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Photochemical Reaction of 9-Chloroacridine in Aerated and Deaerated Ethanol. II. Studies by Means of a Flash Technique

Katsumi Nakamaru, Shigeya Niizuma, and Masao Koizumi
Dapartment of Chemistry, Faculty of Science, Tohoku University, Katahira, Sendai

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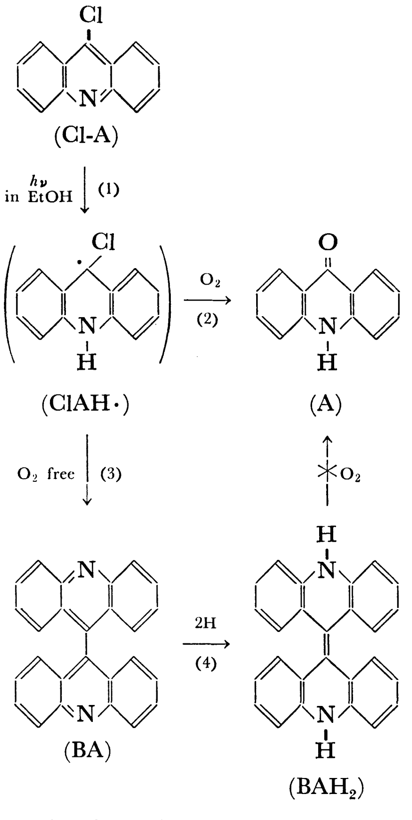
Studies were made on the transient species produced when the aerated and deaerated ethanol solutions of 9-Cl-acridine (9-Cl-A) are flashed. In the deaerated solution, triplet state of 9-Cl-A and a long-lived radical species of unknown structure were detected. It was established that the latter is produced by a reatcion in the singlet excited state of 9-Cl-A (and possibly in the higher triplet ($T_{n-\pi}{}^*$)) and that it produces biacridyl by a bimolecular reaction. In the aerated solution, another radical species of a long life of which structure is still unknown, was detected. It was established that this radical species reacts bimolecularly and produces acridone.

In a previous paper,[1] we have established that irradiation of 9-Cl-acridine in ethanol by 365 nm, produces acridone (A) in the aerated solution, while in the absence of oxygen, mainly biacridan (BAH_2) is produced *via* biacrydyl (BA). The proposed scheme is as follows.



The identification of BA and BAH_2 was established in the previous paper, and there is no doubt on the occurence of process (4). But it is quite unknown how processes (1) and (3) occur, or in other words, whether the splitting of HCl preceeds or follows the dimerization reaction. Still less unknown is the detailed mechanism of the production of acridone. The only information obtained experimentally is that the presence of reductive medium and of oxygen is necessary for the reaction to occur.

In order to elucidate the detailed mechanism of these reactions, we have performed flash photolysis studies for both the aerated and deaerated solutions. For the aerated solution, a certain transient intermediate was detected which produces acridone by a bimolecular reaction. In the deaerated solution, two transient species, long-lived and short-lived were detected and it was established that the long-lived species produces biacridyl bimolecularly. Although we did not succeed in identifying the transient species, the present results are consistent with the conclusion given in the previous paper and are helpful for elucidating the mechanisms of the reactions.

Experimental

Materials. All the materials were purified as described in the previous paper.

Apparatus and Procedures. The apparatus for the flash photolysis is an usual one employed in our laboratory.

Results and Discussion

Deaerated Solution. Two kinds of transient intermediates, short-lived M_1, and long-lived M_2, were detected. It was established that the photoproduct is biacridyl by measuring its spectrum after flashing the sample several times. Although the absorption spectra of M_1 and M_2 overlap with each other to some extent, they can be distinguished rather easily because of their great difference in their lifetimes.

