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Reactive States of Acridine for the Photoreduction in Tetrahydrofuran

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The photoreduction of acridine in tetrahydrofuran (THF) has been investigated by the steady light experiment and also by the flash technique. The quantum yields in the aerated and deaerated solution were 0.12 and 0.36 respectively. The former value is referred to molecular mechanism while the difference of the two, 0.24, to radical mechanism. It was established that the sensitized reaction occurs with biacetyl ($T(n\text{–}\pi^*)$, 19700 cm^{-1}) as a triplet energy donor. The probability factor β with which the produced $T(\pi\text{–}\pi^*)$ of acridine (15840 cm^{-1}) reacts with THF was found to be $\gtrsim 0.6$. Anthracene ($T(\pi\text{–}\pi^*)$, 14700 cm^{-1}) was found to act as a triplet energy acceptor and to reduce the photoreduction. From the decrease of the quantum yield caused by the addition of anthracene, the quantum yield *via* the lowest $T(\pi\text{–}\pi^*)$ of acridine was evaluated as 0.06. By combining this value with the above β-value, the apparent φ_{ST} has proved to be $\lesssim 0.1$. This very small value compared with the φ_{ST} values presented for other solvents (benzene$\gtrsim$0.25, water$\gtrsim$0.24, ethanol$\gtrsim$0.29) leads to the conclusion that in THF, $T(n\text{–}\pi^*)$ is also a reactive state for the photoreduction. Further, an interesting aspect of the radical mechanism was elucidated from the comparison of Φ_R (quantum yield due to radical mechanism) and Φ_{O_2} (quantum yield of oxygen consumption).

There is at present some disagreement as to the reactive state of acridine for the photoreduction in alcohols. In 1965, Kellmann and Dubois[1] reported that in methanol, the $T(n\text{–}\pi^*)$ state in addition to the singlet excited state may participate in the reaction but the lowest $T(\pi\text{–}\pi^*)$ does not. On the other hand, Vander Donkt and Porter[2] concluded that in isopropanol, only the singlet excited state is reactive. That this discrepancy in methanol and in isopropanol really exists was verified by our group[3] using biacetyl as a T-energy acceptor. This was further reconfirmed from the study on the pH dependence of the photoreduction quantum yield.[4] But a little later, Wilkinson and Dubois[5] proposed that only ${}^1L_a(\pi\text{–}\pi^*)$ is a reactive state in ethanol on the basis of the experiments involving external heavy atom effects.

Recently Zanker and Prell asserted that for the photoreduction of 9-methylacridine in ethanol, the singlet $(n\text{–}\pi^*)$ instead of ${}^1L_a(\pi\text{–}\pi^*)$, is a reactive state.[6] According to our results, the quantum yields of photoreduction *via* $T(n\text{–}\pi^*)$ in methanol, ethanol, *n*-propanol and isopropanol are 0.063, 0.019, 0.022 and 0.00 respectively. These results may perhaps be interpreted in terms of the number of α-H atoms and of the steric factors in the reaction. Some workers however seem to have the opinion that the higher T states of short duration are unable to participate in the reaction. One purpose of the present paper is to show another example opposite to such a view.

The second point which we would like to stress is that although all the above workers agree in the point that the lowest $T(\pi\text{–}\pi^*)$ is not reactive in the photoreduction in alcohols, this can not be true in general. For instance, Koizumi *et al.*[7] established that the photoreaction between acridine and acridan in benzene occurs *via* the lowest T-$(\pi\text{–}\pi^*)$ of the former. It is expected therefore, that such a possibility exists also in the photoreduction of acridine in some suitable solvents. The second object of the present paper is to demonstrate such an example. We found that the photoreduction of acridine in tetrahydrofuran (THF) occurs with a high quantum yield and now the lowest $T(\pi\text{–}\pi^*)$ has been established to be reactive in this solvent, and most likely, the higher

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

[2] E. Vender Donkt and G. Porter, *J. Chem. Phys.*, **46**, 1173 (1967).

[3] a) M. Koizumi, Y. Ikeda and T. Iwaoka, *J. Chem. Phys.*, **48**, 1869 (1968). b) M. Koizumi, Y. Ikeda and H. Yamashita, This Bulletin, **41**, 1056 (1968).

[4] K. Nakamaru, S. Niizuma and M. Koizumi, *ibid.*, **42**, 255 (1969).

[5] F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **48**, 2651 (1968).

[6] V. Zanker and G. Prell, *Ber. Bunsenges. Phys. Chem.*, **73**, 791 (1969).

[7] a) S. Niizuma, Y. Ikeda and M. Koizumi, This Bulletin, **40**, 2249 (1967). b) A. Kira and M. Koizumi, *ibid.*, **40**, 2486 (1967).

$T(n\text{-}\pi^*)$ takes part in the photoreduction.

In addition, an interesting feature of the radical process has been elucidated from the review of all our data so far obtained on the quantum yields for photoreduction and for oxygen consumption.

Experimental

Apparatus for the flash photolysis and the steady light experiment, procedures and samples are all essentially similar as in our previous papers. All the steady light experiments were carried out at 25°C. The light intensity for the steady light experiment was usually 2—3×10^{-9} mol cm^{-2} sec^{-1}. As an exciting light, 365 nm was used for the direct photoreduction and 435.8 nm for the sensitized reaction by biacetyl. The reaction was followed by measuring the change in optical density at 365 nm ($\varepsilon=3.75\times10^3$). A Hitachi MPF-2 spectrofluorometer was used for the measurement of the emission spectra. The concentration of oxygen in THF was decided by the manometric method using Bunsen absorption coefficient. The solubility of oxygen in THF, being not found in literature, was measured with an apparatus specially constructed for the present purpose. See Appendix.

