March, 1973]   BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 745—748 (1973)   745

Photochemistry of Acridines. XIX. Photoreduction of Acridine in Mixed Solvents

Mikio Hoshino and Masao Koizumi
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai

(Received March 1, 1972)

The photoreduction of acridine has been investigated in three kinds of mixed solvents, benzene–isopropanol, benzene–methanol and benzene–cyclohexane, all in aerated and deaerated conditions. The following general tendensies have been found for the plot Φ_{rel} *vs.* mole fraction. It is approximately linear or slightly concave upward for molecular mechanism, while convex upward for radical mechanism. This indicates that for molecular mechanism a cage model trapping two radicals (*e.g.* C-radical and alcohol radical) is unsuitable while one act process involving two reactive sites is suitable.

Photoreduction of acridine in H-donating solvents occurs *via* dual mechanisms, molecular and radical. In general, the contribution of excited singlet state and triplet (n-π^*) state to each mechanism depends upon the nature of the solvent. In the case of isopropanol both mechanisms occur only in the singlet excited state, while in methanol both singlet and T(n-π^*) contribute to radical mechanism and molecular mechanism occurs mainly in the singlet excited state.[1] The case is essentially the same with ethanol and n-propanol. However, the feature is quite different in cyclohexane, radical mechanism occurring only in singlet excited state and molecular mechanism only in T(n-π^*).[2] The cause of such behavior still remains unclarified.

Concerning the meaning of radical and molecular mechanisms, the former is a mechanism in which half-reduced acridine is produced as an intermediate and is captured by the oridinary flash technique. In the latter no transient intermediate is observed by the flash technique in contrast to radical mechanism. It is still unknown whether it really occurs as one act or occurs *via* a transient intermediate too short-lived to be captured by the flash technique. Even the possibility that an intermediate in this mechanism is two radicals, *e.g.* acridine semiquinone and alcohol radical trapped in one cage is conceivable. In fact, Zanker and Prell[3] distinguished two mechanisms resembling radical and molecular ones and proposed a cage-like model for the photoreduction of 9-CH_3-acridine by ethanol.

To elucidate the problem, we have studied photoreduction in three mixed solvents, *i.e.*, 2-propanol, methanol and cyclohexane containing various amounts of benzene. They are the three H-donors which display distinct features of the reaction as listed below.

	Molecular mech.	Radical mech.
2-Propanol	singlet	singelt
Methanol	singlet, very littleT(n-π^*)	singlet, T(n-π^*)
Cyclohexane	T(n-π^*)	singlet

If the transient intermediate in molecular mechanism are two radicals trapped in a cage, the contribution of molecular and radical mechanisms will change with a certain correlation depending upon the composition of the solvent. Thus the stability of radicals trapped in the cage will depend upon its structure and nature which varies according to the composition of the solvent. Therfore, if the structure changes in such a way as to make it easy for the two radicals to separate from each other, the molecular mechanism will be transformed to radical mechanism by the amount determined by the cage structure. On the other hand, if the two mechanisms occur independent of each other, or if molecular mechanism occurs *via* a path completely different from the path involving semiquinone, they will show different dependencies upon the composition of the solvent, characteristic of each mechanism.

An outline is given on the method to determine the contribution of singlet excited state and T(n-π^*) state to molecular and radical mechanisms. The quantum yields due to radical (Φ_R) and molecular mechanism (Φ_M) can be discriminated in a simple way. Since the half-reduced acridine is oxidized back entirely to acridine in the aerated solution, the quantum yield experimentally obtained in the aerated solution gives Φ_M, and Φ_R can be obtained as the difference between the quantum yields in the aerated and deaerated solutions.

