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Photochemistry of Acridines. XVIII. Photoreduction by Nonpolar H-donors and the Disproportionation of C-Radicals

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It was found that the photoreduction of acridine in cyclohexane and toluene occurs *via* molecular and radical mechanisms. The T-energy transfer experiments using biacetyl as an energy acceptor have revealed that the molecular mechanism occurs in the $T(n\text{–}\pi^*)$ state, and the radical in the singlet excited state. The effect of the addition of piperylene on the quantum yield of photoreduction was investigated in cyclohexane, methanol, ethanol and isopropanol. The results have been interpreted on the following assumptions. 1) Complete T-energy transfer from acridine to piperylene. 2) No quenching action of piperylene on the singlet excited acridine. 3) Complete transformation of C-radicals of acridine to stable products by piperylene. The results have led to the conclusion that the C-radical undergoes disproportionation in cyclohexane, methanol and ethanol, while it is completely transformed to an acridan-type compound in isopropanol.

Studies on the photoreduction of acridines have been made extensively,[1,4] but most of them dealt with photoreduction in various alcohols. We have investigated the kinetics of photoreduction in nonpolar H-donors such as cyclohexane and toluene. It has been established that both radical and molecular mechanisms occur in these solvents just as in alcoholic solvents.[4l] However, energy transfer experiments with the use of biacetyl have revealed that the radical mechanism occurs mainly in the singlet state while molecular mechanism, in the $T(n-\pi^*)$ state, in contrast to the case with alcoholic solvents.

We have tried using piperylene as a T-energy ac-

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[1] a) V. Zanker and G. Prell, *Ber. Bunsenges. Physik. Chem.*, **73**, 791 (1969). b) V. Zanker and E. Erhardt, *ibid.*, **72**, 267 (1968). c) V. Zanker, E. Erhardt and H. H. Mantsch, *Z. physik. Chem. N. F.*, **58**, 1 (1968).

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

[3] a) A. Kellmann and L. Lindqvist, "The Triplet State," ed by A. B. Zahlan, Cambridge University Press, (1967), p. 439. b) A. Kellmann and J. T. Dubois, *J. Chem. Phys.*, **42**, 2518 (1965).

[4] Our previous paper will be numbered as follows from now on. a) I, S. Kato, S. Minagawa, and M. Koizumi, This Bulletin, **34**, 1026 (1961). b) II, S. Niizuma and M. Koizumi, *ibid.*, **36**, 1629 (1963). c) III, A. Kira, S. Kato, and M. Koizumi, *ibid.*, **39**, 1221 (1966). d) IV, A. Kira, Y. Ikeda, and M. Koizumi, *ibid.*, **39**, 1673 (1966). e) V, S. Niizuma, Y. Ikeda, and M. Koizumi, *ibid.*, **40**, 2249 (1967). f) VI, A. Kira, *Sci. Rep. of Tohoku Univ. Ser.* 1, **69**, No. 3—4, 129 (1966). g) VII, A. Kira and M. Koizumi, This Bulletin, **40**, 2486 (1967). h) VIII, M. Koizumi, Y. Ikeda, and T. Iwaoka, *J. Chem. Phys.*, **48**, 1869 (1968). i) IX, M. Koizumi, Y. Ikeda, and H. Yamashita, This Bulletin, **41**, 1056 (1968). j) X, K. Nakamaru, S. Niizuma, and M. Koizumi, *ibid.*, **42**, 255 (1969). k) XI, A. Kira and M. Koizumi, This Bulletin, **42**, 625 (1969). l) XII, M. Koizumi, S. Niizuma, and Y. Miyashita, *Z. Phys. Chem. N. F.*, **71**, 165 (1970). m) XIII, Y. Miyashita, S. Niizuma, and M. Koizumi, This Bulletin, **43**, 3435 (1970). n) XIV, K. Nakamaru, S. Niizuma, and M. Koizumi, *Z. Phys. Chem. N. F.*, **73**, 113 (1970). o) XV, K. Nakamaru, S. Niizuma, and M. Koizumi, This Bulletin, **44**, 1256 (1971). p) XVI, S. Niizuma, K. Nakamaru, and M. Koizumi, *Chem. Lett.*, **1972**, 59. q) XVII, K. Nakamaru, S. Niizuma, and M. Koizumi, This Bulletin, **45**, 2445 (1972).