Results and Discussion

Broadly speaking, the photoreduction of acridine in THF occurs in the similar way as in alcohol. Thus as shown in Fig. 1, the absorption maximum at 357 nm declines upon irradiation with 365 nm, and a new peak rises at 285 nm with an isosbestic point at 324 nm. Since the absorption maximum of acridan lies at 290 nm, the photoproducts may contain some acridan derivatives and possibly diacridan in addition to acridan. It was established further, that as in alcohols, the photoreduction occurs even in the aerated solution. The quantum yields in the aerated and in the deaerated solutions were respectively 0.12 and 0.36.

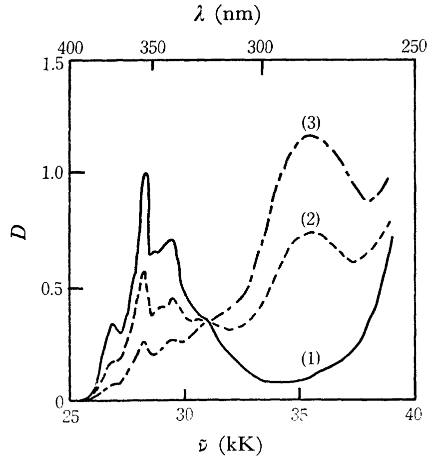

Fig. 1. Change of absorption spectra due to illumination at 365 nm (air-saturated THF solution of acridine).
[A] = 1×10^{-4} M
1) before illumination
2) 4 min 50 sec illumination
3) 10 min 50 sec illumination

The Effect of Oxygen Concentration on the Quantum Yield. Figure 2 shows the plots of $\ln(e^{2.303D}-1)$ against time (D, the optical density at 365 nm) for various concentrations of oxygen up to 2×10^{-3} M. It is seen that the runs for low concentrations of oxygen consist of two linear portions, the earlier portion with almost the same slope as that in the aerated solution and the later one with the slope approaching that in the deaerated solution. These results are similar to those in alcohols,[8] and can be interpreted as follows. Firstly, the reaction proceeds in proportion to the absorption of light. Secondly, the first linear portion corresponds to the period during which the reaction proceeds *via* molecular mechanism, *i.e.*, proceeds as an elementary process or the like, and not *via* semiquinone which, as has already been fully established, is oxidized by oxygen. A sharp breaking point on each run corresponds to the time point where oxygen has been almost exhausted. After the breaking point, the reaction proceeds essentially in the same way as in the deaerated solution, where the molecular and radical mechanisms (the mechanism *via* semiquinone) occur. As shown in Fig. 3, the decrease in acridine concentration during the first period, $-\Delta[\text{A}]$ is proportional to the initial oxygen concentration. This implies that as long as the oxygen concentration is above a certain critical value which is very small, only the molecular mechanism occurs

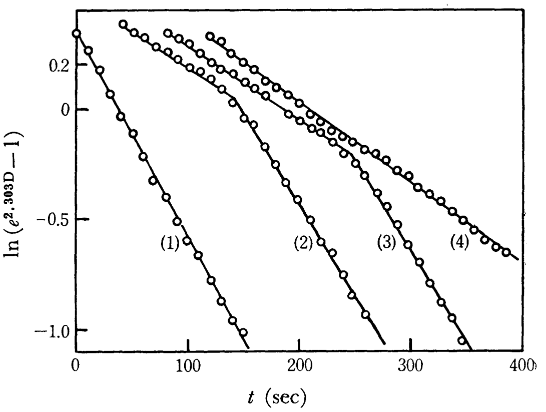

Fig. 2. Plots of $\ln(e^{2.303D}-1)$ *vs.* time for acridine.
[A] = 1×10^{-4} M
(1) Deaerated soln.
(2) $[O_2]=3.4\times10^{-4}$ M
(3) $[O_2]=5.8\times10^{-4}$ M
(4) Aerated soln.

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[8] S. Niizuma and M. Koizumi, This Bulletin, **36**, 1629 (1963).

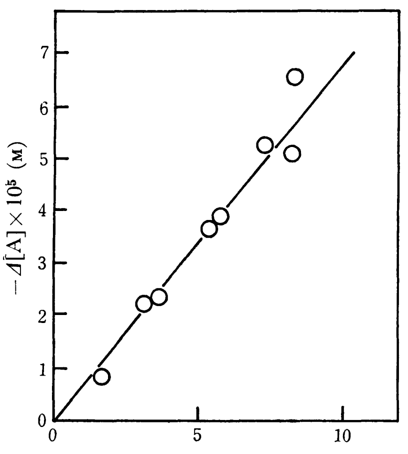

Fig. 3. Plot of the decrease of acridine concentration at the breaking point of the decay curve *vs.* the initial dissolved oxygen concentration.