The contribution of singlet excited state and triplet state T(n-π^*) (the lowest T(π-π^*) of acridine is unreactive) to two mechanisms, $\Phi_M{}^S$, $\Phi_M{}^T$ ($\Phi_M=\Phi_M{}^S+\Phi_M{}^T$), $\Phi_R{}^S$ and $\Phi_R{}^T$ ($\Phi_R=\Phi_R{}^S+\Phi_R{}^T$) can be obtained from the quenching experiment using biacetyl as a quencher.[1,2] The triplet state of biacetyl being located a little lower than acridine T(n-π^*), the triplet energy transfer occurs from the latter to the former at fairly low concentrations of biacetyl. It was established[1] that the singlet excited state of acridine which is considered to be much shorter-lived than that of T(n-π^*) is also deactivated at higher concentrations of biacetyl. Thus, the quenching experiment with biacetyl in the aerated solution can, in principle, distinguish $\Phi_M{}^S$ from $\Phi_M{}^T$. Similarly $\Phi_M{}^T+\Phi_R{}^T$ and $\Phi_M{}^S+\Phi_R{}^S$ can be separated experimentally for the deaerated solution. Since $\Phi_{\mathrm{tot}}=\Phi_M{}^S+\Phi_M{}^T+\Phi_R{}^S+\Phi_R{}^T$, $\Phi_M{}^S+\Phi_M{}^T$, $\Phi_M{}^S$, $\Phi_M{}^T$, $\Phi_M{}^T+\Phi_R{}^T$ and $\Phi_M{}^S+\Phi_R{}^S$ are determined experimentally, $\Phi_M{}^S$, $\Phi_M{}^T$, $\Phi_R{}^S$, and $\Phi_R{}^T$ can be evaluated in general. The procedures are more simplified in many cases.

Experimental

Acridine was purified by recrystallization twice from

---

[1] M. Koizumi, Y. Ikeda, and H. Yamashita, This Bulletin, **41**, 1056 (1968).

[2] M. Hoshino, S. Niizuma, and M. Koizumi *ibid.*, **45**, 2988 (1972).

[3] V. Zanker and G. Prell, *Ber. Busenges.*, **73**, 791 (1969).

aqueous ethanol. Biacetyl was purified by distillation immediately before use. All the solvents used were purified by standard methods. As a light source of 365 nm, a 100 W high pressure mercury lamp was used with suitable filters. All the measurements were made at 25°C.

Results

Quantum Yields of the Photoreduction of Acridine in Mixtures of 2-Propanol–Benzene and Cyclohexane–Benzene. The quantum yields in the mixed solvents of various composition were measured for aerated and deaerated conditions, the former dealing with molecular mechanism. The quantum yields due to radical mechanism were calculated from the difference of the two. In Fig. 1, the relative values of Φ_M and Φ_R for a mixture of benzene and 2-propanol are plotted against the mole fraction. Only singlet excited state participates in the reaction and we have $\Phi_M=\Phi_M^S$ and $\Phi_R=\Phi_R^S$. It is seen that the former is approximately linear or a little concave upward and the latter convex upward. Figure 2 shows the results obtained for a mixture of benzene and cyclohexane. The curves for Φ_M(rel) and Φ_R(rel) are very similar to the corresponding ones in Fig. 1. In this case we have $\Phi_M=\Phi_M^T$ and $\Phi_R=\Phi_R^S$. It is interesting that the characteristic feature of Φ_M(rel) is independent of the reactive state.

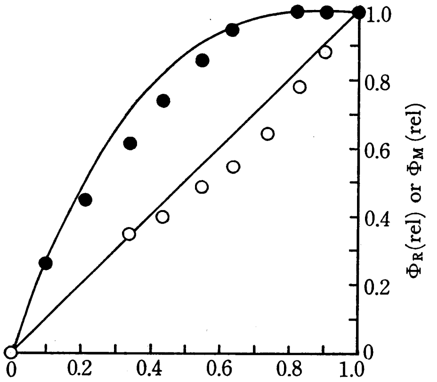


Fig. 1. Plots of Φ_R(rel) (●) and Φ_M(rel) (○) against the mole fraction of 2-propanol. A curve and a straight line are the calculated ones from the following equation by putting $n=3$ and 1 respectively.
$\Phi_{rel}=1-(1-X)^n$