Figure 1 gives the plot of $1/D$ (D, optical density at 460 nm) against time. As will be verified below, the later stage obeys the second order, while the earlier stage deviates greatly from the second order plot. The order of reaction in an early stage was examined by the following procedures; 1) extrapolation of the later linear portion, 2) substraction of the D-value on the extrapolated line (D_{ext}) from D at various time points and 3) plotting of $\log(D-D_{ext})$ or $1/(D-D_{ext})$ against time. As shown in Fig. 1b the $\log(D-D_{ext})$ *vs.* t plot gives a straight line irrespective of the wavelengths. Hence one can conclude that the decay in the early stage obeys the first order. To check the reliability of this procedure and to obtain the correct spectral shape, we plot $(D-D_{ext})$ at various wavelengths against $(D-D_{ext})_{440}$. As shown in Fig. 2 all of them give good linear plots, and the spectral shape could thus be determined accurately. This is given in Fig. 3. All the transient spectra reported below were obtained or checked by the similar

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[1] K. Nakamaru, S. Niizuma, and M. Koizumi, This Bulletin, **44**, 1256 (1971).

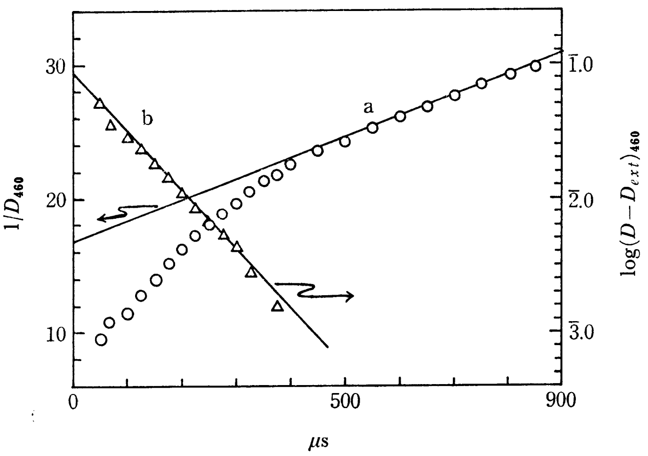


Fig. 1. Analysis of the decay of the two intermediates produced in the degassed solution of 9-Cl-A in ethanol (1×10^{-4} M), at 460 nm (See text).
a: decay of M_2 (long-lived intermediate)
b: decay of M_1 (short-lived intermediate)

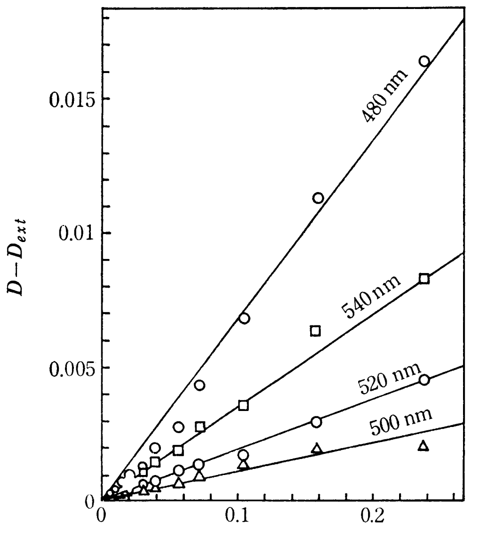


Fig. 2. Plot of $D-D_{ext}$ (at various wavelengths) *vs.* $D-D_{ext}$ (at 440 nm). Degassed solution of 9-Cl-A in ethanol (1×10^{-4} M).

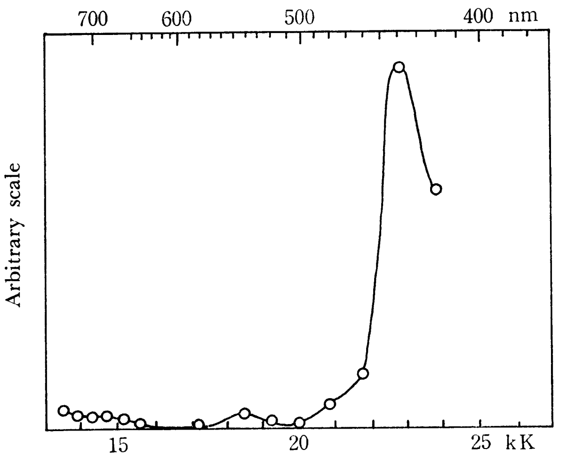


Fig. 3. Spectrum of short-lived intermediate, M_1 obtained in the degassed solution of 9-Cl-A (1×10^{-4} M).