TABLE 1. QUANTUM YIELDS FOR THE PHOTOREDUCTION OF ACRIDINE IN THF

$[O_2]\times10^4$ (M)	Φ_{air}	mean	Φ	mean
20	0.12_1			
20	0.11_5	0.12		
20	0.12_3			
0			0.34_3	
0			0.36_4	0.36
0			0.36_4	

$[O_2]\times10^4$ (M)	Φ_1	Φ_2	$-\Delta[A]\times10^5$ M
1.02	—	0.36_2	—
1.83	0.13_1	0.34_5	0.8_8
3.37	0.11_8	0.30_5	2.2_2
3.95	0.12_4	0.33_1	2.3_3
5.84	0.12_7	0.29_7	3.6_9
6.25	0.12_4	0.29_2	3.9_4
7.91	0.10_0	0.17_5	5.2_9
8.98	0.10_0	0.17_3	5.0_8
9.04	0.09_8	0.19_9	6.5_5
11.3	0.10_0	—	—

and accordingly, $-\Delta[A]$ is the decrease of acridine due to this mechanism during the first stage. The critical value lies in the region, 1.02—1.83×10^{-4} M. Table 1 gives the values of $-\Delta[A]$, the quantum yields for the aerated (Φ_{air}) and deaerated solution (Φ) and those for the various concentrations of oxygen. In the latter cases, the quantum yields for the early stage Φ_1 and for the later stage Φ_2 are tabulated separately.

The quantum yields of oxygen consumption, Φ_{O_2} can be evaluated simply from the following relation,

$$\frac{-d[O_2]}{dt}\Big/\frac{-d[A]}{dt}=\frac{\Phi_{O_2}}{\Phi_1}=\frac{-\Delta[O_2]}{-\Delta[A]} \tag{3}$$

where $-\Delta[O_2]$ can be equated to the initial concentration of oxygen. From the plot of Fig. 3 the value of Φ_{O_2}/Φ_1 was evaluated as 16 and accordingly Φ_{O_2}, as ~2.0. This value suggests the occurrence of chain mechanism for the disappearance reaction of oxygen.

Reaction Sensitized by Biacetyl. In order to know whether the lowest $T(\pi$-$\pi^*)$ can participate in the reaction, the photosensitized reaction by triplet energy transfer using biacetyl as a donor was attempted at first. The T-levels of biacetyl $T(n$-$\pi^*)$ and acridine $T(\pi$-$\pi^*)$ are respectively 19700 cm^{-1} 9) and 15840 cm^{-1}.10) The lifetime of biacetyl $T(n$-$\pi^*)$ in methanol is 0.2×10^{-3} sec3b) and the diffusion controlled rate constant in THF estimated from the Stokes-Einstein relation is 1.4×10^{10} M^{-1}sec^{-1}. Therefore, it is expected that 10^{-4} M of acridine is enough for the complete energy transfer to occur from biacetyl to acridine. This was really verified by the complete quenching of biacetyl phosphorescence in the solution containing 10^{-4} M of acridine. This is shown in Fig. 4.

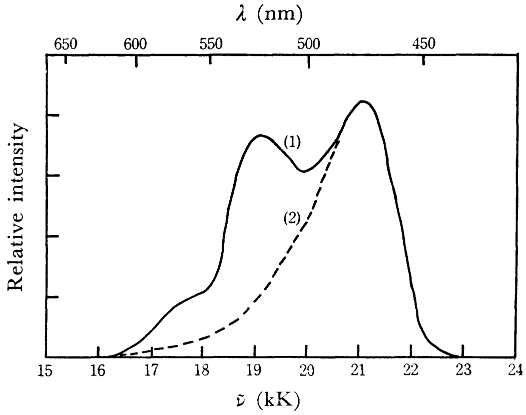

Fig. 4. Emission spectra of biacetyl in the deaerated THF solution (exciting light, 420 nm).
(1) $[B]=1\times10^{-1}$ M
(2) $[B]=1\times10^{-2}$ M, $[A]=1\times10^{-4}$ M

Hence the photosensitized reaction was investigated with the THF solutions containing 10^{-2} M biacetyl and 1×10^{-4} M acridine. The exciting light was chosen at 435.8 nm where there is no absorption of acridine. It is to be noted however, that biacetyl undergoes some unknown reaction in THF gradually when kept in dark for a long time. Hence the sample solution was always prepared immediately before each measurement.

In the aerated solution, the reaction did not occur at all. This is natural since the triplet biacetyl is expected to be quenched completely by $\sim2\times10^{-3}$ M of oxygen.

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9) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

10) D. F. Evans, *J. Chem. Soc.*, **1957**, 1351.

In the deaerated solution the reaction occurred as shown in Fig. 5. In Fig. 6, the relation between the decrease of acridine, $-\Delta[\mathrm{A}]$ as measured by the optical density at 357 nm and the increase of photoproducts, $\Delta[\mathrm{P}]$ measured by the optical density at 285 nm in the present sensitized reaction, is compared with that for the direct reaction. The agreement between the two cases supports that the similar reaction is occurring in the two cases. If one assumes the following scheme,

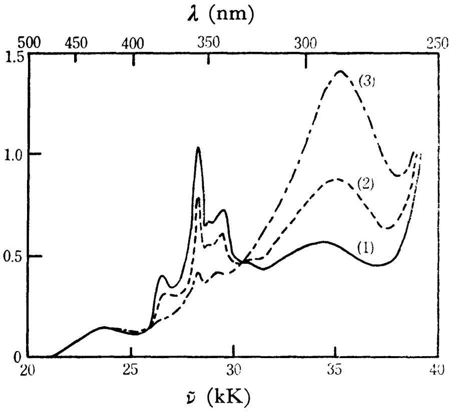

Fig. 5. Change of absorption spectra upon excitation of biacetyl at 435.8 nm (deaerated THF solution).
$[\mathrm{A}]=1\times10^{-4}\,\mathrm{M}$ $[\mathrm{B}]=1\times10^{-2}\,\mathrm{M}$
(1) before illumination
(2) 1 min illumination
(3) 4 min illumination