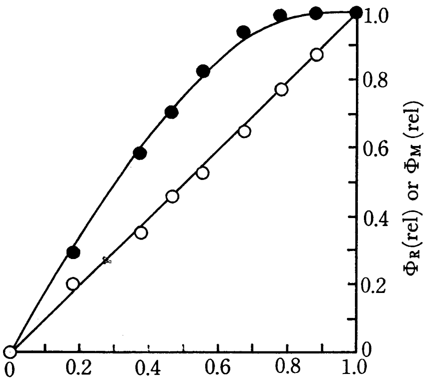


Fig. 2. Plots of Φ_R(rel) (●) and Φ_M(rel) (○) against the mole fraction of cyclohexane. A curve and a straight line are the calculated ones from the following equation by putting $n=3$ and 1 respectively.
$\Phi_{rel}=1-(1-X)^n$

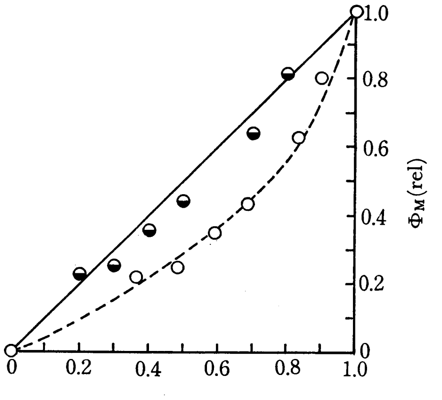


Fig. 3. Plots of Φ_M(rel) against the volume fraction of methanol (◒) and against the mole fraction of methanol (○).

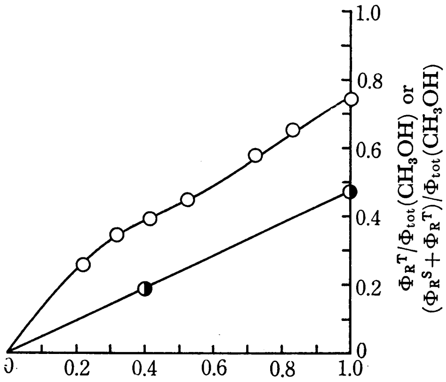


Fig. 4. Plots of Φ_R^T (◑) and $\Phi_R^S+\Phi_R^T$ (○) both divided by $\Phi_{tot}(\mathrm{CH_3OH})$, against the volume fraction of methanol.

Quantum Yields of the Photoreduction of Acridine in a Mixture of Benzene and Methanol. The results are shown in Figs. 3 and 4. The plot for molecular mechanism resembles those of the above two systems though the degree of curvature is somewhat larger, but the plot for radical mechanism is quite different. The shape of the plot $(\Phi_R^T+\Phi_R^S)/\Phi_{tot}(\mathrm{CH_3OH})$ ($\Phi_{tot}(\mathrm{CH_3OH})$ is the value for pure methanol) suggests the superposition of the two components, one resembling the Φ_R plot of the previous systems (convex upward) and the other approximately a straight line.

Anticipating that this is due to the fact that T(n-π^*) in addition to singlet excited state contributes to radical mechanism, we have attempted to discriminate the two contributions Φ_R^T and Φ_R^S. This has been done by examining the effect of the addition of biacetyl on the quantum yields of the photoreduction in the mixed solvent of composition, methanol:benzene=4:6, at which a component convex upward appears to approach a limiting value. In Fig. 5 the inverse of the relative quantum yield (in reference to the Φ-value in the absence of biacetyl) is plotted for the aerated and

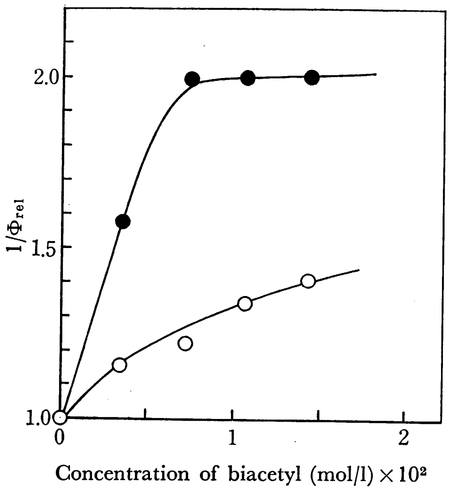


Fig. 5. Plots of $1/\Phi_{rel}$ for the degassed solution (●) and aerated solution (○) against the concentration of biacetyl. Solvent; methanol: benzene=4: 6 (in volume).

