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Primary Processes in the Photoreduction of Acridine in Various Alcohols

Masao KOIZUMI, Yoshinori IKEDA and Hiroshi YAMASHITA

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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The effect of the addition of biacetyl on the quantum yield of photoreduction of acridine in methanol, ethanol, *n*- and iso-propanol has been studied under the aerated and deaerated conditions. From the analysis of the results, the quantum yields for four mechanisms $\Phi^{\mathrm{S}}_{\mathrm{M}}$ (S means that a reactive state is singlet excited states, S*, and M denotes a molecular mechanism), $\Phi^{\mathrm{S}}_{\mathrm{R}}$ (R denotes a radical mechanism), $\Phi^{\mathrm{T}}_{\mathrm{M}}$ (T indicates that a reactive state is a state other than S* and T(π–π*), most likely T(n–π*) and $\Phi^{\mathrm{T}}_{\mathrm{R}}$ have been decided, assuming that oxygen does not deactivate T(n–π*). The values are

for methanol,	$\Phi^{\mathrm{S}}_{\mathrm{M}}(0.027)$	$\Phi^{\mathrm{S}}_{\mathrm{R}}(0.039)$	$\Phi^{\mathrm{T}}_{\mathrm{M}}(0.006)$	$\Phi^{\mathrm{T}}_{\mathrm{R}}(0.057)$
for ethanol,	$\Phi^{\mathrm{S}}_{\mathrm{M}}(0.043)$	$\Phi^{\mathrm{S}}_{\mathrm{R}}(0.067)$	$\Phi^{\mathrm{T}}_{\mathrm{M}}(0)$	$\Phi^{\mathrm{T}}_{\mathrm{R}}(0.019)$
for *n*-propanol,	$\Phi^{\mathrm{S}}_{\mathrm{M}}(0.030)$	$\Phi^{\mathrm{S}}_{\mathrm{R}}(0.036)$	$\Phi^{\mathrm{T}}_{\mathrm{M}}(0)$	$\Phi^{\mathrm{T}}_{\mathrm{R}}(0.022)$
for isopropanol,	$\Phi^{\mathrm{S}}_{\mathrm{M}}(0.03)$	$\Phi^{\mathrm{S}}_{\mathrm{R}}(0.058)$	$\Phi^{\mathrm{T}}_{\mathrm{M}}(0)$	$\Phi^{\mathrm{T}}_{\mathrm{R}}(0)$

The quenching constants of biacetyl on the fluorescence of acridine have been found to agree with the ones on the reaction at S* in all alcohols; the rate constants approximate diffusion controlled. In addition it has been confirmed by a flash method that biacetyl does not attack the T(π–π*) nor the semi-reduced acridine; this justifies the present method of analysis.

It is well known that acridine dissolved in some H-containing solvents, undergoes photoreduction and yields acridan, its derivatives or diacridan according to the experimental conditions.[1-5] Since all these products have no absorption from 350 to 400 mμ where the absorption of acridine is large, disappearance of acridine can be followed very accurately by the change in the optical density at 365 mμ and some interesting feature of the reaction was obtained from such kinetic studies.[6,7] Recent flash photolytic investigations performed by our group,[8] have revealed that two independent primary processes are involved in this photoreduction. One is a radical mechanism in which half-reduced acridine is formed as an intermediate, and the other is a mechanism in which acridan or its derivative (perhaps a compound in which a solvent fragment is attached to 9-position[3-5] is produced so quickly that no intermediate is observed by an ordinary flash technique. This mechanism was designated conventionally as a molecular mechanism.

Kellmann and Dubois, on the other hand, proposed that the reactive state of acridine in methanol is most likely the n–π* triplet state instead of the lowest π–π* triplet state.[9] They did not, however, exclude the possibility of singlet excited state participating in the reaction. We also confirmed by energy transfer experiments, using eosine as triplet energy acceptor, that the lowest triplet is not a reactive state.[10]

Under such status, we have planned to make the experiments which will make clear the contributions of singlet excited state and of n–π* triplet state to the entire reaction and the experiments which will decide for each state the contribution of radical and molecular mechanisms. Such experiments consist of investigating the effect of biacetyl (used as a triplet energy acceptor) concentration on the rate of photoreduction both in the absence and in the presence of oxygen. We have made such studies using methanol, *n*- and iso-propanol as H-containing solvents, and have obtained some interesting results. It was not a long while since we had finished the present experiments that a paper by Van der Donckt and Porter appeared,[11] which has raised some doubt on the conclusion of Kellmann and Dubois; they have

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1) V. Zanker and P. Schmidt, *Z. physik. Chem. N.F.*, **17**, 11 (1958).

2) A. Kellmann, *J. Chem. Phys.*, **57**, 1 (1960).

3) M. Giurgea, G. Mihai, V. Topa and M. Musa, *J. Chimie Physique*, **61**, 619 (1964).

4) F. Mader and V. Zanker, *Chem. Ber.*, **97**, 2418 (1964).

5) H. Gyth, P. Cerutti and H. Schmid, *Helv. Chim. Acta*, **48**, 1395 (1965).

6) S. Kato, S. Minagawa and M. Koizumi, This Bulletin, **34**, 1026 (1961).

7) S. Niizuma and M. Koizumi, *ibid.*, **36**, 1629 (1963).