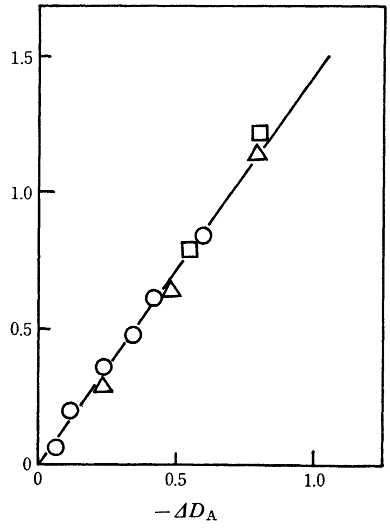

Fig. 6. The relation between the decrease of acridine and the increase of photoproducts.
☐ Direct reaction (aerated soln.)
△ Direct reaction (deaerated soln.)
○ Sensitized reaction

$$\mathrm{B} + h\nu \longrightarrow {}^1\mathrm{B}^* \qquad I_{\mathrm{abs}}$$
$$^1\mathrm{B}^* \longrightarrow {}^3\mathrm{B} \qquad \varphi^{\mathrm{B}}_{\mathrm{ST}} I_{\mathrm{abs}}$$
$$^1\mathrm{B}^* \xrightarrow{k_1} \mathrm{B} + h\nu_{\mathrm{f}}$$
$$^3\mathrm{B} \xrightarrow{k_2} \mathrm{B} + h\nu_{\mathrm{p}}$$
$$^3\mathrm{B} \xrightarrow{k_3} \mathrm{B}$$
$$^3\mathrm{B} + \mathrm{A} \xrightarrow{k_4} \mathrm{B} + {}^3\mathrm{A}$$
$$^3\mathrm{A} + \mathrm{RH}_2 \xrightarrow{k_5} \mathrm{Prod}$$
$$^3\mathrm{A} \xrightarrow{k_6} \mathrm{A}$$

where $^1\mathrm{B}^*$, $^3\mathrm{B}$ and $^3\mathrm{A}$ are respectively the singlet excited state of biacetyl, the n-π^* triplet of biacetyl and the π-π^* triplet of acridine. RH_2 stands for THF which acts as a reducing agent. The steady state method gives the following equation,

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = \varphi_{\mathrm{ST}}\cdot\chi\cdot\beta\cdot I_{\mathrm{abs}} \qquad (4)$$
$$\chi = k_4[\mathrm{A}]/(k_2+k_3+k_4[\mathrm{A}])$$
$$\beta = k_5[\mathrm{RH}_2]/(k_5[\mathrm{RH}_2] + k_6)$$

Putting $\varphi^{\mathrm{B}}_{\mathrm{ST}}\simeq1$[9] and $\chi=1$, the following zeroth order rate formula is expected to hold, which enables us to evaluate the value of β.

$$[\mathrm{A}] = [\mathrm{A}]_0 - \beta I_{\mathrm{abs}}t \qquad (5)$$

In reality however, this does not hold satisfactorily as shown in Fig. 7. Perhaps it may be due to the occurrence of some side reactions involving biacetyl. Thus the exact value of β could not be decided and only its lower limit was estimated as $\beta\gtrsim0.6$.

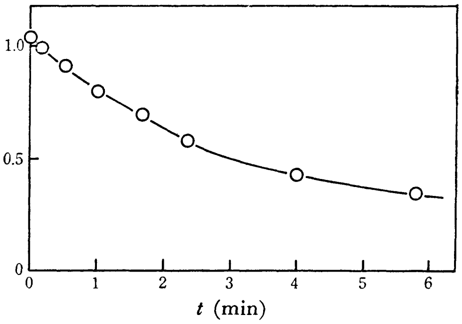

Fig. 7. Plot of D at 357 nm *vs.* time for the biacetyl sensitized reaction.

The Effect of the Addition of Anthracene as a *T*-Energy Acceptor. Although the above results support the occurrence of photoreduction at the lowest $T(\pi$-$\pi^*)$ of acridine, there still remains some suspicion that the reaction is not due to T-T energy transfer but due to some other type of sensitization, for instance, a reaction involving half-reduced biacetyl.[2] To get further evidence, the effect of the addition of a triplet energy acceptor on the photoreduction was examined. As such a substance, anthracene $T(\pi$-$\pi^*)$ of which is located at 14700 cm^{-1}[11] was employed. Anthracene has

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[11] J. Nag-Chaudhuri, L. Stoessell and S. P. McGlynn, *J. Chem. Phys.*, **38**, 2027 (1963).

however, the absorption in the region common to acridine, and care should be paid on its inner filter effect.

Generally, the information on the energy transfer can be obtained directly by the flash technique. But before doing this, the feature of the transient species produced by the flash illumination in THF solutions of acridine alone, anthracene alone and of the two, were examined preliminarily. The transient spectra of acridine, 1×10^{-4} M in THF, resemble those obtained in ethanol[12] and in benzene[7b] very well, and the peaks at 440 nm and at 520 nm are safely assigned to the T–T absorption and to semiquinone. The first order decay constant of the former could not be measured very accurately but was estimated about $\sim1\times10^4$ sec^{-1}. The second order decay constant of semiquinone measured at 520 nm was $\sim4\times10^5\,\varepsilon$ M^{-1} sec^{-1}. The transient absorption for anthracene alone 1×10^{-5} M and for the mixture of anthracene 1×10^{-5} M and acridine 1×10^{-4} M were compared. The former agrees very well with T–T absorption in literature,[13] and its decay is of the second order in agreement with Linschitz *et al.*[14] The decay constant was measured at 425 nm and was decided as $8.1\times10^4\,\varepsilon$ M^{-1} sec^{-1}. The agreement of the main peak position in the two solutions suggested the almost complete energy transfer from acridine to anthracene.