deaerated solutions, against biacetyl concentrations. The plot for the aerated solution deals with molecular mechanism to which singlet excited state mainly contributes. It is natural that the curve still increases at about 10^{-2}M. The plot for the deaerated solution apparently consists of two parts, one with a steep slope in the lower concentration region of biacetyl and the other with a very gradual slope in the higher concentration region. It is appropriate to relate the former to T(n-π^*) and the latter to the singlet excited state. We can estimate from the plot for the deaerated solution the value of Φ_R^T for the mixed solvent at methanol: benzene=4: 6, which was found to be 0.025_6. The value of Φ_R^T in pure methanol is 0.057—0.063.[1,2] The values of $\Phi_R^T/\Phi_{tot}(CH_3OH)$ are obtained by dividing the above two values by Φ_{tot} for pure methanol, 0.128.

It is seen that the contribution of T(n-π^*) to radical mechanism is approximately linear with respect to the volume fraction of methanol. Substracting this portion from the $(\Phi_R^R+\Phi_R^T)/\Phi_{tot}(CH_3OH)$, we obtain the Φ_R^S-values. The plots Φ_R^S(rel) *vs.* mole fraction and volume fraction are given in Fig. 6. The curves are convex upward and the limiting value is reached at a mole fraction of methanol of about 0.8.

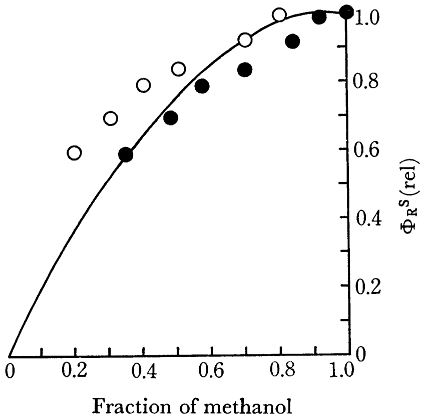


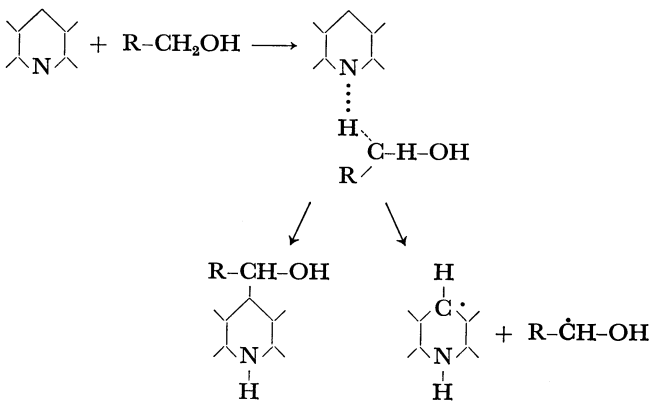
Fig. 6. Plots of Φ_R^S(rel) against the mole fraction (●) and against the volume fraction (○). The curve is a calculated one from the following equation by putting $n=2$.
$\Phi_{rel}=1-(1-X)^n$

Discussion

From the present results we can say that the Φ_R(rel) *vs.* X plot and the Φ_M(rel) *vs.* X plot are not related with each other at all and that the two plots show their own characteristic dependency on the mole fraction. Therefore a cage model involving two radicals can not be adopted. Since the concentration of H-donor is high enough under the present conditions (from $X=0.1$ to pure solvent), the behavior of semiquinone will not be affected by the composition of the solvent in view of a long lifetime of semiquinone (>msec).[4] Accordingly the present results deal mainly with the characteristics of the primary processes for molecular and radical mechanisms, which essentially depend on the nature of H-donor.

