_2 && [2] \\ &\quad\searrow\!\longrightarrow A + AH_2 && [3] \end{aligned}$$

(A, acridine; A*, singlet excited state of acridine; A^T, triplet acridine; AH_2, acridan; $(AH)_2$, diacridan)

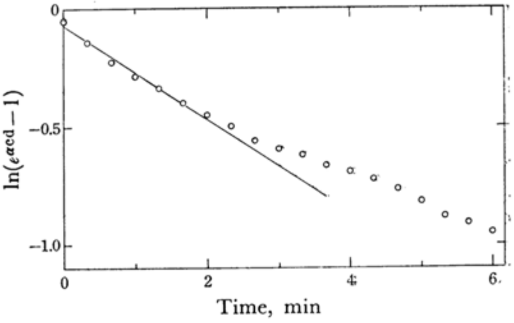

Fig. 3a. $\ln(e^{\alpha cd}-1)$ *vs.* t plot.
$[A]=5\times10^{-5}$ M
$[AH_2]=5\times10^{-3}$ M (Degassed benzene solution)

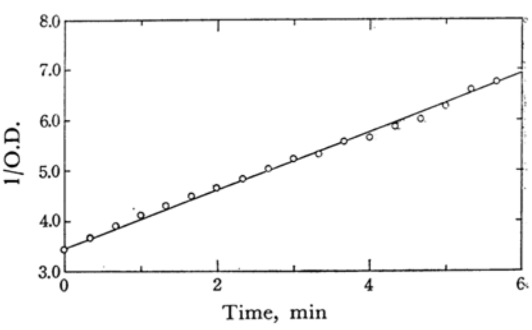

Fig. 3b. Second order plot (1/O.D. *vs.* t).
$[A]=5\times10^{-5}$ M
$[AH_2]=5\times10^{-3}$ M (Degassed benzene solution)

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[7] V. Zanker and H. Schnith, *Chem. Ber.*, **92**, 2210 (1959); A. Kellmann, *J. Chim. Phys.*, **57**, 1 (1960).

the reaction rate is expected to be simply proportional to the absorption of light. But this does not fit the experimental results. As Fig. 3a shows, the linearity of the $\ln(e^{\alpha cd}-1)$ *vs.* t[4] plot does not hold at all, whereas a simple second-order rate formula reproduces the experimental results rather well as seen in Fig. 3b. It is unknown at the present stage whether this rate formula reflects the true reaction scheme or it only holds as a mere approximation. Although the exact rate law is still uncertain, the following characteristic features are induced from more than twenty experiments. 1) The variation of acridan concentration from 5×10^{-5} M to 1×10^{-2} M, keeping the concentration of acridine constant, does not affect the reaction rate at the initial stage. 2) The less the acridan concentration is, the sooner the rate begins to fall. 3) The quantum yield, Φ at the initial stage is 8.4×10^{-2}. 4) The variation of acridine concentration also scarcely affects the initial slope of the $\ln(e^{\alpha cd}-1)$ *vs.* t plot.

The Effect of the Addition of Diacridan on the Rate. The possibility of the occurrence of a backward reaction, for example, $AH+(AH)_2\rightarrow AH+A+AH_2$ was examined in the following way. A benzene solution containing 5×10^{-5} M of acridine and 1×10^{-3} M of acridan was illuminated for 40 minutes. The concentration of acridine which was reduced to about 1/6 of the original, was again raised to $\sim5\times10^{-5}$ M by adding a suitable quantity of acridine. (The procedure was performed through a breakable seal). This solution, when illuminated, showed a small rate which was almost identical with that of the last stage of the first run. Thus the nonlinear relation between $\ln(e^{\alpha cd}-1)$ and t, as seen in Fig. 3a may perhaps be due to a retarding effect of the reaction product.