ceptor to confirm the above result. We found that the compound acts as a radical scavenger as well as T-energy acceptor which indicates that the C-radical in cyclohexane, ethanol and mehtanol undergoes disproportionation. The results with the latter two solvents are in complete agreement with our previous conclusion.[4m] In the case of isopropanol it was found that semiquinone is most likely reduced further to acridan by isopropanol or by the isopropyl radical.

In view of the present results and another unpublished one concerning φ_{ST}, the values of Φ^{S}_{M}, Φ^{S}_{R}, Φ^{T}_{M}, and Φ^{T}_{R} previtusly published[4i] have been criticized and corrected to some extent.

Experimental

Acridine was recrystallized twice from aqueous ethanol. Biacetyl was purified by distillation immediately before use. Piperylene used was a mixture of *cis*- and *trans*-forms, and was subjected only to distillation. Ethanol, cyclohexane, and isopropanol were purified by the usual method. Methanol, G. R. grade of Wako Junyaku was used without further purification. The apparatus and procedures were described previously.[4d,m]

Results and Discussion

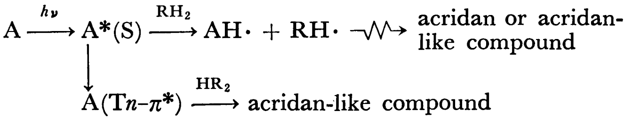
Photoreduction of Acridine in Cyclohexane and Toluene. Photoreduction of acridine in cyclohexane which occurs upon irradiation at 365 nm is distinct. In the couse of the reduction, gradual decrease of acridine peak at 356 nm and a well-defined isosbestic point at 320 nm were observed. The feature of the reaction is similar to that in alcohols, occurring both in the deaerated and aerated solutions. The product has an absorption peak at 278—279 nm which differs slightly from that of acridan dissolved in cyclohexane (a peak at 282~283 nm). It is likely that the product is a mixture of acridan and an acridan-type compound.

The kinetic runs, *i. e.*, the plots $\ln(10^{D}-1)$ *vs.* t always give good straight lines. From the slopes the quantum yields in the deaerated and aerated solutions were obtained as $\Phi_{dea}=0.14_4$—0.14_9 and $\Phi_{aer}=0.05_1$, respectively. These values are a little larger than those in methanol and ethanol. The contributions of the molecular and radical mechanisms are 35 and 65%, respectively, of the entire reaction.

To determine the contribution of singlet excited state and triplet n–π^* state to the molecular and radical mechanisms, the effect of the addition of biacetyl as a T-energy acceptor was examined. Experiments were carried out in the same way as in alcohols[4i] for both the aerated and dearearated solutions. They are given in Fig. 1. It is seen that the quantum yeild in the aerated solution Φ_M decreases remarkably with the increase in biacetyl concentration. Judging from the concentration of biacetyl, this quenching is mostly related to T(n–π^*). This is in sharp contrast to alcohol systems in which the molecular mechanism scarcely occurs or not at all in T(n–π^*).