Quantitative Investigation on the Energy Transfer. The energy transfer from acridine $T(\pi$–$\pi^*)$ to anthracene was investigated quantitatively under various conditions using the flash technique involving the emission measurement.[15] For this purpose, the yields of triplet anthracene $[^3\mathrm{An}]_0$ were investigated at a fixed acridine concentration, $[\mathrm{A}]=1\times10^{-4}$ M and at various anthracene concentrations up to 2×10^{-5} M. Under such a condition, the inner filter effect of anthracene may be neglected to a first approximation. The yield of triplet anthracene $[^3\mathrm{An}]_0$ for which conventionally the quantity 50 μsec after flashing was taken,[15] consists in general of the two portions, the one due to the direct excitation of anthracene, $[^3\mathrm{An}]_d$ and the other due to energy transfer from acridine, $[^3\mathrm{An}]_e$. Thus,

$$[^3\mathrm{An}]_0 = [^3\mathrm{An}]_d + [^3\mathrm{An}]_e \tag{6}$$

Under the above assumption the efficiency of energy transfer can be studied from the effect of anthracene concentration on $[^3\mathrm{An}]_e$, and to do this it is necessary to know the magnitude of $[^3\mathrm{An}]_d$. This was performed as follows. $[^3\mathrm{An}]_d$ which is equated to $\varphi_{\mathrm{ST}}^{\mathrm{An}}\int I_{\mathrm{abs}}^{\mathrm{An}}\mathrm{d}t$, is proportional to the integrated fluorescence intensity during a flash because of the following relation,

$$\int I_{\mathrm{F}}\,\mathrm{d}t \propto \phi_{\mathrm{F}}\int I_{\mathrm{abs}}^{\mathrm{An}}\,\mathrm{d}t$$

in which ϕ_{F} is the fluorescence quantum yield. The fluorescence of anthracene was measured at 405 nm where there is no absorption of acridine and of anthracene. Figure 8 gives the relationship between $\int I_{\mathrm{F}}\,\mathrm{d}t$ (at 405 nm) and D_0 (at 425 nm) measured at various flash intensities for the solution of anthracene alone. It is obvious that the relation

$$D_0 = \gamma\int I_{\mathrm{F}}\,\mathrm{d}t \tag{7}$$

holds satisfactorily and that the parameter γ can be evaluated correctly from the plot. This relation can be used to know the quantity of $[^3\mathrm{An}]_d$ for the mixed solution of acridine and anthracene, because acridine is nonfluorescent in THF.

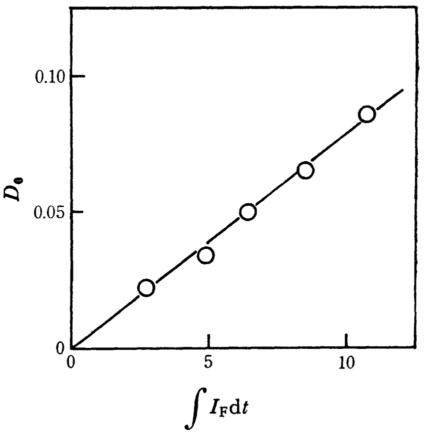

Fig. 8. Plot of D_0 at 425 nm *vs.* $\int I_{\mathrm{F}}\mathrm{d}t$ at 405 nm for the THF solution of anthracene.

Now in practice, it is more convenient to make argument in terms of the optical densities, and for this purpose equation (6) is to be rewritten as follows using eq. (7).

$$D_0 = D_0^{\mathrm{A}} + D_{0\mathrm{e}}^{\mathrm{An}} + \gamma\int I_{\mathrm{F}}\,\mathrm{d}t \tag{8}$$

where D_0, $D_{0\mathrm{e}}^{\mathrm{An}}$ and D_0^{A} are respectively the entire optical density at 425 nm, that due to anthracene produced by energy transfer and that due to acridine. The values of $D_0^{\mathrm{A}}+D_{0\mathrm{e}}^{\mathrm{An}}$ thus obtained are in general written as follows,

$$D_0^{\mathrm{A}} + D_{0\mathrm{e}}^{\mathrm{An}} = \{\varepsilon_{^3\mathrm{A}}[^3\mathrm{A}]_0 + \varepsilon_{^3\mathrm{An}}[^3\mathrm{An}]_e\}d \tag{9}$$

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

[13] M. W. Windsor and J. R. Novak, "The Triplet State," ed. A. B. Zahlan, Cambridge University Press, Cambridge (1967), p. 229.

[14] H. Linschitz, C. Steel and J. A. Bell, *J. Phys. Chem.*, **66**, 2574 (1962).

[15] K. Kikuchi, H. Kokubun and M. Koizumi, This Bulletin, **49**, 1545 (1968).

In the special case that [An]=0,

$$D_{00}^{\mathrm{A}} = \varepsilon_{^3\mathrm{A}}[{}^3\mathrm{A}]_{00}d \tag{10}$$

From these two equations and using the relation $[{}^3\mathrm{A}]_{00}=[{}^3\mathrm{A}]_0+[{}^3\mathrm{An}]_0$, one gets

$$\Delta D_{0\mathrm{e}} = D_0^{\mathrm{A}} + D_{0\mathrm{e}}^{\mathrm{An}} - D_{00}^{\mathrm{A}} = \{(\varepsilon_{^3\mathrm{An}}-\varepsilon_{^3\mathrm{A}})[{}^3\mathrm{An}]_e\}d \tag{11}$$

which shows that $\Delta D_{0\mathrm{e}}$ is a measure of $[{}^3\mathrm{An}]_e$.