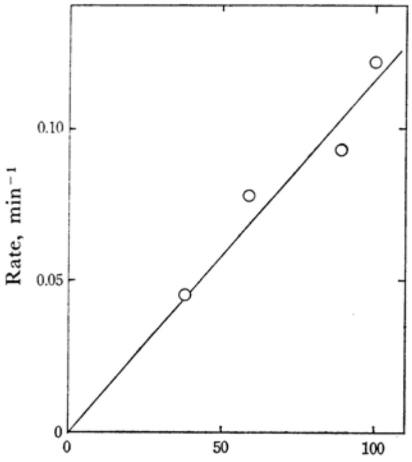

Fig. 4. Effect of light intensity on the rate of the decrease of acridine concentration (degassed benzene solution).
$[A]=5\times10^{-5}$ M
$[AH_2]=1\times10^{-3}$ M

The Effect of Light Intensity. This was examined by placing a wire screen in front of the reaction vessel. (As is shown in Fig. 4, the rate is approximately proportional to the light intensity.)

Concluding Remarks about the Reaction in the Degassed Solution. The present experiments lead to the following scheme for the entire reaction. No effect of light intensity on the quantum yield, precludes any excited intermediate participating in the reaction.

$$A \rightarrow A^*$$

$$A^* \rightarrow A^T$$

$$A^T + AH_2 \xrightarrow{k_1} 2AH \qquad [1]$$

$$2AH \rightarrow (AH)_2 \qquad [2]$$

$$2AH \rightarrow AH_2 + A \qquad [3]$$

$$\left(\begin{array}{l} AH + (AH)_2 \rightarrow AH + A + AH_2 \\ A^T + (AH)_2 \rightarrow A + AH_2 + A \end{array}\right) \qquad \begin{array}{r}[4]\\ [5]\end{array}$$

The reactions in parentheses are the backward reactions which have not yet been decided. The finding that Φ in the initial stage is independent of the acridan concentration above 5×10^{-5} M, leads $k_1>k_d\times2\times10^4$, where k_d is the first order decay constant of the triplet state of acridine. With the value of k_d, $2\times10^3\,\text{sec}^{-1}$,[8] $k_1>4\times10^7\,\text{M}^{-1}\,\text{sec}^{-1}$.[8]

The Reaction in the Aerated Solution

The photochemical reaction between acridine and acridan in the benzene solution containing dissolved oxygen, consists of the oxidation of acridan into acridine.

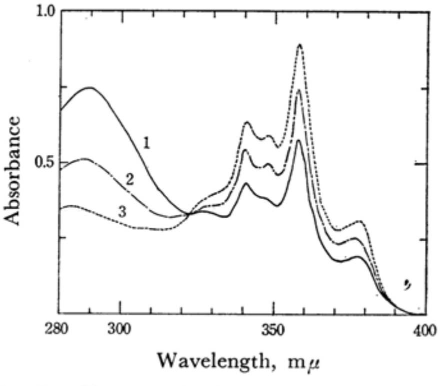

Fig. 5. Change of absorption spectra due to irradiation (Air-saturated benzene solution).
$[A]=5\times10^{-5}$ M
$[AH_2]=5\times10^{-5}$ M
1) before illumination
2) 40 min after irradiation
3) 90 min after irradiation

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[8] To be published. The above value of k_1 is consistent with the one from the flash experiment.

Figure 5 gives a typical example for the change in the absorption spectra during the course of the reaction. It is evident that the decline of acridan peak at 290 mμ is accompanied with the increase in the absorption near 360 mμ. An isosbestic point is seen at 322 mμ.

The $\ln(e^{\alpha cd}-1)$ *vs.* t plot is satisfactorily linear indicating that the rate is simply proportional to the absorption of light.

