BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 625—630 (1969)

Photochemistry of Acridine and Acridan. Two Isomeric Forms of Acridine Semiquinone

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(Received July 11, 1968)

A transient species characterized by the absorption peaks at 350 mμ and 560 mμ has been found in the flash photolysis of acridan in both benzene and methanol solutions. This species has been proved to be different from the acridine semiquinone reported already, but has been identified as another acridine semiquinone radical on the basis of its direct conversion to acridine and also from its low reactivity to oxygen which denies the possibility of being triplet acridan. Thus it is concluded that two isomeric forms of acridine semiquinone exist. From the result of the flash photolysis of biacridan, the one reported previously has been identified definitely with a radical having a hydrogen atom attached to the nitrogen atom of acridine. Therefore, the newly discovered one is most likely a radical with a hydrogen atom attached on the 9 carbon atom of acridine.

In previous papers,[1,2] acridine semiquinone with the absorption maxima at 278 mμ and ~520 mμ has been found in flash photolysis studies of acridine in alcohols. Judging from the results of steady-illumination studies,[3] the formation of semiquinone was also expected in the photoreduction of acridine by acridan (dihydroacridine) in inert solvents, but the transient species in this case showed some difference against the semiquinone described above both in its spectral and in kinetic features.[4] Under such circumstances, it is most desirable to study further the transient absorption spectra observed in the photoreduction of acridine in various conditions, and in particular, in the photodehydrogenation of acridan.

In the present work, the photoreaction of acridan was studied with the flash method in a non-polar solvent, benzene and also in a polar solvent, methanol, both of which had been used in the previous investigations. In addition, the transient species produced photochemically in benzene solutions of acridine and acridan was investigated in more detail. It has been found that the results are interpreted satisfactorily by regarding a new transient band from acridan as an isomer of the acridine semiquinone. Furthermore, the structure of the semiquinone found in the photoreduction of acridine was determined by comparing its spectrum with the transient spectrum in the photolysis of biacridan.

Experimental

Apparatus. A flash photolysis apparatus used in the present work was constructed recently at the Institute of Physical and Chemical Research.

The excitation source consisting of two U-shaped xenon flash lamps connected in series were fired with the electric charge stored in two or three 1 μF-capacitors at 6 to 10 kV. A half-intensity duration was 15 μs at 9 kV and 3 μF. A quartz cylinder 10 cm in length and with an inner diameter of 8 mm, was used as a sample cell. Liquid or solution filters were set between the lamps and the cell; filter cells were of quartz with a size of $106 \times 52 \times 8$ mm³. Details of the apparatus are described elsewhere.[5]

Illumination Conditions. Samples were illuminated by the 64 to 94 J flash through filters. Methanol solutions were excited through a plastic filter with a ~250 mμ cut off. For benzene solutions of acridan, a liquid benzene filter was employed to eliminate the photo-excitation of the solvent. In the solutions of acridine and acridan, only the former was excited by using a Toshiba UV-D2 filter. Biacridan dissolved in dimethylsulfoxide (DMSO) was illuminated through the plastic filter described above. Although the solvent, DMSO, absorbs considerably under this condition, the excitation of the solvent did not disturb the observation of the transient spectra.

Samples. Acridan was prepared by reducing acridine with sodium amalgam and recrystallized three times from a methanol-water mixture after removing insoluble

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

2) A. Kira, *Sci, Rep. Tohoku Univ.*, **49**, 129 (1966).

3) S. Niizuma, Y. Ikeda and M. Koizumi, This Bulletin, **40**, 2249 (1967).

4) A. Kira and M. Koizumi, *ibid.*, **40**, 2486 (1967).

5) A. Kira and K. Nishi, *Rep. IPCR*, **44**, 56 (1968) (in Japanese).

precipitates. Acridine was recrystallized three times from an ethanol-water mixture.

Biacridan was photochemically prepared and recrystallized from dimethylsulfoxide.[6]

Benzene fractionally distilled from a guaranteed reagent of Wako Pure Chemicals Co. was used throughout the present work; it gave slower decays of the transient species in the photolysis of acridan than a Dotite "Primasol" benzene without further purification.