8) A. Kira, S. Kato and M. Koizumi, *ibid.*, **39**, 1221 (1966).

9) A. Kellmann and J. T. Dubois, *J. Chem. Phys.*, **42**, 2518 (1965); A. Kellmann, *J. Chimie Physique*, **63**, 936 (1966).

10) A. Kira, Y. Ikeda and M. Koizumi, This Bulletin, **39**, 1673 (1966).

11) E. Van der Donckt and G. Porter, *J. Chem. Phys.*, **46**, 1173 (1967).

claimed that an excited singlet state is an only reactive state in the photoreduction of acridine in *isopropanol*.

According to our present results, however, four alcohols behave more or less in different manner and in particular, isopropanol and methanol show distinctly different features in the effect of biacetyl on the photoreduction, which lead to the conclusion that the reactive states is in the former case only singlet excited state in agreement with Porter's conclusion, whereas in the latter case, are singlet and $T(n-\pi^*)$ state as Kellmann and Dubois proposed. Hence it seems timely to report the details of our experiments although we have not yet succeeded in interpreting the unexpected differences found in four kinds of alcohols.

Since Dubois and Kellmann's conclusion was based on the assumption that inhibiting action of biacetyl is due to the energy transfer according to $A^{T(n-\pi^*)}+B\rightarrow A+B^T$ (where A is acridine and B is biacetyl), it is desirable to examine whether biacetyl does not affect the lowest $T(\pi-\pi^*)$ of acridine by a different mechanism than energy transfer and further to examine whether it does not react with the half reduced acridine. Therefore we have investigated at first by the flash technique using methanol and ethanol as solvents, the effect of the addition of biacetyl on the decays of $T(\pi-\pi^*)$ of acridine and of the half reduced acridine. In addition, we have made investigations on the effect of the addition of biacetyl on the yield of $T(\pi-\pi^*)$, AH and AH_2, the results of which have supported the view of Kellmann and Dubois to some extent. These experiments are described in Part I. In Part II, the steady illumination experiments are described. The data, being more accurate than those from flash experiments, are analysed and interpreted on the basis of four alternative processes, and the quantum yields Φ_M^S, Φ_R^S, Φ_M^T and Φ_R^T (where S and T denote singlet excited state and $T(n-\pi^*)$ state and where M and R denote respectively molecular and radical) are separately decided.

Part I.[*1] Flash Photolysis Studies

Experimental

Apparatus, procedures and samples are essentially similar as in the previous papers.[8,10] The decays and yields of $T(\pi-\pi^*)$ of acridine and of the half-reduced form of acridine were examined respectively at 440 and at 278 mμ (or in some cases as 520 mμ). The yield of acridan was investigated from the increase of optical density at 290 mμ. The concentration of acridine was always 4.8×10^{-5} M and the concentration of biacetyl was changed from zero to 1.1×10^{-2} M. By using a suitable filter only acridine was excited.

Results and Discussion

T-T Absorption Spectra of Biacetyl. Transient absorption spectra of biacetyl in methanol are shown in Fig. 1.

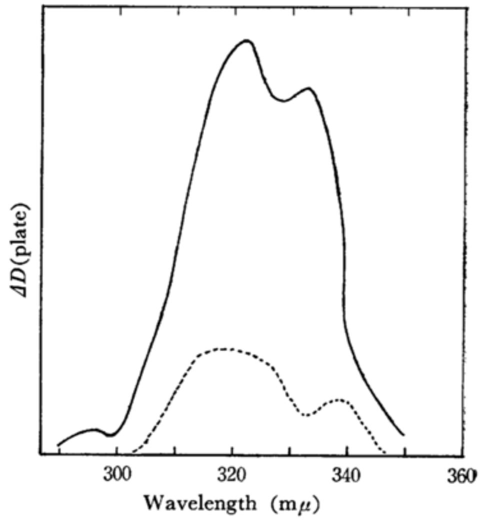

Fig. 1. Transient absorption spectra of biacetyl. —— after 93 μsec, - - - after 360 μsec

The decay at 320 mμ is of the first order with a rate constant $k\simeq4\times10^3\text{sec}^{-1}$. The comparison with the data in literatures[9,12,13] confirms that this species is the triplet state of biacetyl.

The Effect of the Addition of Biacetyl on the Decay of $T(\pi-\pi^*)$ of Acridine. The decay was not essentially affected by the addition of biacetyl up to 1.1×10^{-2}M. Some of the values of the first order rate constants are given in Table 1.

The Effect of the Addition of Biacetyl on the Decay of Half Reduced Acridine. The decay of half reduced acridine is second order and the rate

TABLE 1. RATE CONSTANT OF THE DECAY OF $T(\pi-\pi^*)$, $k\times10^{-4}(\text{sec}^{-1})$

$[B]_M$	0	1.1×10^{-4}	1.1×10^{-3}	5×10^{-3}	1.1×10^{-2}
Methanl	1.1	1.1	1.1	1.1	1.1
	1.2	1.1	1.2	1.1	1.1
Ethanol	0.8	0.8	0.6	0.7	0.7
	0.9	0.8	0.7	0.7	0.8

[*1] Experiments were made by Yamashita.