The Effect of Oxygen Concentration on the Rate. The $\ln(e^{\alpha cd}-1)$ *vs.* t plots for different oxygen concentrations are shown in Fig. 6. When the oxygen concentration is higher than 7—8$\times 10^{-4}$, the linear relation holds during the entire course of the reaction. With the decrease in the oxygen concentration, this linearity ceases to hold at an earlier stage and the magnitude of $\ln(e^{\alpha cd}-1)$ begins to decrease. This is expected naturally since Reaction $A+AH_2\rightarrow(AH)_2$ may occur after the exhaustion of the dissolved oxygen.

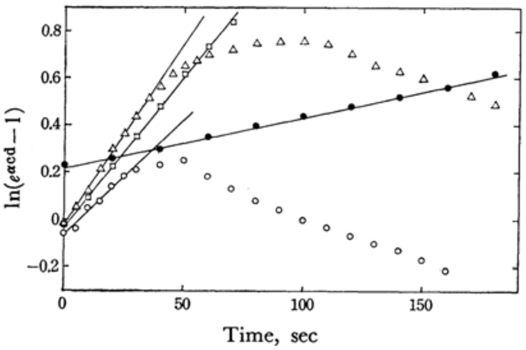

Fig. 6. $\ln(e^{\alpha cd}-1)$ *vs.* t plots for various oxygen concentrations.
$[A]=5\times10^{-5}$ M
$[AH_2]=1\times10^{-3}$ M
$[O_2]$
○ $1.3_8\times10^{-4}$ M △ $2.0_4\times10^{-4}$ M
□ $4.6_8\times10^{-4}$ M ● $3.3_0\times10^{-3}$ M

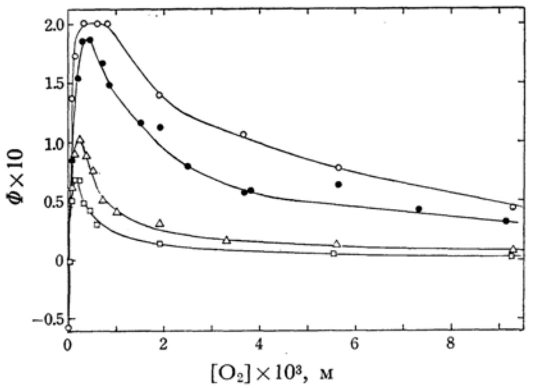

Fig. 7. Effect of oxygen concentration on the quantum yield of acridine formation.
$[A]=5\times10^{-5}$ M
$[AH_2]$
□ 5×10^{-4} M △ 1×10^{-3} M
● 5×10^{-3} M ○ 1×10^{-2} M

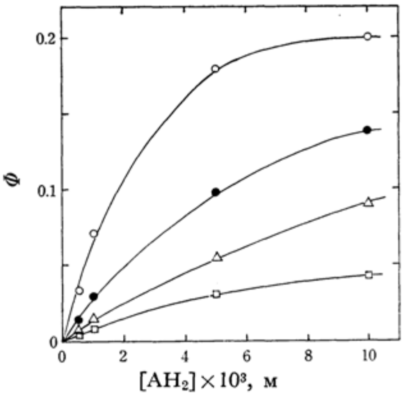

Fig. 8. Dependence of the quantum yield of acridine formation of the concentration of acridan.
$[A]=5\times10^{-5}$ M
$[O_2]$
○ 5×10^{-4} M ● 2×10^{-3} M
△ 5×10^{-3} M □ 9×10^{-3} M

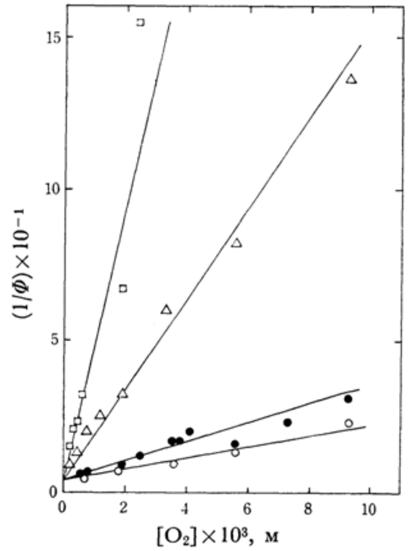

Fig. 9. $1/\Phi$ *vs.* $[O_2]$ plot.
$[A]=5\times10^{-5}$ M
$[AH_2]$
□ 5×10^{-4} M △ 1×10^{-3} M
● 5×10^{-3} M ○ 1×10^{-2} M