A plausible model for molecular mechanism is either (1) a one act process involving two reactive sites (N and 9-C of acridine) or (2) a consecutive reaction with a very short-lived intermediate (first, N-atom and secondly 9-C atom react).

For the latter, it is likely that the step of intermediate formation is common to radical mechanism as written schematically below,



It is thus expected that M- and R-mechanisms are related to each other in a certain way. If the first step is essential in determining the feature of reaction, the solvent dependence should be common to both mechanisms, whereas if the second step is the key-process, a similar deduction to that for the cage model should hold. Both expectations contradict the experimental results and it is thus most likely that the M- and R-mechanisms occur *via* different paths from the start.

In order to discuss the solvent dependence of Φ_M and Φ_R quantitatively, we should know the lifetime of the excited state. However, acridine is nonfluorescent in nonpolar solvents and the lifetime of the singlet excited state cannot be measured. Still less knwon is the solvent dependence of the lifetime.

We have found that the feature in the solvent dependence of M- and R-mechanisms is not related to the existence of OH group in a H-donor molecule which

---

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

is attached to N of acridine *via* H-bonding. This seems reasonable for M-mechanism for which two site reaction occurs as one step but not so for radical mechanism, since the existence of specific interaction in the form of H-bonding is suspected to favor the reaction in which N of acridine is attacked by H-atom. One is tempted to consider that the upward convex shape of the Φ_R *vs.* X plot is due to this specific interaction which suppresses the dilution effect of benzene. However, this view does not hold because a similar dependence of Φ_R on X has been obtained in the case of cyclohexane for which no such interaction exists. It is therefore inferred that the relative positions of acridine and H-donor together with their configurations necessary for R-mechanism to occur are taken newly after acridine is excited and irrespective of the ground state configuration. This is reasonable because a hydrogen atom to be detached from alcohol is a α-H atom and not one of the OH group. Thus it is considered that for the reaction to occur, a molecule of H-donor must occupy a specific site, orientation and configuration relative to N of acridine. When such an effective encounter is realized, the reaction will occur with certain probability. Assuming the constant lifetime of the excited state, the rate can be determined by the number of occurrences of such an encounter.

If such a view is adopted, the Φ_R *vs.* X relation will be treated approximately by a site-jumping model. Neglecting energy factor and assuming that the probability for H-donor to occupy this effective configuration is merely proportional to mole fraction, the relative quantum yield for radical mechanism can be given by

$$\Phi_{\rm rel} = 1 - (1-X)^n$$

where X is a mole fraction and n is the number of effective encounters (number of jumping) during the excitation.

This model is too crude to treat the present results quantitatively, but it seems suitable as one step in a mathematical approach to the problem. If one applies the formula to the present results, the values of n for radical mechanism are evaluated as follows. The numbers in parentheses are the values of n when volume fractions are used instead of mole fractions.

2-propanol	$n = 3$ (3)
cyclohexane	$n = 2$ (2)
methanol	$n = 2$ (3)

The results appear to be reasonable.

If the same model is applied to molecular mechanism the value of n becomes 1 or less than 1. However, the concave upward curve may partially be due to the excess inhibiting action of benzene. For instance, a larger size of benzene molecule than of methanol will reduce the occurrence of effective encounter.

The results obtained strongly suggest that M- and R-mechanisms are two independent reactions occurring *via* different paths from the start. However, the reasons for the following behaviors still remain unclarified.

1) T(n-π^*) participates in the case of methanol but not isopropanol.

2) Only R-mechanism occurs in S* in the case of cyclohexane while both R- and M-mechanisms occur in S* in the case of methanol.

3) Only M-mechanism occurs in T(n-π^*) in the case of cyclohexane, while R-mechanisms mainly occurs in T(n-π^*) in the case of methanol.

4) Linear relation holds between $\Phi_R{}^T$ and the volume fraction for methanol in contrast to the convex upward curve of $\Phi_R{}^{S*}$ *vs.* volume fraction in general.