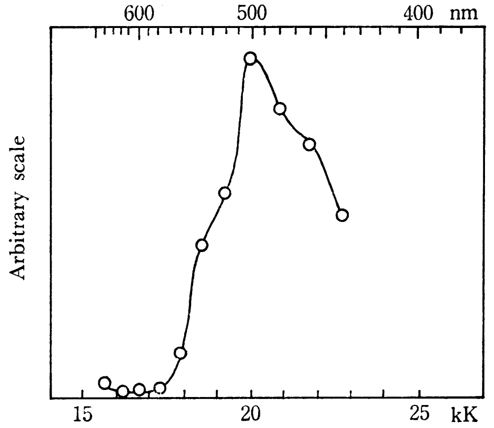


Fig. 4. Spectrum of long-lived intermediate, M_2 obtained in the degassed solution of 9-Cl-A (1×10^{-4} M).

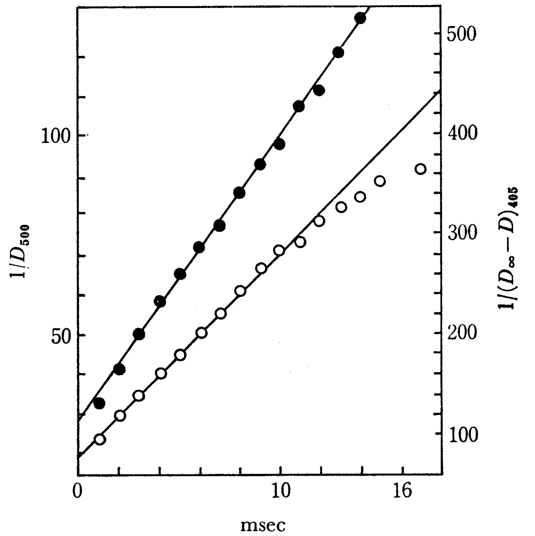


Fig. 5. Second-order plot for the decay of M_2 (at 500 nm) and for the build-up of BA (at 405 nm). Degassed solution of 9-Cl-A in ethanol (1×10^{-4} M).
○: $1/D_{500}$, ●: $1/(D_\infty-D)_{405}$

method as described above. The success of the above procedure implies that there is no interrelation between M_1 and M_2. M_1 may safely be identified as the triplet state on the basis of its lifetime (rate constant, 7.4×10^3 sec^{-1}) and a somewhat similar spectral shape as that of acridine triplet. Hence it is likely that M_2 is produced by a reaction in the singlet excited state of 9-Cl-A(and possibly in the high triplet (n-π^*)).

Figure 4 gives the spectral shape of M_2 as obtained by the similar method as described above. Figure 5 gives the decay of M_2 and the build-up of BA plotted according to the second order rate formula. The former was measured at 500 nm while the latter at 405 nm. The inclinations of the plots which give $k/\varepsilon d$ are for the former 1.8×10^4 sec^{-1} and for the latter 2.8×10^4 sec^{-1}. Figure 6 gives the relation between the decrease of M_2 and the increase of BA, as measured by the change in the optical densities respectively at 500 nm and at 405 nm. It is seen that the plot of D_{500} *vs.* $(D_\infty-D)_{405}$ gives a good straight line passing through the origin. We can conclude from Figs. 5 and 6 that BA is produced from M_2 accord-