Figure 7 gives the relation between the values of the quantum yield (for the yield of acridine), as obtained from the initial slope of the $\ln(e^{\alpha cd}-1)$ *vs.* t plot, and oxygen concentrations. Of course the negative values of Φ correspond to the disappearance of acridine. The general feature is that Φ increases very rapidly with the addition of a small amount of oxygen, but after reaching a maximum, it gradually decreases. Thus it is certain that oxygen or some other gaseous substance(s) in the air exhibit a retarding effect on the reaction. This is also seen from Fig. 8 where Φ is plotted against acridan concentration, keeping the oxygen concentration constant. Figure 9 shows that a good linear relation exists between $1/\Phi$ and oxygen concentration. Of course this relation holds only when the oxygen is in excess. The following formula reproduces the above results.

$$\Phi = \text{const.} \times \frac{\beta[\mathrm{AH_2}]}{\alpha[\mathrm{O_2}]+\beta[\mathrm{AH_2}]} \tag{1}$$

The value of const. is 0.25 and the ratio of α and β is 3.3

The Effect of Light Intensity. The quantum yield was found to be almost independent of the light intensity.

Discussion on the Reaction Scheme. It is reasonable to consider that a reactive state of acridine is the lowest π-π^* triplet state, since the reaction occurs with the concentrations of oxygen and acridan as low as 10^{-5} M. Equation (1) seems to suggest that oxygen merely deactivates the triplet acridine. If this assumption is adopted, Eq. (1) may be interpreted on the basis of the following A scheme.

Scheme A

$$\mathrm{A} + h\nu \rightarrow \mathrm{A}^* \qquad I_{ab}$$

$$\mathrm{A}^* \rightarrow \mathrm{A^T} \qquad I_{ab}\times\varphi_{\mathrm{ST}}$$

$$\mathrm{A^T} \xrightarrow{k_d} \mathrm{A}$$

$$\mathrm{A^T} + \mathrm{AH_2} \xrightarrow{k_1} 2\mathrm{AH} \qquad [1]$$

$$\mathrm{A^T} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{A} + \mathrm{O_2} \qquad [6]$$

$$2\mathrm{AH} \xrightarrow{k_3} (\mathrm{AH})_2 \qquad [2]$$

$$\searrow\xrightarrow{k_4} \mathrm{A} + \mathrm{AH_2} \qquad [3]$$

$$\mathrm{AH} + \mathrm{O_2} \xrightarrow{k_5} \mathrm{A} + \mathrm{HO_2} \qquad [7]$$

where φ_{ST} is a quantum yield of intersystem crossing. When the concentration of oxygen is high enough, Process (6) outweighs Processes (1) and Φ will be given by

$$\Phi = \varphi_{\mathrm{ST}}\frac{\gamma k_1[\mathrm{AH_2}]}{k_d+k_1[\mathrm{AH_2}]+k_2[\mathrm{O_2}]} \tag{2}$$

where γ is an unknown factor related with any possible reactions between $\mathrm{AH_2}$ and $\mathrm{HO_2}$. From the experimental results, $\gamma\varphi_{\mathrm{ST}}=0.25$, $k_d\approx 0$ and $k_2/k_1=3.3$.

Although the above interpretation apparently seems reasonable, it is rather curious that oxygen plays only a mere deactivator without causing any sensitized action on acridan. The following alternative scheme B which is none the less hypothetical, contains no such difficulty. For simplicity, only the processes occurring at high concentrations of oxygen will be written.