A G. R. methanol submitted to the fractional distillation was used; a "spectral" methanol which we purchased was found to contain some amines as a stabilizing agent.

Dimethylsulfoxide was twice fractionally crystallized from a Wako reagent grade reagent.

Solutions were degassed by the usual freeze-pump-thaw method. The procedure was repeated at least three times. When the distillation of a soluent between two traps was made as the method of degassging, some acridan was converted to acridine in the case of methanol.

Results and Discussion

Comparison of the Transient Spectra in Various Systems.

Transient absorption spectra for acridan are shown in Figs. 1 and 2. The peaks are situated at 352 and 557 mμ in a benzene solution and at 350 and 564 mμ in a methanol solution. Hereafter, we will call them the 350 mμ- and the 560 mμ-band respectively. These two bands decay similarly in the second order, as will be described later, and it appears that they are ascribed mainly to the one same species. They were also observed in the aerated solutions, though the intensities were somewhat reduced. The decay of the transient absorption in aerated solutions had duration times of the order of 10^{-4} sec. This suggests that a species giving rise to these bands has low reactivity to oxygen, because, if it were to react with oxygen with the diffusion-controlled rate constant, 10^{10} M^{-1} sec^{-1}, the duration time in aerated solutions containing $\sim 2\times 10^{-3}$M oxygen (for both solvents) would be of the order of 10^{-7} sec. The predominant final product was identified with acridine from its absorption spectra; an example for benzene solution is shown in Fig. 3. Furthermore, in methanol which is transparent in the near UV region, an intense maximum at 250 mμ characteristic of acridine was also observed. As shown in Fig. 4, the formation of acridine was found to proceed in parallel with the fade-out of the transient absorption at 560 mμ, in both deaerated and aerated methanol solutions.

According to previous papers,[1,2] the spectra of acridine semiquinone obtained in the photoreduction of acridine in deareated alcohol solutions have the maxima at $\sim$480 and $\sim$520 mμ in the visible

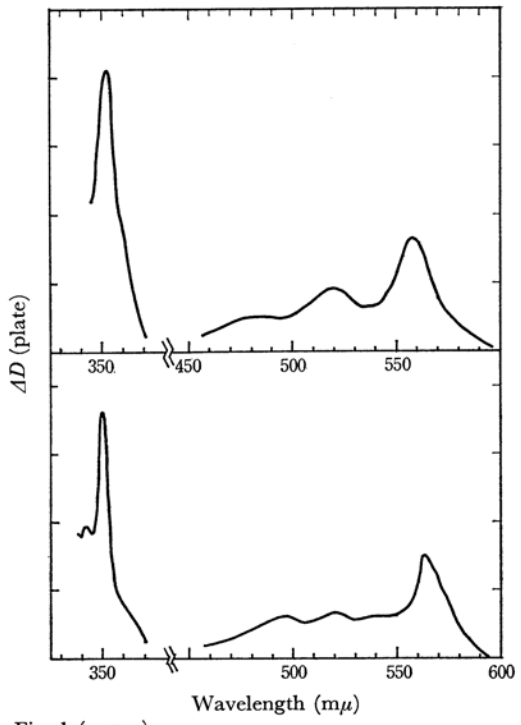


Fig. 1 (upper).
A transient spectrum observed in a deaerated benzene solution of 1×10^{-4} M acridan (t: 50 μsec), and
Fig. 2 (lower).
One observed in a deaerated methanol solution of 5×10^{-5} M acridan (t: 50 μsec). Both spectra were photographed on the same plate. The wavelength response of the plate (Fuji, Neopan.) is not corrected (also for Figs. 5 and 6).