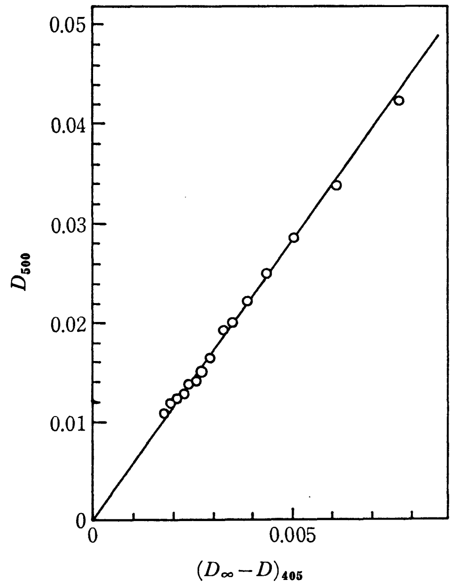
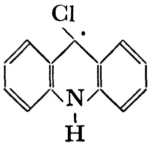
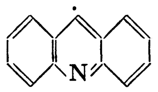


Fig. 6. Relation between the quantity of the intermediate M_2 and that of BA in the degassed solution of 9-Cl-A in ethanol (1×10^{-4} M).

ing to a bimolecular reaction. As to the identification of M_2, there are two possibilities. One is a half-reduced 9-Cl-acridine (I). In this case splitting of hydrogen chloride occurs during or after dimerization. Another possible structure is (II). This is produced when the splitting of HCl from (I) preceeds dimerization. Discrimination of the two will be possible if we undertake the similar experiments using other 9-halogenated acridines.


(I)


(II)

The Aerated Ethanol Solution. Only one transient species with a rather long lifetime was detected. The product after flashing was identified as acridone by measuring the UV spectrum. A transient species has a spectral shape as given in Fig. 7. Since it is common that no T-T absorption is observed in the aerated solution, this transient species is attributed to some kind of radical species. Comparing Fig. 7 with Fig. 4, we can conclude that this radical species is different from M_2. We call it M_3 for the sake of convenience.

In Fig. 8 the decay of M_3 measured at 520 nm and the build-up of acridone as measured at 400 nm are plotted as a second order process. Since at 400 nm, the spectra of M_3 and acridone overlap to some extent, $(D_\infty-D)_{400}$ was plotted against time. It is evident that the decay of M_3 and the build-up of acridone run parallel. This was confirmed further by Fig. 9 where $(D_\infty-D)_{400}$ and D_{520} at corresponding time points are plotted. The plot is a good straight line. We can conclude therefore, that acridone is produced from some unknown radical species M_3 bimolecularly.

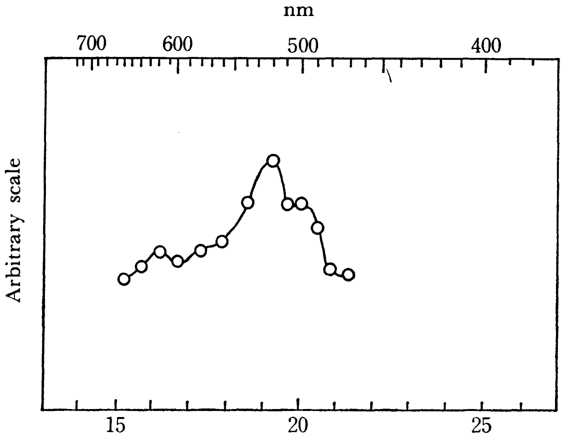


Fig. 7. Spectrum of intermediate M_3 obtained in the aerated solution of 9-Cl-A in ethanol (1×10^{-4} M).