12) G. Porter and M. W. Windsor, *Proc. Roy. Soc.*, **A245**, 238 (1958).

13) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

TABLE 2. RATE CONSTANT OF THE DECAY OF HALF-REDUCED ACRIDINE

	[BA]$_M$		0	1.1×10^{-4}	1.1×10^{-3}	5.0×10^{-3}	1.1×10^{-2}
$k\times10^{-8}$ (M^{-1} sec^{-1})	Methanol		4	4	3	4	4
	Ethanol	exp. 1	4	3	4	5	3
		exp.	2	3	2	3	4

constant was evaluated from the plot of $1/D$ against t, D being measured at 520 mμ. The results are shown in Table 2. The analysis of the changes in the optical density at 278 mμ by the method employed in the previous paper,[8] also gave essentially the similar results. Thus the possibility of such a reaction $AH+B\rightarrow A+BH$ occurring, can safely be ruled out. The results given in Tables 1 and 2 justifies Kellmann and Dubois' interpretation of their results.

The Effect of [B] on the Yield of T(n–π^*) of Acridine. If the reactive state is T(n–π^*), then there is a possibility that the yield of T(π–π^*) is increased by the addition of biacetyl as inferred from the following reasoning. It is quite reasonable to presume that the intersystem crossing occurs *via* the following scheme,[14]

$$\begin{tikzcd} S^*(\pi\text{-}\pi^*) \arrow[r] & T(n\text{-}\pi^*) \arrow[r, "k_d'"] \arrow[d, "k_r'"] & T(\pi\text{-}\pi^*) \\ & \text{reaction} & \end{tikzcd}$$

In the absence of biacetyl, a portion of T(n–π^*) disappears through the reaction with the solvent; this portion, if biacetyl is present, will be affected by biacetyl according to $A^{T(n-\pi^*)}+B\rightarrow B^T+A$. The produced B^T then gives its excitation energy back again to acridine according to $B^T+A\rightarrow B+A^{T(\pi-\pi^*)}$ (The occurrence of such a process was demonstrated by Kellmann and Dubois and was reconfirmed by the present authors (see Part II).). Then the quantum yields of the production of T(π–π^*), $\phi_{\pi\pi}$ should be given by the following equations, provided biacetyl does not affect the intersystem crossing.

In the absence of B

$$\phi_{\pi\pi} = k_d'/(k_r'+k_d')\cdot\phi_{n\pi}.$$

In the presence of B

$$\phi_{\pi\pi} = (k_d'+k[B])/(k_r'+k_d'+k[B])\cdot\phi_{n\pi}.$$

The results are shown in Fig. 2, where the optical densities at 440 mμ immediately after flashing, are plotted against [B].

It seems that there is a slight increase at the largest biacetyl concentration, but in view of the crudeness of the data one should say rather that there is no essential effect. This suggests $k_r'\ll k_d'$. By the way, the optical densities at 440 mμ immediately after flashing in methanol, ethanol and isopropanol are respectively ~0.36, ~0.33 and ~0.37. Thus the yields are essentially the same in three alcohols. These data may be of some importance for the general discussion.

The Effect of [B] on the Yield of AH. The lifetime of singlet excited state of acridine in ethanol is 7.2×10^{-10} sec,[15] and that of T(n–π^*) was estimated by Kellmann and Dubois as $\sim10^{-8}$sec. Therefore, if the reactive state were only S*, the addition of $\sim10^{-2}$M of biacetyl would scarcely affect the yield of AH. On the other hand, if the reactive state were only T(n–π^*), the addition of this magnitude of biacetyl should decrease the yield to some extent. The yield of AH was estimated from the

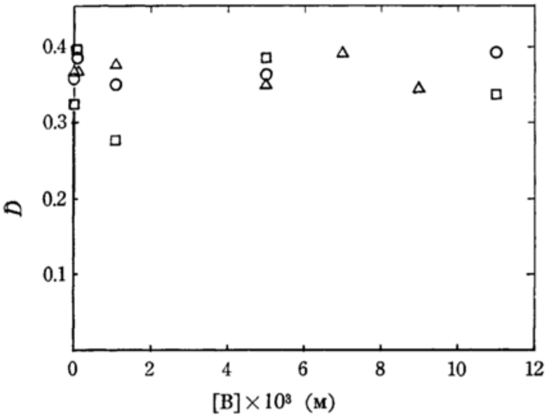

Fig. 2. Influence of the concentration of biacetyl on the yield of the lowest triplet of acridine (in terms of optical densities at 440 mμ).
○ methanol, □ ethanol, △ isopropanol

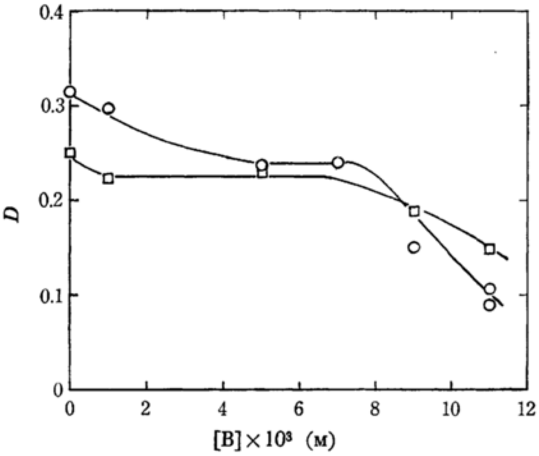

Fig. 3. Influence of the concentration of biacetyl on the yield of semi-reduced acridine (in terms of optical densities at 278 mμ).
○ methanol, □ ethanol

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[14] M. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1963).