Figure 9 gives the plot of $\Delta D_{0\mathrm{e}}$ *vs.* [An]. It can be concluded from Fig. 9 that the energy transfer occurs completely above 5×10^{-6} M of anthracene. It is to be added that the decay of triplet anthracene in the mixed solution is $\sim 0.8\times10^4\ \mathrm{sec}^{-1}$ and is very much larger than that in the solution of anthracene alone. This may suggest the attack of some intermediates originating from acridine upon triplet anthracene, but this does not invalidate the above treatment.

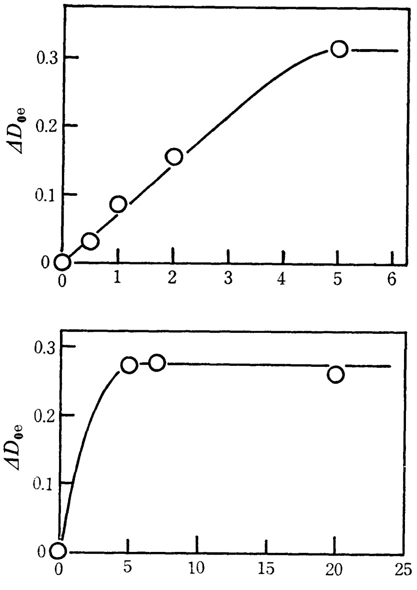

Fig. 9. Plots of $\Delta D_{0\mathrm{e}}$ *vs.* [An].
upper: lower concentration region
lower: higher concentration region

Dependence of the Quantum Yield on the Anthracene Concentration. This was investigated by varying the concentration of anthracene from 5×10^{-7} to 1.4×10^{-4} M and by fixing the concentration of acridine at 1×10^{-4} M. It was found that the solution of anthracene alone undergoes the photoreaction but the quantum yield is less than 10^{-2} and can be neglected in the present case. The inner filter effect was corrected on the basis of the following equation,

$$\ln(e^{2.303D_0}-1) - \ln(e^{2.303D}-1) = \Phi I_0\alpha\left(t-\int_0^t \frac{D_{\mathrm{An}}}{D}\mathrm{d}t\right)\times10^3 \tag{12}$$

where α is the molar absorption coefficient of acridine at 365 nm, where D and D_0 are the optical densities at t and $t=0$ and where D_{An} is the optical density of anthracene. The other notations are the usual ones. Thus the correct value of Φ can be obtained only by changing the time axis by $-\int_0^t D_{\mathrm{An}}/D\cdot\mathrm{d}t$. It was checked that this correction was very satisfactory. The quantum yields at various anthracene concentrations are given in Table 2.

TABLE 2. QUANTUM YIELDS AT VARIOUS ANTHRACENE CONCENTRATIONS

[An] (M)	Φ	$-\Delta\Phi$
0	0.36	—
5×10^{-7}	0.35_7	0.00_3
1×10^{-6}	0.33_0	0.03_0
2×10^{-6}	0.31_4	0.04_6
5×10^{-6}	0.29_8	0.06_2
5×10^{-6}	0.31_2	0.04_8
7×10^{-6}	0.30_6	0.05_4
1×10^{-5}	0.32_1	0.03_9
2×10^{-5}	0.30_2	0.05_8
2.5×10^{-5}	0.29_3	0.06_7
5×10^{-5}	0.28_5	0.07_5
9×10^{-5}	0.26_8	0.09_2
1.4×10^{-4}	0.25_1	0.10_9

It is obvious that the addition of anthracene causes a decrease in the quantum yield. Assuming that this decrease is due to the energy trnasfer from acridine $T(\pi\text{-}\pi^*)$ to anthracene, the analysis can be made on the following scheme,

$$\mathrm{A} + h\nu \longrightarrow \mathrm{A}^* \qquad I_{\mathrm{abs}}$$

$$\mathrm{A}^* + \mathrm{RH}_2 \longrightarrow \mathrm{Prod} \qquad \Phi^* I_{\mathrm{abs}}$$

$$\mathrm{A}^* \longrightarrow {}^3\mathrm{A} \qquad \varphi_{\mathrm{ST}} I_{\mathrm{abs}}$$

$${}^3\mathrm{A} \xrightarrow{k_1} \mathrm{A}$$

$${}^3\mathrm{A} + \mathrm{RH}_2 \xrightarrow{k_2} \mathrm{Prod}$$

$${}^3\mathrm{A} + \mathrm{An} \xrightarrow{k_3} \mathrm{A} + {}^3\mathrm{An}$$

$${}^3\mathrm{An} \xrightarrow{k_4} \mathrm{An}$$

where ${}^3\mathrm{A}$ is the lowest $T(\pi\text{-}\pi^*)$ of acridine and A* stands conventionally for the other reactive states (singlet excited state and $T(n\text{-}\pi^*)$) and where ${}^3\mathrm{An}$ is the anthracene triplet state. The total quantum yield consists of two parts, one due to A^* (Φ^*) and the other due to ${}^3A$ (Φ_T). In the absence of anthracene,

$$\Phi_0 = \Phi^* + \Phi_T^0$$

and in the presence of anthracene (assuming that anthracene quenches only $T(\pi\text{-}\pi^*)$),

$$\Phi = \Phi^* + \Phi_T$$

Then,

$$-\Delta\Phi = \Phi_0 - \Phi = \Phi_T^0 \frac{k_3[\mathrm{An}]}{k_1+k_2[\mathrm{RH_2}]+k_3[\mathrm{An}]} \qquad (13)$$

and

$$1/-\Delta\Phi = 1/\Phi_T^0(1+1/(k_3[\mathrm{An}]\tau)) \qquad (14)$$
$$(1/\tau = k_1+k_2[\mathrm{RH_2}])$$