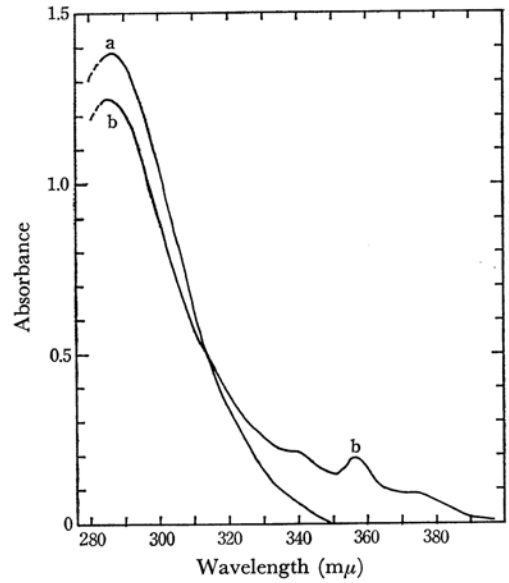


Fig. 3. The original (a) and final (b) spectra in the illumination of 1×10^{-4} M acridan in a deaerated benzene solution. The sample was illuminated 6 times with a 9 kV-3 μF flash.

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

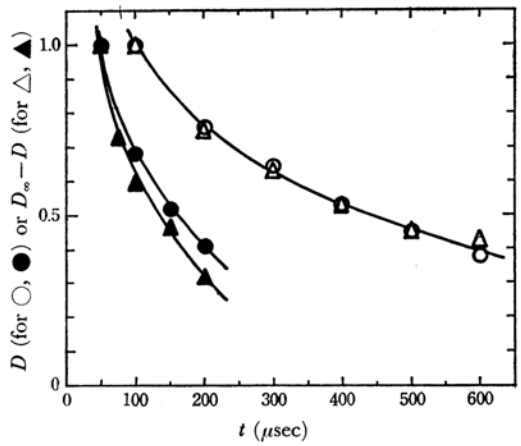


Fig. 4. The decay in the transient absorption (564 mμ) and the increase in the acridine absorption (250 mμ).
●, 564 mμ and ▲, 250 mμ for deaerated solution;
○, 564 mμ and △, 250 mμ for aerated solution.
Each pair of curves is normalized at the initial measuring point. (In methanol, the reaction proceeds faster in the deaerated condition than in the aerated one).

region, but no appreciable band near 560 mμ. This semiquinone is so sensitive to oxygen that its spectrum completely vanishes in aerated solutions. Thus, the predominant transient species with 350 and 560 mμ bands found in the present investigation is quite distinguished from the acridine semiquinone previously reported.

As seen in Fig. 1, a weak maximum is perceived at 520 mμ in deaerated benzene solutions. Upon aeration, the intensity at 520 mμ was reduced to one eighth of the deaerated one, while the intensity at 560 mμ to one fourth. This suggests that the 520 mμ band in the present system is partially ascribed to the transient species reported in the previous paper. A maximum at 520 mμ was not observed clearly in a methanol solution.

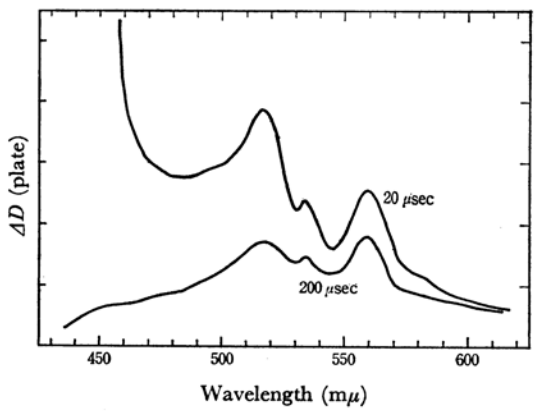


Fig. 5. Transient spectra in the photoreaction of acridine with acridan in deaerated benzene solution.

It was reported, in another previous paper,[4] that when acridine was excited by a flash in the benzene solutions containing acridan, a band with a maximum near 560 mμ as well as the 520 mμ band appeared. In that paper, however, both 520 and 560 mμ bands were attributed, tentatively or rather implicitly, to a single transient species. Hence the transient spectra in this system were examined in more detail under the condition that acridine was selectively excited. The spectra in the deaerated solutions given in Fig. 5 reconfirm the previous result. Thus the short-lived transient absorption is the T-T absorption of acridine with an intense peak at 440 mμ,[4] and the long-lived one consists of the 520 and 560 mμ bands. However, in view of the findings already described, a more reasonable interpretation is that the transient species consist of two components, the oxygen-sensitive and the oxygen-insensitive ones. This has actually been proved in the following way. The intensity ratio of the 520 mμ band to the 560 mμ band was examined in various oxygen concentrations. The results are given in Table 1, which shows definitely that oxygen attacks the 520 mμ band more efficiently.