It has been found that the radical mechanism is scarcely affected by the adition of biacetyl in this concentration region. As shown in Fig. 1, the calculated values for $(\Phi/\Phi_0)_{dea}$ fit fairly well the experimental ones on the assumption that only Φ_M is decreased by the above amount. It is thus concluded that the radical mechanism occurs mainly in the singlet excited state. This is also remarkable in view of our previous results where T(n–π^*) contributes to radical mechanism to some extent in the case of methanol and ethanol.[4i]

The photoreduction of acridine in cyclohexane occurs mainly according to the following scheme,



$$\begin{tikzcd} A \arrow[r, "h\nu"] & A^*(S) \arrow[r, "RH_2"] \arrow[d] & AH\cdot + RH\cdot \arrow[r, squiggly] & \text{acridan or acridan-like compound} \\ & A(Tn\text{–}\pi^*) \arrow[r, "HR_2"] & \text{acridan-like compound} & \end{tikzcd}$$

The reason for such a difference between alcohols and cyclohexane is unknown at the present stage but it might possibly be related to the presence or absence of the OH group which interacts specifically with N of acridine. We thus carried out similar experiments to those above, replacing cyclohexane with toluene. The relative quantum yields for the aerated and deareated solutions obtained as a function

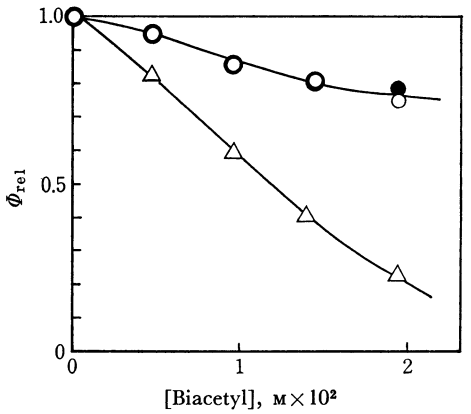


Fig. 1. Dependence of Φ_{rel} on biacetyl concentration for the aerated (Φ_M) and the deaerated ($\Phi_M+\Phi_R$) cyclohexane solutions.

△: Φ_M, ○: $\Phi_M+\Phi_R$, ●: ($\Phi_M+\Phi_R$)-values calculated on the assumption that Φ_R is not affected by biacetyl.

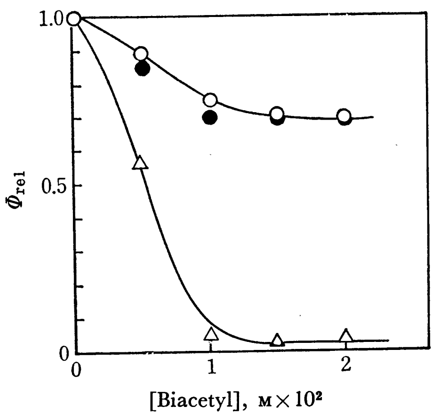


Fig. 2. Dependence of Φ_{rel} on biacetyl concentration for the aerated (Φ_M) and the deaerated ($\Phi_M+\Phi_R$) toluene solutions.

△: Φ_M, ○: $\Phi_M+\Phi_R$, ●: ($\Phi_M+\Phi_R$)-values calculated on the assumption that Φ_R is not affected by biacetyl.

of biacetyl concentration are given in Fig. 2. It is seen that biacetyl acts as a more effective quencher in aerated toluene than in aerated cyclohexane. This might be due to the difference in viscosity. All other results were much the same as those with cyclohexane. Thus we might say that in nonpolar solvents having no such group as OH, molecular mechanism does not occur in the singlet state but occurs in the T(n–π^*) state and that radical mechanism occurs mainly in the singlet state.

Reevaluation of the Values of Φ^S_M, Φ^S_R, Φ^T_M *and* Φ^T_R. Since these values were reported,[4i] the values of $\Phi_R=\Phi^S_R+\Phi^T_R$ for ethanol and methanol were found to agree respectively with the quantum yeilds of oxygen consumption during the photoreduction of acridine in the aerated ethanol and methanol solutions,a reasonable interpretation being given. This confirmed the reliability of our values for $\Phi^S_R+\Phi^T_R$,[4m] but not of our individual values of Φ^S_R and Φ^T_R.