[15] H. Kokubun, to be published.

optical densities at 278 mμ directly after flashing. The results are shown in Fig. 3. Although the data are not very accurate, still there is a clear tendency that the yield decreases with the increase of [B]. At 5×10^{-3} M of B, the decrease in methanol and ethanol is approximately ∼1/4 and 1/8 and at 1×10^{-2}M of B it is ∼2/3 and 1/2. These results strongly suggest the participation of T(n–π*) state in these two solvents.

The Effect of [B] on the Yield of AH_2. This was examined from the similar reasoning as above. The yield of AH_2 was evaluated from the optical density at 290 mμ a long time after flashing, D^{290}_{∞}. The results are shown in Fig. 4. The decrease in the yield of AH_2 by adding 5×10^{-2}M of biacetyl in methanol and ethanol are equally about 1/3 while at 1×10^{-2}M of the added biacetyl, it is respectively ∼2/3 and 1/2. Although the above data are not very accurate, they lead us to suspect that T(n–π*) as well as S* participates in the reaction. It may be added that the above data in combination with the oxygen effect on the yield of AH_2[8] enable us in principle, to evaluate Φ^S_M, Φ^S_R, Φ^T_M and Φ^T_R. But since it is difficult to get the exact data from the flash photolytic experiments, it seems wiser to leave the quantitative investigation to the steady light studies.

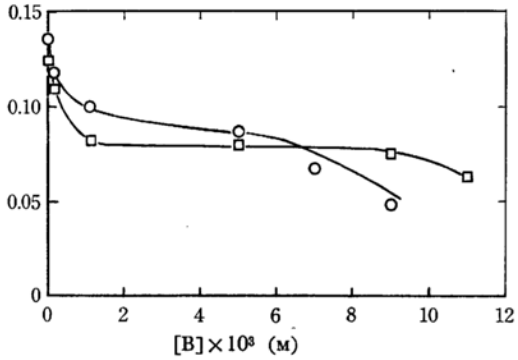

Fig. 4. Influence of the concentration of biacetyl on the yield of the product (in terms of optical densities at 290 mμ).
○ methanol, □ ethanol

Part II.*2 Steady Light Experiment

Preliminary Experiments for the Effect of the Addition of Biacetyl on the Photochemical Reduction of Acridine. Figure 5 shows a typical example of the spectral change when the deaerated solution of acridine, 1×10^{-4} M in methanol containing some quantity of biacetyl, is irradiated by 365 mμ. In the early stage of irradiation, the peak of acridine declines accompanied with the rise in the height of the peak at ∼290 mμ. An isosbestic point is seen at ∼325 mμ. The above behavior substantiates that the similar photoreduction as in the absence of biacetyl is occurring in the early stage. In the later stage, however, the absorption around 350 mμ gradually rises again and the absorption in the shorter wavelength region declines with no isosbestic point. This suggests the occurrence of some unknown reaction between biacetyl and acridan. Such a phenomenon was observed in all the alcohols investigated but it was most prominent in methanol. The similar phenomenon was observed in the air-saturated solution. It was checked that the alcoholic solution of biacetyl alone scarcely undergoes any reaction even by the irradiation for one hour.

Figure 6 gives some typical examples of the $\ln(e^{\alpha cd}-1)$ *vs.* t plots. In consistence with the above spectral change, the plots are satisfactorily linear in the early stage indicating the occurrence of a simple photoreduction of acridine whereas in the later stage they gradually deviate and finally show slow and apparently linear increase. The above results ensure us to investigate the retarding effect of biacetyl by

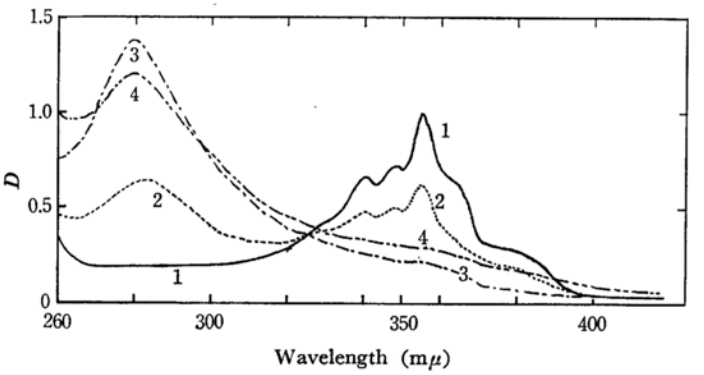

Fig. 5. Spectral change caused by the irradiation of the acridine solution of methanol containing biacetyl.
[acridine]$=1\times10^{-4}$ M [B]$=5\times10^{-3}$ M
1 before irradiation, 2 after 1 min irradiation, 3 after 6 min irradiation, 4 after 60 min irratiation

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*2 The experiments were performed by Ikeda.