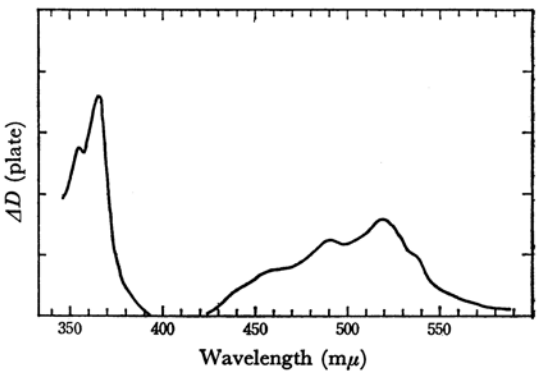
Biacridan (Compound III in Fig. 7), which is hardly soluble in methanol and benzene, was dissolved in DMSO and its transient spectrum

Table 1. The dependence of the transient absorption intensity on the oxygen concentration

1×10^{-4}M Acridine and 1×10^{-4}M acridan in benzene solutions

$[O_2]$ (M)	D^{520}	D^{560}	D^{520}/D^{560}
0	0.416	0.301	1.38
6.3×10^{-5}	0.254	0.242	1.05
1.3×10^{-4}	0.095	0.100	0.95
2.2×10^{-4}	0.044	0.052	0.85

D is the optical density for 10 cm path and the superscript denotes the wavelength (mμ).

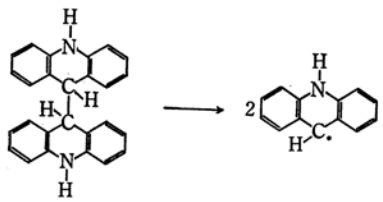


Fg. 6. A transient spectrum from biacridan in a deaerated DMSO solution (t: 200 μsec).

obtained upon flashing was examined. As Fig. 6 shows, the spectrum lacking the 560 mμ band, agrees with that obtained in the photoreduction of acridine in alcohols. The two bands located at ~520 mμ and at 350 mμ decay in a similar way and may be attributed to the same species. The bands in Fig. 6 were not observed in aerated solutions. The main final product was identified with acridine from the absorption spectrum. The yield of acridine was found to increase by a factor of two by the aeration. This is similar to the previous observation made in the photoreduction of acridine in alcohols. These findings substantiate the conclusion that the same transient species are produced in the photolysis of biacridan and in the photoreduction of acridine in alcohols.

Assignment of the Two Species. It is clear from the above experimental facts, that there are two kinds of long-lived species other than T-states, that is, the one without the 560 mμ band and the other with the 560 mμ band. Only the former is produced in the photolysis of biacridan and in the photoreduction of acridine in alcohols, while in benzene solutions both are produced in the reaction of excited acridine and acridan and, in the photolysis of acridan the latter is the main species.

Since there is no other type of dissociation conceivable for biacridan than the following one,



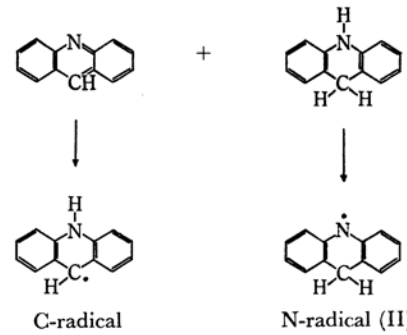
Biacridan (III) C-radical (I)

Fig. 7

the above results unambiguously lead to the assignment that the transient species without 560 mμ band is the radical with an unpaired electron on 9-carbon atom (C-radical).