From recent measurements of the values of intersystem crossing probabilities of acridine in methanol, ethanol and isopropanol, our Φ^S_R and Φ^T_R values for ethanol appeared to be somewhat unreliable[5] and we reinvestigated our previous method. Taking ethanol as an example, the values of Φ^T_R,Φ^S_R and Φ^S_M (Φ^T_M is zero for ethanol) were determined in the following way from the plots given in Fig. 3. Φ^S_M was determined from the quantum yield of photoreduction in the areated solution. The value of $\Phi^S_M+\Phi^S_R$ was evaluated from the intercept of part b of the plot for the dearated solution. However, the slopes of part b of the Φ_0/Φ *vs.* [Biacetyl] plots (k_q) for the deaerated solutions in methanol, ethanol and isopropanol were always larger than the corresponding slopes of the aerated solutions. The latter agreed very well with the quenching constants of acridine fluorescence by biacetyl. We mentioned that somewhat larger values for the deaerated solutions might be due to participation of the T(n–π^*) state. From this viewpoint it would be more reliable to use the slopes of the aerated solutions and to calculate the $\Phi^S_M+\Phi^S_R$ value from the intercept of the dotted line shown in Fig. 3.[6] The recalculated values of Φ^S_M, Φ^S_R, Φ^T_M and Φ^T_R (italicized) are listed in Table 1 along with the old values.

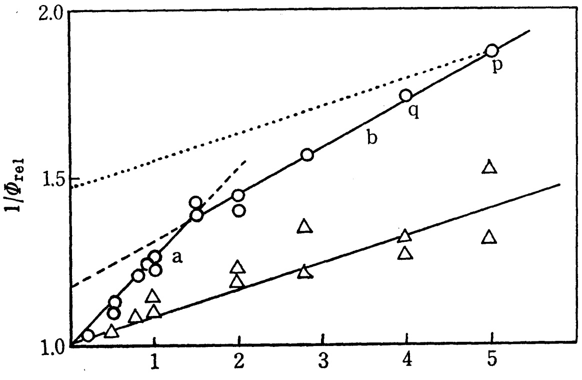


Fig. 3. Plot of $1/\Phi_{rel}$ *vs.* [Biacetyl] for the aerated and deaerated ethanol solution of acridine.
○: deaerated, △: aerated.

The new values of Φ^S_M,Φ^S_R, and Φ^T_R for n-propanol and ethanol are about the same percentage of the Φ_{total}-value. Although the difference between the new and old values is not so great, except in the case of ethanol, and could be considered within experimental accuracy, most of the results, particularly for ethanol, might be well comprehended on the basis of the new data.

Effect of the Addition of Piperylene on the Photoreduction Quantum Yield in Cyclohexane. It is well-known that piperylene ($CH_3-CH=CH-CH=CH_2$) acts as a good T-energy acceptor.[7] Therefore in order to reconfirm the results obtained

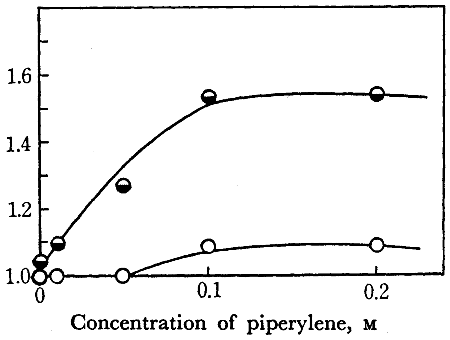


Fig. 4. Plot of Φ_{rel} *vs.* piperylene concentration in the aerated and deaerated solution of acridine in cyclohexane.
○: aerated, ◒: deaerated.

Table 1. Separate quantum yields due to different mechanism

	Φ^S_M	Φ^S_R	Φ^T_M	Φ^T_R	Φ_{total}
Methanol	0.027 (21%) 0.027 (21%)	*0.032* (24%) 0.039 (30%)	0.006 (5%) 0.006 (5%)	*0.063* (50%) 0.057 (45%)	0.128
Ethanol	0.043 (33%) 0.043 (33%)	*0.043* (33%) 0.067 (52%)	0 0	*0.043* (33%) 0.019 (15%)	0.129
1-Propanol	0.030 (34%) 0.030 (34%)	0.030 (34%) 0.030 (40%)	0 0	*0.028* (31%) 0.022 (25%)	0.088
Isopropanol	0.03 (35%) 0.03 (35%)	0.058 (65%) 0.058 (65%)	0 0	0 0	0.088

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[5] It has been found that the apparent inconsistence is also due to another quite different fact.