Since the flash experiment has already demonstrated that the energy transfer is complete above 5×10^{-6} M of anthracene, it is desirable to apply the above equation at lower concentrations. But in such a region the effect was so small that the reliable data could not be obtained. In fact, Table 2 shows that the values of $-\Delta\Phi$ in the region 5×10^{-6}—2.5×10^{-5} M of anthracene, are almost constant and are 0.06. The further decrease in the higher concentration of anthracene might be due to the quenching of $T(n\text{-}\pi^*)$. Figure 10 gives the plot of $1/\Phi$ *vs.* log [An] and the plot of $1/-\Delta\Phi$ *vs.* [An] which was drawn under the assumption that Φ_T^0 is equal to 0.06. The value of $k_3\tau$ obtained from the latter plot is 3.5×10^6 M^{-1} and by putting $k_3=1.4\times10^{10}$ M^{-1} sec^{-1}, one gets $\tau=2.5\times10^{-4}$ sec. Although these values are not very reliable, the latter value is compared with the result obtained by the flash experiment.

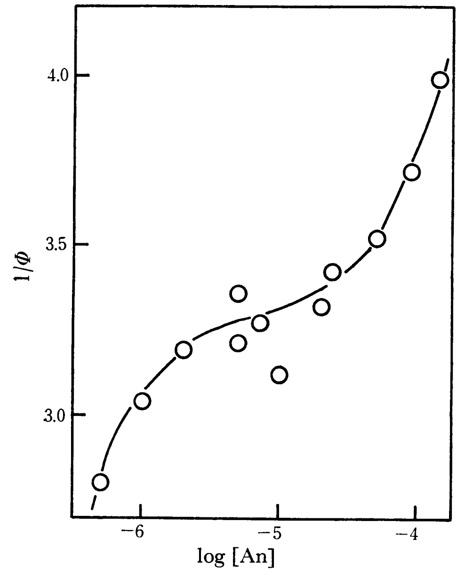

Fig. 10a. Plot of $1/\Phi$ *vs.* log [An].

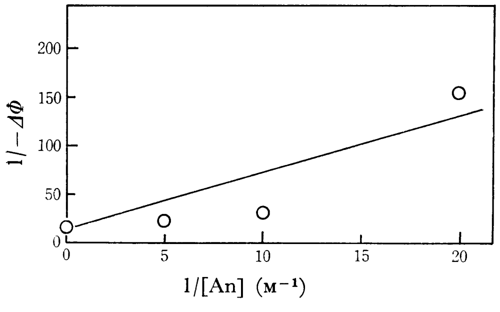

Fig. 10b. Plot of $1/-\Delta\Phi$ *vs.* 1/[An].

Conclusion

The present work has established that the quantum yields of the photoreduction of acridine in the aerated and in the deaerated THF solution are respectively 0.12 and 0.36. The former occurs by molecular mechanism, and the latter by radical mechanism in addition to molecular one. The contribution of radical mechanism is thus 0.24. We have not yet succeeded in deciding the contribution of different excited states to the above two processes. But it has been demonstrated that a certain portion is due to the reaction involving $T(\pi\text{-}\pi^*)$. Thus firstly, the sensitized reaction has been found to occur by using biacetyl as a sensitizer, of which the triplet level is lower than acridine $T(n\text{-}\pi^*)$ but higher than its $T(\pi\text{-}\pi^*)$. Furthermore, it has been shown by the flash technique that anthracene above 5×10^{-6} M, deactivates $T(\pi\text{-}\pi^*)$ of acridine completely and that the quantum yield of photoreduction of acridine decreases by about 0.06 ($=\Phi_T$) by the addition of anthracene of the same concentration. Combining the value of Φ_T with the probability factor $\beta\gtrsim0.6$ with which the $T(\pi\text{-}\pi^*)$ state reacts with THF, it can be concluded that the φ_{ST} value in the present system appears to be $\lesssim0.1$.

On the basis of this value, further conclusion

Table 3. Quantum yields in various solvents

	Φ_{total}	Φ_{M} (%)	Φ_{R} (%)	$\Phi_{T(\pi-\pi^*)}$ (%)	$\Phi_{\mathrm{O_2}}$
THF	0.36	0.12 (33)	0.24 (67)	0.06 (17)	2
Methanol	0.128	0.033 (25) (S 0.027, T 0.006)	0.096 (75) (S 0.039, T 0.057)	0	0.096
Ethanol	0.129	0.043 (30) (S only)	0.086 (70) (S 0.067, T 0.019)	0	0.086
n-Propanol	0.088	0.030 (35) (S only)	0.058 (65) (S 0.036, T 0.022)	0	—
Isopropanol	0.089	0.031 (35) (S only)	0.058 (65) (S only)	0	0.16

S: Singlet excited state, T: $T(n\text{-}\pi^*)$ state.