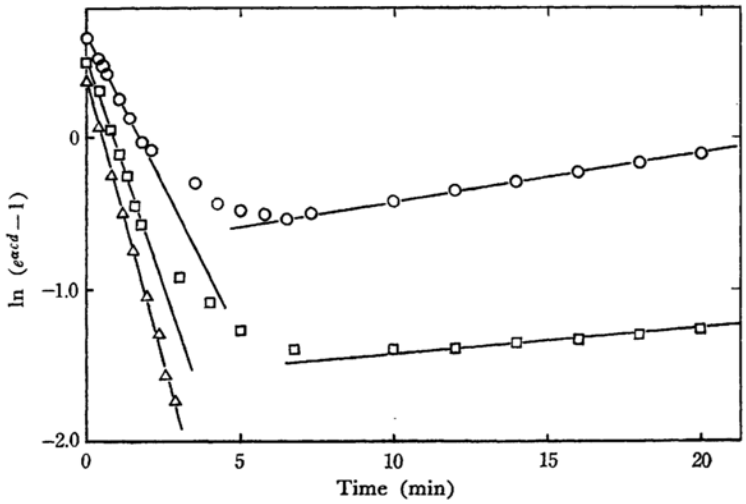

Fig. 6. ln($e^{\alpha cd}-1$) vs. t plots (25°C).
[A]$=1\times10^{-4}$ M, ○ [BA]$=0$ M, □ [BA]$=2\times10^{-3}$ M, △ [BA]$=1\times10^{-2}$ M

comparing the initial slope of the ln($e^{\alpha cd}-1$) vs. t plots.

The Effect of [B] on the Quantum Yield of Photoreduction. This was investigated for four kinds of alcohols and for both the aerated and deaerated solutions. Some corrections were made for the absorption of biacetyl when its concentration was high. The values of quantum yields for the four kinds of alcohol (in the absence of biacetyl) were redetermined and were found essentially the same as the previously reported ones.[6,7] In Fig. 7, some of the plots of Φ_0/Φ vs. [B] (Φ_0, the quantum yield in the absence of biacetyl) are given.*3

It is quite astonishing that the plots are essentially different in the four alcohols. Thus in methanol the plot clearly consists of two linear portions a and b, for both the aerated and deaerated conditions. In ethanol and *n*-propanol the similar curve as in methanol is obtained only in the deaerated solutions, but in the aerated solutions, the plot consists of a single straight line the slope of which is of the similar magnitude as the ones for the b-parts of the above mentioned plots. In the case of isopropanol the plot for both the aerated and deaerated solutions is satisfactorily reproduced by a single straight line.

From the above results, one may safely conclude that in the case of methanol, ethanol and *n*-propanol (for the latter two alcohols only in the deaerated condition) the two states participate in the reaction, whereas in isopropanol and the aerated solutions of ethanol and *n*-propanol only one state is involved in the reaction. It is most plausible that the latter state is a singlet excited state and the former two states are S* and T(n–π*). These conclusions agree with that of Kellmann and Dubois for methanol on one hand, and that of Porter for isopropanol.

Quenching Action of Biacetyl on the Fluorescence of Acridine. To confirm the participation of S* in the reaction further, the quenching action of B on the fluorescence of acridine has been studied and has been compared quantitatively with the retarding effect of B on the photoreduction (in the high concentration region of B). In Fig. 8, the emission spectra for the following three solutions are given (a) [A]$=1\times10^{-4}$ M, (b) [B]$=5\times10^{-2}$ M and (c) [A]$=1\times10^{-4}$ M, [B]$=5\times10^{-2}$ M. The absorption spectra of biacetyl are also dipicted for later consultation.

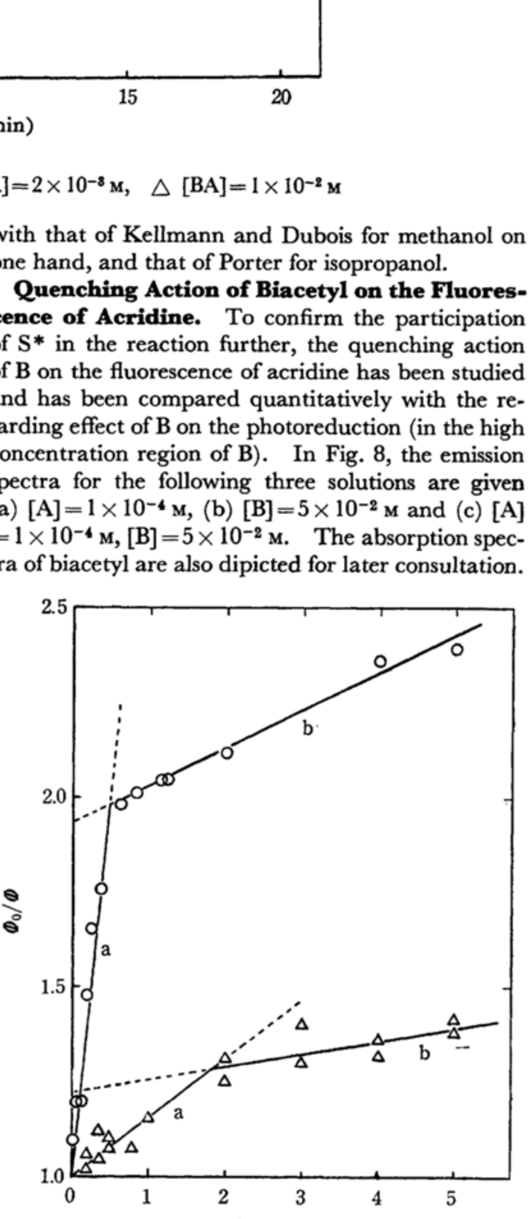

Fig. 7-1

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*3 Comparing these results with the ones in the flash experiment, one may say that the effect of [B] agrees in the two cases for methanol but the disagreement for ethanol seems to exceed the experimental error