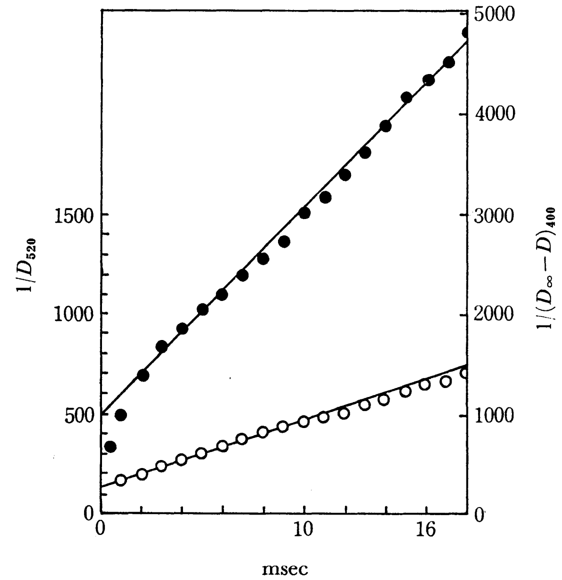


Fig. 8. Second-order plot for the decay of M_3 (at 520 nm) and for the build-up of acridone (at 400 nm). Aerated solution of 9-Cl-A in ethanol (1×10^{-4} M).
○: $1/D_{520}$, ●: $1/(D_\infty-D)_{400}$

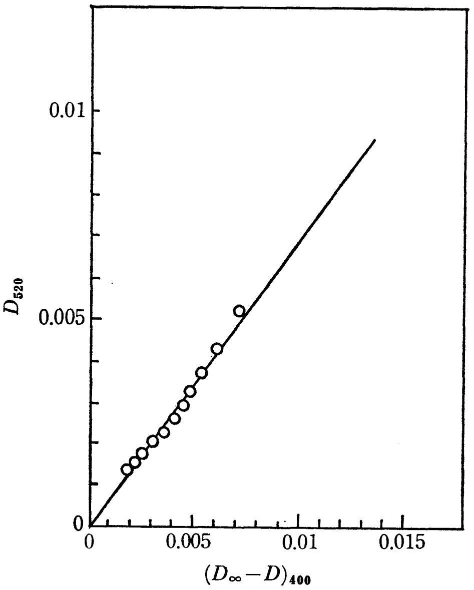
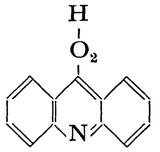
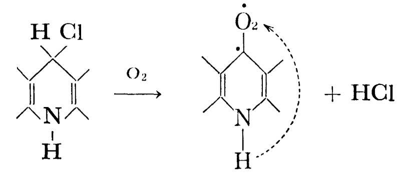


Fig. 9. Relation between the quantity of the intermediate M_3 and that of acridone in the aerated solution of 9-Cl-A in ethanol (1×10^{-4} M).

The identification of M_3 will become easier when M_2 is identified and so was not attempted at the present stage. Only provisional discussions will be given below. Judging from the fact that M_3 gives rise to acridone bimolecularly and that oxygen is involved in the reaction, it seems very probable that HO_2 group is attached to acridine structure in some way. If one assumes M_2 has a structure (II) and further assumes that (II) is formed even in the presence of exygen, then it is conceivable that (II) reacts with oxygen, and the resulting peroxiradical deprives hydrogen atom from ethanol producing the following hydroperoxide. This will produce acridone bimolecularly. On the other hand, if M_2 has structure (I), it is expected to be oxidized back to 9-Cl-acridine from analogy to acridine, rather than attacked by oxygen at 9-position. Another possibility is primary production of 9-Cl-acridan *via* molecular mechanism and the attack of oxygen at 9-position. But this is also improbable because acridan type product was not detected in the steady light reaction of 9-Cl-acridine.[1]





The identification of M_2 and M_3 is most desirable to establish the mechanism of the general photoreaction of 9-Cl-acridine. Furthermore it will be interesting to investigate the transient radical species of photoreaction of BA at various acidities in view of great difference of stability in $BAH_2^{+}\cdot$ and $BAH\cdot$ reported in a previous paper.[2] These studies will be made in near future.

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[2] S. Niizuma, K. Nakamaru, and M. Koizumi, *Chem. Lett.*, **1972**, 59.