Hitherto most workers[6-8] have considered, perhaps from chemical intuition, that the acridine semiquinone is the C-radical. In fact, the production of biacridan has been ascertained[6,9-11] in the photoreduction of acridine in hydrogen donating solvents and this may be regarded to support the formation of the C-radical as an intermediate. But the first confirmative evidence that only the C-radical is produced in the photoreduction of acridine in alcohols has been afforded in the present work.

As for the other transient species, it is most reasonable to assign it as an isomeric semiquinone with an unpaired electron on nitrogen atom (N-radical), because it is produced accompanied with the C-radical in the course of the photochemical reaction between acridine and acridan in inert solvents; the C-radical, in analogy with the photoreduction of acridine in alcohols, may be produced from acridine through a hydrogen atom transfer from acridan to acridine. This hydrogen atom is the one located either in 9-carbon or nitrogen atom in acridan and one may say, to be consistent with the experimental result, that the latter is more easily detached than the former. The main reaction may then be written as follows.



C-radical N-radical (II)

Fig. 8

This interpretation is also supported by the type of hydrogen abstraction in the photolysis of acridan in which the species with 560 mμ band seems to be the principal intermediate. The view that the 560 mμ band is ascribed to an isomeric semiquinone is also supported by the fact that, in the photolysis of acridan, the formation of acridine proceeds in parallel with the fade-out of the 560 mμ band.

More direct proof for the above assignment of the N-radical analogous to the proof for the C-radical was attempted but was unsuccessful, since appropriate compounds which may give rise to the N-radical, for example, *N,N'*-biacridan or *N*-halogenated acridan were not available. Attempts for preparing the N-radical by the radiolysis method are now in progress.

Although there is scarcely any doubt that the 560 mμ band is due to the N-radical, it might be added that all other conceivable assignments can be rejected from the experimental facts. These will be described below briefly.

Firstly, this species can not be assigned as the triplet acridan, because in the photoreaction of acridine with acridan, the triplet energy transfer,[12]

7) R. C. Kaye and H. I. Stonehill, *J. Chem. Soc.*, **1951**, 27.

8) R. A. Jackson and W. A. Waters, *ibid.*, **1958**, 4632.

9) A. Kellmann, *J. Chim. Phys.*, **63**, 936 (1966).

10) M. Giurgea, G. Mihai, V. Topa and M. Musa, *ibid.*, **61**, 619 (1964).

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

12) F. Wilkinson, "Advances in Photochemistry," Vol. III, Interscience Pub., New York (1964), p. 241.

$$A^T + AH_2 \longrightarrow A + AH_2^T$$

where a superscript T represents the triplet state, is, in all probabilities, not possible, since the energy levels of the triplet state are for acridine[13] and acridan[14] respectively 14800 cm^{-1} and 24200 cm^{-1}. In addition, the poor reactivity of this species to oxygen, does not agree with the generally accepted properties of the triplet state of organic molecules.

The second conceivable possibility is the formation of radical cation from acridan; but the absorption spectrum of acridan cation produced by a radiolysis method was found to be quite different.[15]

The final possibility is the formation of a certain molecular complex of the C-radical with acridine or acridan or alternatively dimerization of the C-radical. These possibilities are, however, safely denied from the concentration effect of certain substances on the relative intensity ratio of 560- to 520 mμ-band. For example, values of this ratio were 0.7 in the direct excitation of a benzene solution of 1×10^{-4}M acridan and 1.6 in the acridine excitation of a benzene solution containing 1×10^{-4}M acridine and 1×10^{-4}M acridan. In these experiments, the initial optical densities at 520 mμ were 0.40 and 0.15 respectively. These results preclude the possibility of the 560 mμ species being the radical dimer, because if it were the case, the dimer concentration should be proportional to the square of the monomer concentration in contradiction to the above data.