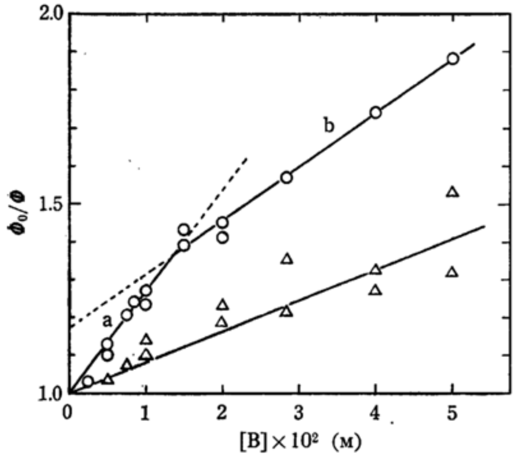

Fig. 7-2

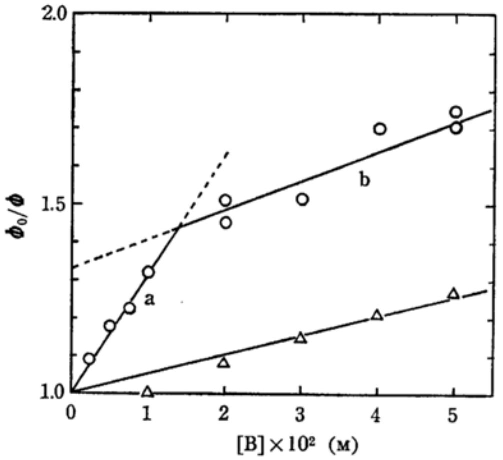

Fig. 7-3

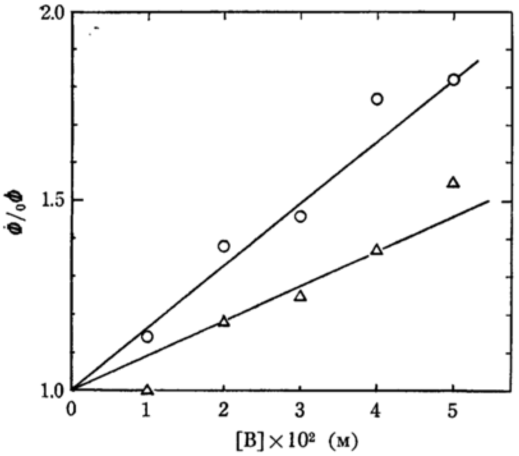

Fig. 7-4

Fig. 7. Plots of Φ_0/Φ against the concentration of biacetyl (25°C).
1 methanol, 2 ethanol, 3 *n*-propanol, 4 isopropanol

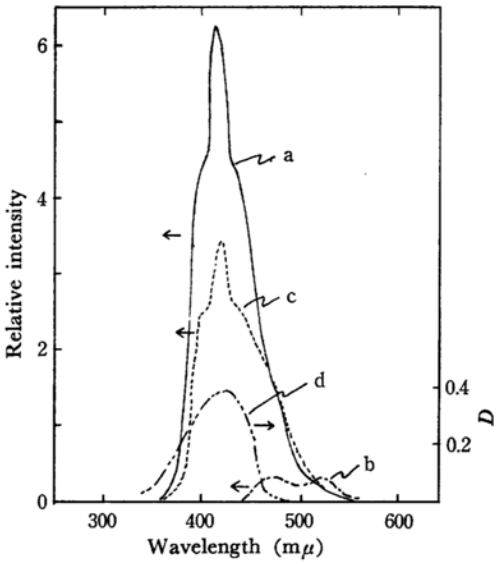

Fig. 8. Emission spectra of acridine, biacetyl and the mixture of the two in the deaerated methanol solution (exciting light, 365 mμ).
a) [A]$=1\times10^{-4}$ M, b) [B]$=5\times10^{-2}$ M,
c) [A]$=1\times10^{-4}$ M, [B]$=5\times10^{-2}$ M
d) absorption spectra of biacetyl.