can be made on the reactive states in the present system. Table 3 lists the present result with those obtained by our group in the past. From the results in alcohols, one may say that molecular mechanism occurs mainly at singlet excited state. This may perhaps be true for THF. Then the Φ_R value of 0.24 includes 0.06 of $\Phi_{T(\pi\text{-}\pi^*)}$ and the remaining part 0.18 may be due to the reaction at both singlet excited and $T(n\text{–}\pi^*)$ states. It is highly unlikely that this is due only to singlet excited state in view of the φ_{ST} values estimated from the previous work. Thus the value of φ_{ST} in benzene and in water was estimated respectively as $\gtrsim 0.25$[7a] and $\gtrsim 0.24$.[16] Furthermore it has been decided recently by Kikuchi that the φ_{ST} value in ethanol is 0.27.[17] This value, however, is concerned with the $T(\pi\text{–}\pi^*)$ state which is produced under the condition that the reaction *via* $T(n\text{–}\pi^*)$ is occurring as shown in the above table. Thus the true φ_{ST} value in ethanol is $\gtrsim 0.27+0.019=0.29$. At any rate, it seems that the φ_{ST} value does not vary so much according to solvents, and it lies in the range 0.25—0.3. Hence, it is very unlikely that the true φ_{ST} value in THF is so small as $\lesssim 0.1$. It may be concluded that this low value is due to the participation of $T(n\text{–}\pi^*)$ in the reaction to some considerable extent. Further decrease in the quantum yield by the addition of anthracene$>2\times10^{-5}$ M, is also consistent with this conclusion. Determination of the reliable φ_{ST} values of acridine in various solvents are now in progress.

At the end, some consideration will be added on the quantum yields of the oxygen consumption, Φ_{O_2}. In table 3 are added the Φ_{O_2} values in THF and in alcohols, the values in alcohols being recalculated from the old data.[8] It is remarkable that the values of Φ_{O_2} in methanol and ethanol do agree exactly with the Φ_R values. This is interpreted very satisfactorily as follows. Acridine semiquinone AH and the solvent radical RH produced by radical mechanism in these solvents mainly undergo disproportionation reaction separately, as has been substantiated to some extent in the previous paper.[12] Oxygen when existent, is considered to be consumed mainly by the following processes,

$$AH + (O_2) \longrightarrow A + HO_2,\ 2HO_2 \longrightarrow H_2O_2 + O_2$$

where (O_2) denotes the oxygen involved in the oxidative species.

Then for each two semiquinone molecules, one acridan molecule is produced in the absence of oxygen while in the presence of oxygen, one oxygen molecule is exhausted. Thus the material balance is in excellent agreement with the above data. On the other hand, for isopropanol and especially for THF, the Φ_{O_2} values are much larger than those of Φ_R. It is suggested that in these solvents, the following reactions may occur as proposed by Stockhausen *et al.*,[18] in the presence of oxygen.

$$RH + O_2 \longrightarrow RHO_2 \quad (1)$$

$$RHO_2 + RH_2 \longrightarrow RHO_2H + RH \quad (2)$$

$$RHO_2 + RHO_2 \longrightarrow \text{Prod} \quad (3)$$

If process (2) predominates over process (3) then the chain type-reaction will become possible. In fact, it really occurs in THF, as has been clearly demonstrated by the Φ_{O_2} value larger than unity.

Appendix

Measurement of the Solubility of Oxygen in THF. Since no data on the solubility of oxygen in

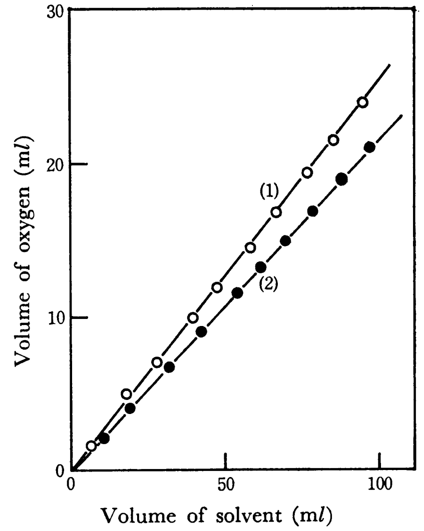

Fig. 11. The relation between the volume of solvent and that of oxygen dissolved in it.
(1) THF (2) Benzene

Table 4. Solubility data of oxygen

	Rate of dropping (m*l*/min)	α	mean	α in literature
Methanol	0.75	0.229		
	1.5	0.228	0.229	0.227[20]
	2.0	0.229		
Benzene	1.5	0.203	0.204	0.205[21]
	2.0	0.205		
THF	1.0	0.236		
	1.9	0.234	0.235	—
	2.5	0.236		

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[16] K. Uchida and M. Koizumi, This Bulletin, **35**, 1875 (1962).

[17] K. Kikuchi, H. Kokubun and M. Koizumi, The 23rd Annual Meeting of Chem. Soc. Japan, April in 1970.

[18] K. Stockhausen, A. Henglein and G. Beck, *Ber. Bunsenges. Phys. Chem.*, **73**, 567 (1969).

THF are found in literature, the measurement was made with an apparatus constructed according to the direction recommended by Morrison and Billet,[19] which in principle is based on the saturation method.

Result. The measurement was made at 25°C. The analysis was made by plotting the volume of dissolved gas against that of solvent. Some examples are shown in Fig. 11. From the slope of the plot, the solubility, L was evaluated and Bunsen coefficient was obtained from the following relation.

$$\alpha = L\frac{273}{273+t}$$

As a check Bunsen coefficients of oxygen in methanol and benzene were measured. The results are given in Table 4, together with the data in literature.

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[19] T. J. Morrison and F. Billet, *J. Chem. Soc.*, **1948**, 2033. R. Battino and H. L. Clever, *Chem. Rev.*, **66**, 395 (1966).

[20] C. B. Kretschmer, J. Nowakowska and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946).

[21] J. Horiuchi, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)* **17**, 125 (1931).