Some Aspects of the Kinetic Behaviors of the Two Semiquinones. Acridine-Acridan in Benzene. In the previous paper,[4] the second order rate constant for the decay of acridine semiquinone in the deaerated condition was estimated by analyzing the change in the optical density at 520, 560 and 350 mμ. The rate constant was interpreted to be related with Processes

$$2AH \longrightarrow (AH)_2$$
$$2AH \longrightarrow A + AH_2$$

The semiquinone treated in the previous paper, however, was the species produced by the reaction between acridine and acridan in benzene solutions and it has been proved by the present work that the species is not a single species but consists of the C-radical (AH) and N-radical (AH'). Hence the rate constants reported in that paper should be considered to be a kind of averaged one for the following processes,

$$AH + AH \longrightarrow AH_2 + A$$
$$\longrightarrow (AH)_2$$
$$AH + AH' \longrightarrow A + AH_2$$
$$AH' + AH' \longrightarrow A + AH_2$$
$$(\longrightarrow (AH')_2?) \quad etc.$$

Some of the ε-values are also concerned with both AH and AH'. It is impossible to analyze the data according to the above scheme.

As for the aerated solution, an attempt to evaluate the rate constant for $AH+O_2\rightarrow A+HO_2$ was unsuccessful in the previous paper. This was attributed to the complicated nature of the reaction. For instance, Reaction $AH+O_2\rightarrow A+HO_2$ and Reaction $AH_2+O_2^*\rightarrow AH+HO_2$, where O_2^* is the singlet oxygen, occur simultaneously. Besides the real situations are even more complicated because there are two radical species AH and AH'. It will practically be impossible to evaluate the rate constants for $AH+O_2\rightarrow A+HO_2$ and $AH'+O_2\rightarrow A+HO_2$ separately as long as the acridine-acridan system is concerned.

Acridan in Benzene. In Figs. 9 and 10 some of the typical decay curves of the transient absorption in benzene solutions of acridan are shown. The decay curves are drawn in terms of $D-D_{A\infty}$, where D is the observed optical density and $D_{A\infty}$, the one of acridine produced by one flash (at $t=\infty$), since the following relation holds where ε_R and ε_A

$$D - D_{A\infty} = l(\varepsilon_R - \varepsilon_A)[R]$$

are respectively the molar extinction coefficient of a radical and acridine.*1 It is evident that the decay obeys the second order satisfactorily. The rate constants at 560 mμ and at 356 mμ can be compared from the slopes in Fig. 10 and the values of D_i and D_A; it was found that the value at the former wavelength was always larger by about several ten %. This suggests that the C-radical, which also absorbs at 356 mμ, might be somewhat more stable than the N-radical in the deaerated condition. It is interesting that the above result eliminates the quick conversion of the type $AH \rightleftarrows AH'$ in this case. Because, if for instance, AH' converts to AH by the following reaction with a high rate,

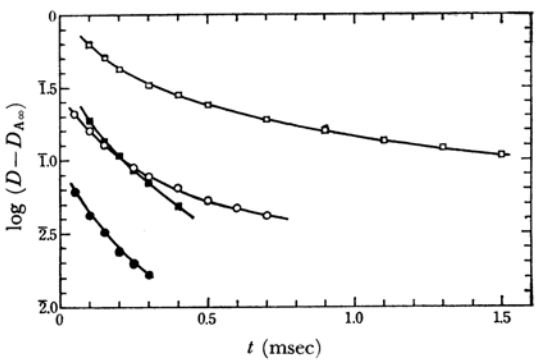


Fig. 9. Decay curves of the transient absorption in a benzene solution of acridan.
□, 356 mμ and ○, 560 mμ in deaerated solution,
■, 356 mμ and ●, 560 mμ in aerated solution.

13) D. F. Evans, *J. Chem. Soc.*, **1957**, 1351.
14) H. Kokubun and K. Kikuchi, private communication.
15) T. Shida and A. Kira, to be published.

*1 At 560 mμ, both $D_{A\infty}$ and ε_A are zero, since acridine does not absorb.