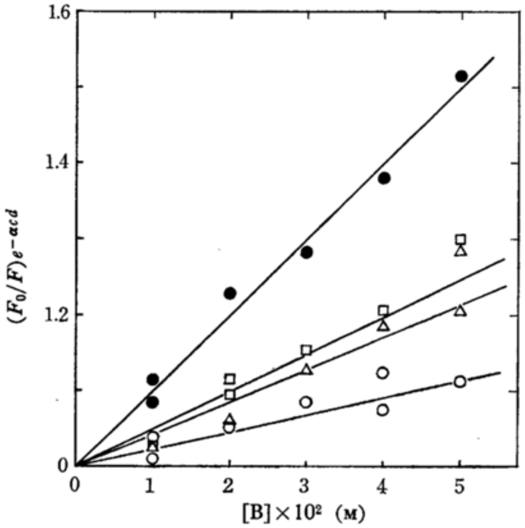

Fig. 9. Stern-Volmer plots for quenching of fluorescence of acridine by biacetyl.
○ methanol, □ ethanol, △ *n*-propanol,
● isopropanol

As is well known, the emission of B consists of fluorescence (shorter wavelength) and phosphorescence[16] (longer wavelength). It is apparent from the emission spectra of System C, that biacetyl quenches the fluorescence of acridine and that the phosphorescence of biacetyl is quenched by acridine. The latter

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[16] H. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

phenomenon is due to the process $B^T+A\rightarrow B+A^{T(\pi-\pi^*)}$ as Kellmann and Dubois have established.[9] Systematic studies on the quenching action of B have been made at the emission peak, 410 mμ of acridine, choosing 365 mμ as an exciting light. Stern-Volmer plots for the four alcohols are shown in Fig. 9. The quantity for the ordinate, $(F_0/F)e^{-\alpha cd}$ contains a correction term, $e^{-\alpha cd}$ for the reabsorption of fluorescence by biacetyl (*cf.* Fig. 8) where α is the absorption coefficient of biacetyl at 410 mμ, where c is the concentration of biacetyl and where d is the length of fluorescence light path. d is approximated as 1/2 cm. From the slopes one can evaluate $k_Q\tau$; approximating τ as 10^{-9}sec for all the alcohols, one obtains the rate constant k_Q for the quenching process. The results are given in Table 3.

TABLE 3

		k_q(M^{-1}sec^{-1})	k_Q(M^{-1}sec^{-1})
Methanol	(dea)	1.2×10^{10}	0.3×10^{10}
	(aer)	0.4×10^{10}	
Ethanol	(dea)	1.4×10^{10}	0.7×10^{10}
	(aer)	0.8×10^{10}	
n-Propanol	(dea)	0.8×10^{10}	0.5×10^{10}
	(aer)	0.5×10^{10}	
Isopropanol	(dea)	1.7×10^{10}	1.0×10^{10}
	(aer)	0.9×10^{10}	

It is worthwhile to note that the k_Q-values are essentially the same for the aerated and deaerated solutions.

Quantitative Discussion about the Retarding Effect of B on the Photoreduction. Since the reaction occurring in the high concentration region of B is considered to be concerned with S*, the reaction scheme for it may be written as follows,

$$A + h\nu \rightarrow A^* \quad I_{ab}$$
$$A^* \rightarrow A \quad k_d$$
$$A^* + RH_2 \rightarrow \text{Prod} \quad k_r$$
$$A^* + B \rightarrow A + B \quad k_q$$

where A* is the singlet excited state of acridine. The following relations are derived straightforwardly.

$$\Phi = k_r/(k_r + k_d + k_q[B]) \qquad (1)$$

$$\Phi_0 = k_r/(k_r + k_d) \qquad (2)$$

$$\Phi_0/\Phi = 1 + (k_q/(k_d + k_r))[B] \qquad (3)^{*4}$$

Since $k_r+k_d=1/\tau$, k_q can easily be evaluated from the plots given in Fig. 7. The results are given in Table 3. The agreement between k_q and k_Q are satisfactory especially for the k-values for the aerated solutions. Somewhat larger k_q values for the deaerated solutions might be due to the participation of the T(n–π*) state. Rate constants for the encounter-controlled reaction evaluated from the relation $k=8\boldsymbol{R}T/3000\,\eta$ for methanol, ethanol and n-propanol are respectively 1.2×10^{10}, 0.6×10^{10}, 0.3×10^{10} M^{-1}sec^{-1}. These values are close to those of k_q amd k_Q. Thus the above results lead to the conclusion that the part of the reaction occurring in the high concentration of biacetyl, is concerned with S* and that biacetyl quenches the reaction at an encounter-controlled rate.

The participation of T(n–π*) state is very prominent only in the case of the deaerated methanol. Hence the accurate treatment can be made only on this case. If one assumes that biacetyl does not affect the intersystem crossing, equations corresponding to (1) and (2) are

$$\Phi = \frac{k_r'}{k_r' + k_d' + k_q'[B]}\varphi_{ST} \qquad (1')$$

$$\Phi_0 = \frac{k_r}{k_r' + k_d'}\varphi_{ST} \qquad (2')$$

where φ_{ST} is the quantum yield of intersystem crossing S*→T(n–π*). The similar relation to (3) exactly holds also in this case. Making a suitable correction for the participation of the singlet excited state and assuming the calculated k_q' value, one can evaluate the lifetime of T(n–π*). The result is 8.9×10^{-8}sec which agrees with the one proposed by Kellmann and Dubois.