[6] From the Φ *vs.* [Biacetyl] plot, it seems appropriate to draw the dotted line from a point located in a p∼q region. If it is drawn from the neighborhood of q, the Φ^T_R and Φ^S_R-values become about 10% smaller and greater, respectively.

[7] G. H. Hammond, J. Salticel, A. A. Lamola, N. J. Turro, I. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Datton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

from the effect of the addition of biacetyl, we have made similar experiments using piperylene. It was confirmed that the spectral change and the $\ln(10^D-1)$ *vs.* t plots run just as in the absence of piperylene.

The effect, however, was found to be contrary to expectation. Thus the quantum yield does not decrease but increases with addition of piperylene both in the aerated and deaerated solutions (Fig. 4). The increase is especially remarkable for the deaerated solution, the Φ-value reaching 10^{-1} M piperylene about one and a half times the value in the absence of piperylene. The increase for the aerated solution is about 10%. Thus

Φ_{dea}(in the presence of piperylene) $=0.22$
Φ_{aer}(in the presence of piperylene) $=0.05_6$

as compared with

Φ_{dea}(in the absence of piperylene) $=0.146$
Φ_{aer}(in the absence of piperylene) $=0.051$

from which $\begin{matrix}\Phi_R=0.095\\ \Phi_M=0.051\end{matrix}$

The above result for the deaerated solution may be interpreted in the following way. The concentration of piperylene is so high that the T-energy transfer from acridine to piperylene is considered to be practically complete. However, piperylene acts as a radical scavenger and the intermediate produced is stabilized most likely as follows,

$$AH\cdot + P \rightarrow AH - P\cdot \qquad (1)$$

$$2AH - P\cdot \rightarrow (AH - P)_2$$
$$\text{or } AH - P\cdot + AH\cdot \rightarrow AH - P - AH \qquad (2)$$

The essential point is that all the intermediates are stabilized without reconverting to acridine. If we assume that acridine semiquinone undergoes the following disproportionation as in the case of ethanol and methanol,[4m)]

$$2AH \rightarrow A + AH_2\ , \qquad (3)$$

then the addition of piperylene is expected to double the value of $\Phi_R^{\S}$. Hence the expected value of

Φ_{dea}(in the presence of piperylene) $=0.19$.

Taking the experimental error into account, the agreement is fairly satisfactory.

It is to be noted that two assumptions have been made:

1) the complete quenching of T(n–π^*)
2) no quenching action of piperylene on the singlet excited acridine.

The result for the aerated solution is difficult to explain, because the features of reaction seem to be very complicated. Firstly, much higher concentrations of piperylene than that of oxygen make the deactivation of $T(n\text{–}\pi^*)$ by piperylene predominant. Whether oxygen or piperylene acts as a deactivator does not matter as long as both act as simple deactivators. The complication may be caused by various types of reaction involving semiquinone. It is expected that competition occurs between reaction (1) and the following reaction

$$AH\cdot + O_2 \rightarrow A + HO_2\cdot \qquad (4)$$

High concentrations of piperylene make reaction (1) more favorable. The intermediate produced by this reaction may also be attacked in part by oxygen;

$$AH - P\cdot + O_2 \rightarrow AH - P - O_2\cdot \qquad (5)$$

and the product is expected to act as an oxidizing agent toward acridine semiquinone. Moreover radicals produced from cyclohexane will be oxidized to peroxyradical which again acts as an oxidizing agent. Thus the eventual reactions consist of the recovery of acridine and the formation of an acridan-like compound. Quantitative treatment is far outside our scope. What we can say is only that the result is reasonable at least qualitatively on the basis of the above reasoning.