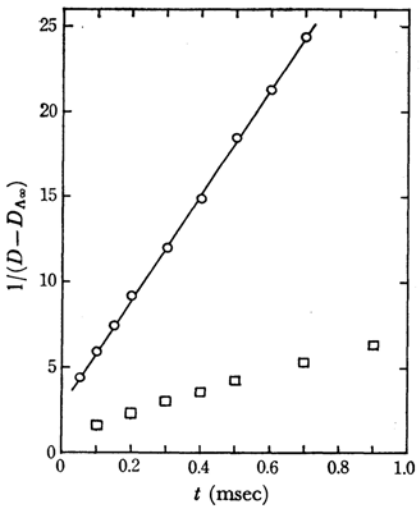
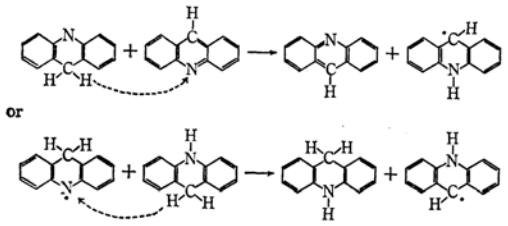


Fig. 10. The second-order plots for the decay curves given in Fig. 9. The symbols are the same as those in Fig. 9.



the apparent decay at 560 mμ should not obey a simple second order.

The true second order rate constant can be evaluated if one assumes that AH′ disappears according to the reaction

$$AH' + AH' \longrightarrow A + AH_2 \qquad (1)$$

If this is correct, ε^{560} (AH′) can be estimated from the value of $D_\infty{}^{356}$ (for acridine). The result was $1.3\times10^4 M^{-1}cm^{-1}$ and the rate constant for Reaction (1) was found to be $k_1\sim4\times10^9 M^{-1}sec^{-1}$. However there is no assurance that all AH′ disappears according to Reaction (1); on the contrary, it is more likely that a certain radical species produced by the reaction of hydrogen atoms with the solvent molecules participates in the reaction. In fact the k-value found for the methanol solution was different and appreciably larger than for the benzene solution. Therefore, it is also doubtful whether the above rate constant is concerned with only Reaction (1).

In the aerated solution, such a complication is supposed to be largely eliminated, because oxygen is likely to attack such radical species, and the disappearance of AH′ may perhaps occur mainly through Reaction $AH'+O_2\rightarrow A+HO_2$ (2) and Reaction (1). In fact, the decay curves under the aerated condition was found to be practically the same in benzene and in methanol. From the above reasoning, it may be allowed to put the rate formula as follows,

$$-\frac{dD}{dt}=\frac{2k_1}{\varepsilon_R l}D^2+k_2[O_2]D \qquad (3)$$

where k_1 and k_2 are the rate constants of Reactions (1) and (2) respectively. Dividing Eq. (3) by D, one gets

$$-\frac{d\log D}{dt}=\frac{2k_1}{\varepsilon_R l}D+k_2[O_2] \qquad (4)$$

Hence the plot of the gradient in Fig. 9 against the optical density gives $k_2[O_2]$ as an intercept on the ordinate. The value of k_2 thus obtained is $2\times10^5 M^{-1}sec^{-1}$ for both benzene and methanol solutions. According to the previous paper,[1] the corresponding value for the C-radical in ethanol is $1.2\times10^9 M^{-1}sec^{-1}$. The value of k_2 for the N-radical is not very reliable, and yet it is quite certain that the reactivity of C- and N-radical against oxygen is profoundly different.

The authors are grateful to Dr. Masashi Imamura for generous support and helpful discussions, and to Dr. Tadamasa Shida for useful suggestions.

Note Added after the Preparation of This Paper. We have found in a newly arrived Zeit. für physik. Chem. N. F., a paper of Zanker *et al.*[16] They gave some evidence for the photochemical formation of N-radical of some acridan derivatives in the rigid ethanol at low temperatures. For example, the transient band with the 575 mμ max for 9-C_2H_5 and 9-CH_3 acridan corresponds most likely to the 560 mμ band of our N-radical of acridine and also to the 570 mμ band in alcohols at low temperatures, reported by Niizuma and Koizumi.[17]

16) V. Zanker, E. Erhardt and H. H. Mantsch, *Z. physik. Chem., N. F.*, **58**, 1 (1968).

17) S. Niizuma and M. Koizumi, This Bulletin, **41**, 1090 (1968).