Analyzing the experimental data along the above reasoning, the values of $(k_d+k_r)/k_r$ or $(k_d'+k_r')/k_r'\cdot\varphi_{ST}$ may be evaluated. The results are given in Table 4. The reliable value of φ_{ST} is still unknown. If one assumes $\varphi_{ST}\simeq0.3$,[*5] k_d' is several times larger than k_r' in the case of the deaerated methanol. In ethanol and n-propanol the ratio is considered to be still larger. This is consistent with the result obtained from the flash experiment, that

TABLE 4

		S* $(k_d+k_r)/k_r$	n–π* $(k_d'+k_r')/k_r'\varphi_{ST}$
Methanol	(dea)	15	17
	(aer)	37	~170
Ethanol	(dea)	8.3	~ 50
	(aer)	23	—
n-Propanol	(dea)	15	~ 50
	(are)	33	—
Isopropanol	(dea)	11	—
	(are)	32	—

[*4] In the presence of O_2, k_d+k_r should be replaced by $k_d''+k_r''$ with $k_r''<k_r$, but the sum of the two rate constants is the same.

[*5] The maximum quantum yield for the photochemical reaction between acridine and acridan in benzene solution is ~0.25.[17] (In this case, the reactive state of acridine is T(π–π*).) Furthermore, acridine-sensitized photooxidation of leucouranine in the aqueous solution leads to $\varphi_{ST}=0.24$ provided the efficiency for the reaction between T(π–π*) of A and leuco-uranine is 1.[18]

17) This Bulletin, **40**, 2249 (1967).

18) *Ibid.*, **35**, 1875 (1962).

TABEE 5. SEPARATE QUANTUM YIELDS OF THE FOUR PROCESSES

	Φ^{S}_{M}	Φ^{S}_{R}	Φ^{T}_{M}	Φ^{T}_{R}	Φ_{total}
Methanol	0.027(20%) (0.009)	0.039(30%) (0.013)	0.006(5%) (0.002)	0.057(45%) (0.019)	0.128 (0.043)
Ethanol	0.043(30%) (0.022)	0.067(55%) (0.034)	0 (0)	0.019(15%) (0.010)	0.129 (0.065)
n-Propanol	0.030(35%) (0.015)	0.036(40%) (0.018)	0 (0)	0.022(25%) (0.011)	0.088 (0.044)
Isopropan-	0.03(35%) (0.031)	0.058(65%) (0.058)	0 (0)	0 (0)	0.089 (0.089)

the yield of $T(\pi-\pi^*)$ is scarcely affected by the addition of biacetyl.

Evaluation of Φ^{S}_{M}, Φ^{S}_{R}, Φ^{T}_{M} and Φ^{T}_{R}. From the results given in Fig. 7, one can estimate these quantities if one assumes that $T(n-\pi^*)$ is not deactivated by oxygen contained in the aerated solution. Singlet excited state of acridine is not affected by oxygen as has been verified in the present experiment. That AH is not attacked by biacetyl is also verified by the present flash experiment.

Taking methanol for instance, the evaluation can be made in the following way. The quantum yield for the deaerated solution in the absence of biacetyl gives $\Phi^{S}_{M}+\Phi^{S}_{R}+\Phi^{T}_{M}+\Phi^{T}_{R}$. The aerated solution in the absence of biacetyl gives $\Phi^{S}_{M}+\Phi^{T}_{M}$, since oxygen quickly reverts semi-reduced acridine to acridine. The extrapolation of the b-part of the plot for the deaerated solution to $[B]=0$, gives $\Phi^{S}_{M}+\Phi^{S}_{R}$ and the similar extrapolation of b-part of the plot for the aerated solution gives Φ^{S}_{M}. From these values, each Φ can be determined separately. The results are given in Table 5. The second column for each alcohol is the respective value allotted to one α-H atom.

Although the data are not very accurate and still provisional, it is believed that the general feature will not be altered by more accurate experiments. Generally speaking, the singlet excited state makes a more important role than $T(n-\pi^*)$ for the photoreduction of acridine. There seems to be a tendency that more of the $T(n-\pi^*)$ reacts with alcohols with the increase of the number of α-hydrogen atoms. Molecular mechanism does not occur or scarcely occurs in $T(n-\pi^*)$ state. The reaction at S^* increases in the order, methanol$<$ethanol$<$isopropanol for both molecular and radical mechanisms when the number of α-hydrogen is taken into account. This agrees with the general tendency of these alcohols when they act as hydrogen donors. Although conspicuous difference in methanol and isopropanol, *i.e.* the result that in methanol about 50% of the total reaction occurs at $T(n-\pi^*)$ whereas in isopropanol the entire reaction occurs at S^*, cannot be interpreted in the present stage, one may say at least in the following way. Firstly, any reactions at singlet excited states may not affect the value of φ_{ST} so much since $\Phi^{S}_{M}+\Phi^{S}_{R}$ is rather small, *i.e.* ~ 0.1 at most. In fact, as mentioned in Part I, the yield of $T(\pi-\pi^*)$ is essentially the same in methanol, ethanol and isopropanol. This is naturally expected if Φ_{ST}-$(n-\pi^*)$ is about equal and if $T(n-\pi^*)$ produced mostly goes to $T(\pi-\pi^*)$. The latter remark has been verified in the present experiment.

Hence, the cause for the difference in methanol and isopropanol should be sought in the step of reaction of $T(n-\pi^*)$ with an alcohol molecule. Steric effect might be a factor chiefly controlling the situation. To make clear the cause of this difference, it is desirable to extend such studies to other solvents. It is also desirable to make experiments using other triplet energy donors and acceptors. Further it is hoped that the reliable value of φ_{ST} is determined.