The value of $\Phi_{aer}=0.056$ is only about 30% of $\Phi_R\times 2=0.19$ which is expected if all the intermediates produced by reaction (1) undergo reaction (2).

Effect of the Addition of Piperylene on the Quantum Yield of the Photoreduction of Acridine in Methanol. In order to make clearer the reactions in the presence of piperylene and to confirm the assumptions made above, photoreduction in methanol has been investigated. The experiments and the analysis of the reuslts were made in the same way as in the case of cyclohexane.

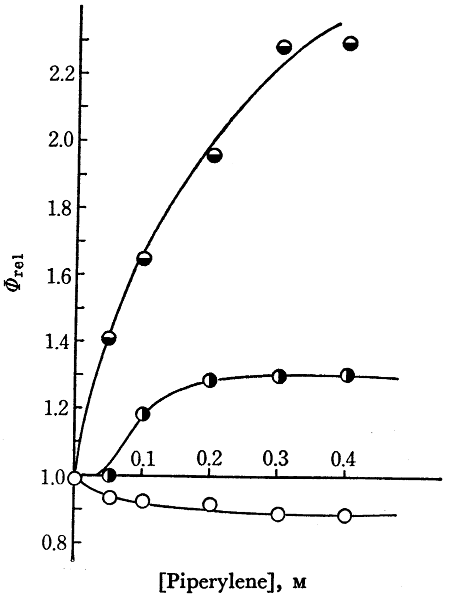


Fig. 5. Plot of Φ_{rel} *vs.* piperylene concentration in the aerated and deaerated solution of acridine in methanol.
◓: for the first stage } aerated.
◑: for the later stage }
○: deaerated.

For the aerated solutions, the plots $\ln(10^{+D}-1)$ *vs*, t consist of two steps, the slopes in the later stage being about 1/2 of those in the early one. This suggests the complicated nature of the entire reaction. It is more suitable to adopt the slopes in the early stage (up to about 15% decrease of acridine) because of the anticipated participation of the reaction products in the later stage. The results are shown in Fig. 5. It is seen that in contradistinction to the result for cyclohexane, a remarkable increase of Φ_{aer} occurs, *i. e.*, the Φ_{aer} value reaches 2.3 times that in the absence of piperylene. The value of Φ_{dea} decreases by about

10%. Thus

Φ_{dea}(in the presence of piperylene) $=0.115$
Φ_{aer}(in the presence of piperylene) $=0.07_6$

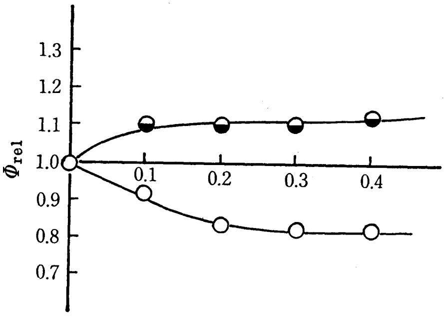
The value of Φ_{dea} is discussed as follows. According to our previous result,[4m] acridine semiquinone undergoes mainly disproportionation in methanol. It is likely as in cyclohexane that in the presence of piperylene, all the acridine semiquinone is stabilized to an acridan-like compound. If we further assume, as before, the complete quenching of T(n–π^*) and no quenching action of piperylene on the singlet excited state of acridine, the values calculated using the data in Table 1 are

$\Phi_{dea}=0.32\times 2+0.027=0.091$...with the new data
$\Phi_{dea}=0.039\times 2+0.027=0.105$...with the old data

Both values agree with the experimental one within about twenty percent.

On the other hand, Φ_{aer}(in the presence of piperylene is 75—80% of the value expected on the assumption that reaction (2) overwhelms reaction (4) or other types of reaction recovering acridine.

Effect of the Addition of Piperylene on the Photoreduction of Acridine in Ethanol and Isopropanol. The results for ethanol are shown in Fig. 6. Thus



[Piperylene], M

Fig. 6. Plot of Φ_{rel} *vs.* piperylene concentration in the aerated and deaerated solution of acridine in ethanol. ◒: aerated, ○: deaerated.