Scheme B

$$\mathrm{A} \rightarrow \mathrm{A}^*$$

$$\mathrm{A}^* \rightarrow \mathrm{A^T}$$

$$\mathrm{A^T} \xrightarrow{k_d} \mathrm{A}$$

$$(\mathrm{A^T} + \mathrm{AH_2} \rightarrow 2\mathrm{AH}) \qquad [1]$$

$$\mathrm{A^T} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{A} + \mathrm{O_2}^* \qquad [6]$$

$$\mathrm{O_2}^* + \mathrm{AH_2} \xrightarrow{k_6} \mathrm{AH} + \mathrm{HO_2} \qquad [8]$$

$$\mathrm{O_2}^* + \mathrm{M} \xrightarrow{k_7} \mathrm{O_2} + \mathrm{M} \qquad [9]$$

$$(\mathrm{AH} + \mathrm{O_2} \xrightarrow{k_8} \mathrm{A} + \mathrm{HO_2}) \qquad [10]$$

In this scheme, oxygen is assumed rather conventionally, to be excited to singlet oxygen,[9] but the interpretation holds quite the same for Schenck's type oxygen adduct.[10] If the concentration of oxygen is high enough, Reaction [6] outweighs Reaction (1) and the oxidation proceeds *via* [8].[*1] M in [9] may be oxygen or some other gaseous substance(s) in the air which deactivate singlet oxygen. The above scheme leads the following equation

$$\Phi = \varphi_{\mathrm{ST}} \times \frac{k_2[\mathrm{O_2}]}{k_d + k_2[\mathrm{O_2}]} \times \frac{\gamma' k_6[\mathrm{AH_2}]}{k_7[\mathrm{M}] + k_6[\mathrm{AH_2}]} \tag{3}$$

[*2]

where γ' is an unknown factor which is related with the behavior of $\mathrm{HO_2}$. Replacing $k_7[\mathrm{M}]$ with $k_7[\mathrm{O_2}]$ and further neglecting k_d to meet the ordinary condition, one gets

$$\Phi = \gamma'\varphi_{\mathrm{ST}}\frac{k_6[\mathrm{AH_2}]}{k_7[\mathrm{O_2}] + k_6[\mathrm{AH_2}]} \tag{4}$$

This is also of the same form as Eq. (1). Further studies are necessary in order to determine whether scheme A or scheme B is correct. In any case, however, it is interesting to note that the values of $\gamma\varphi_{\mathrm{ST}}$ and $\gamma'\varphi_{\mathrm{ST}}$ agrees with a tentiative value of Φ_{ST} for acridine in the aqueous solution.[11] This strongly suggests that γ or γ' is unit and further that a parameter for mere deactivation of $\mathrm{A^T}$ with oxygen is also unnecessary.

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9) C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879 (1964); E. T. Corey and W. O. Taylor, *ibid.*, **86**, 3881 (1964).

10) For instance, G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957).

[*1] For Reaction [6] to outweigh Reaction [1] at $[\mathrm{O_2}] \sim 10^{-4}$ M and at $[\mathrm{AH_2}] \sim 10^{-3}$ M, k_2 should be $>4\times10^8\ \mathrm{M^{-1}\,sec^{-1}}$, since $k_1 \geq 4\times10^7\ \mathrm{M^{-1}\,sec^{-1}}$.

[*2] Strictly speaking, another parameter related with mere deactivation of the triplet acridine by oxygen, should be included. This does not, however, change the general type of the formula.

11) K. Uchida and M. Koizumi, This Bulletin, **35**, 1875 (1962). In Uchida's paper (This Bulletin, **36**, 1097 (1962)) which delt with the photosensitized oxidation of leuco-uranine by acridine, somewhat similar retarding effect of an excess oxygen, to the one observed here, is seen in Figs. 2 and 3 in his paper. The fact, however, was not taken into consideration there; it will be interesting to reinvestigate this point.