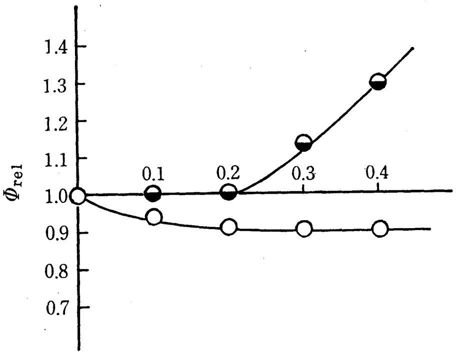
Φ_{dea}(in the presence of piperylene) $=0.10_7$
Φ_{aer}(in the presence of piperylene) $=0.04_7$

If we make the same assumptions as in the case of cyclohexane and methanol. Φ_{dea} is expected to be 0.129 with the new data but 0.177 with the old one. Thus the experimental value is about 20% less for the former.

The value of Φ_{aer} is about 30% of the value expected if reaction (2) overwhelms reaction (4) or similar oxidizing reactions.

The results for isopropanol are given in Figure 7. This system is considered to be simple in one sense because only singlet excited state participates in the reaction. From the plots given in Fig. 6.

Φ_{dea}(in the presence of piperylene) $=0.08_0$



[Piperylene], M

Fig. 7. Plot of Φ_{rel} *vs.* piperylene concentration in the aerated and deaerated solution of acridine in *iso*-propanol. ◒: aerated, ○: deaerated.

But a reliable value of Φ_{aer} can not be obtained from the plot. In our previous paper,[4m] we could not make any conclusion about the behavior of acridine semiquinone in isopropanol. Hence it is quite unknown whether $2AH \rightarrow A+AH_2$ or $AH+RH \rightarrow AH_2+R$ or $AH+RH_2 \rightarrow AH_2+RH$ occurs predominantly. If we assume that disproportionation is predominant, Φ_{dea} should reach $0.058\times 2+0.03=0.15$ which exceedes very much the experimental value of Φ_{dea}. If one considers that for other alcohols and for cyclohexane the calculated values of Φ_{dea} (on the assumption of disproportionation of semiquinone) agree with the experimental Φ_{dea}-value within *ca.* 20%, the disagreement in the present case is too large to attribute it to the experimental error. It seems therefore more likely to consider that the reaction

$$\begin{aligned} &AH + \text{isopropanol} \rightarrow AH_2 + (CH_3)_2C - OH \\ &\quad\text{or } AH + RH \rightarrow AH_2 + R \qquad (6)\end{aligned}$$

mainly occurs in isopropanol. This is not unreasonable in view of the high reactivity of isopropanol. If we assume reaction (6), the experimental value of Φ_{dea} is about 10% less than the calculated one, $0.058+0.03=0.088$. This may be within experimental error, but one can safely say that even if piperylene deactivates singlet excited state the amount does not exceed 10% or so of Φ^S in isopropanol. The results for other solvents are consistent with this conclusion. Thus the second assumption made at the start has been substantiated to some extent.

In conclusion, we can say firstly that in nonpolar solvents with a hydrogen atom easily detachable, radical mechanism mainly occurs in the singlet excited state and molecular mechanism in T(n–π^*). This may be due to the non-existence of a specific interaction between acridine and H-donor. Under such conditions, a two site reaction like molecular mechnaism may not be able to occur during the lifetime of singlet excited state. A little longer lifetime of T(n–π^*) may be favorable for the occurrence of this mechanism in T(n–π^*).

Secondly, the results obtained from the experiments concerning piperylene effects have led to the conclusion that in the case of methanol, ethanol and cyclohexane, the half-reduced radical of acridine mainly undergoes disproportionation while in the case of isopropanol it is highly probable that semiquinone is further reduced by isopropanol or by isopropyl radical.