BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2486—2492 (1967)

Photochemical Reaction between Acridine and Acridan in the Presence and in the Absence of Oxygen. II. Studies by the Flash Technique

Akira KIRA[*1] and Masao KOIZUMI

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

(Received March 30, 1967)

Flash photolytic studies have been made to elucidate the behavior of the intermediates and to obtain the rate constants of the elementary reactions, which are related to the reactions between acridine and acridan in benzene solutions. Two transient species, triplet and semireduced acridine, have been detected. The elementary reactions the rate constants of which have been measured are:

$$\begin{array}{lll} A^T \rightarrow A & [1] & k_1 = 1\text{—}2\times10^3\,\text{sec}^{-1} \\ A^T + A^T \rightarrow & [2] & k_2 = 6.0\times10^9\,\text{M}^{-1}\text{sec}^{-1} \\ A^T + O_2 \rightarrow (A + O_2^*) & [3] & k_3 = 6\times10^9\,\text{M}^{-1}\text{sec}^{-1} \\ A^T + AH_2 \rightarrow 2AH & [4] & k_4 = 3\times10^8\,\text{M}^{-1}\text{sec}^{-1} \\ 2AH \rightarrow (AH)_2 & [5] & \multirow{2}{*}{$k_5 + k_6 = 2\text{—}3\times10^9\,\text{M}^{-1}\text{sec}^{-1}$} \\ \quad \hookrightarrow A + AH_2 & [6] & \end{array}$$

The quantity of AH produced in the presence of a small quantity of oxygen decreases with an increase in the oxygen concentration; if one assumes that Reaction [3] is mere deactivation, the decrease in acridine is too large to be expected from the values of k_3 and k_4. Hence, it has been inferred that O_2^* (or some other reactive intermediate) oxidizes AH_2. The decrease in the yield of AH with the increase in the oxygen concentration has been attributed to the deactivation of O_2^* by a third substance. The other kinetic data have been found to be consistent with this scheme.

In a previous paper1) a photochemical reaction between acridine and acridan in the degassed and in the aerated benzene solution was reported. It was found that diacridan is produced in the former case, whereas in the latter case the net reaction is the production of acridine. Further, studies of the oxygen concentration effect on the latter reaction revealed that the rate shows a sharp maximum at $\sim10^{-4}$ M of oxygen under otherwise similar conditions. Two schemes were tentatively presented in an attempt to interpret this effect. In the present paper, flash photolytic studies will be made to elucidate the behavior of the intermediates produced in the reaction, on the basis of which the mechanism of the overall reactions, including the two schemes mentioned above, will be discussed. We believe that there is no work on a similar subject reported in the literature except for the preliminary report of Livingston *et al.*2)

Experimental

The flash apparatus and the procedure were similar to those described in a previous paper,3) except for the use of a filter transmitting 315 to 390 mμ. The light absorption of acridan is negligible under the usual conditions ($[AH_2] \leq 6\times10^{-5}$ M, $[A] \simeq 3\times10^{-5}$ M). Experiments involving oxygen were made by dissolving air at the desired pressures.

Results and Discussion

Transient Species in the Benzene Solution of Acridine. Scarcely any permanent reaction occurs by the repeated illumination of the degassed solution of acridine.

Transient Absorption Spectra. The transient spectra at 93 μsec after flashing, which extend from 380 to 520 mμ, agree moderately well with those in the aqueous acridine solution reported by Jackson and Porter.4) These are ascribed to the triplet state of acridine; it is perhaps the π-π^* state because of the resemblance with the spectra of the anthracene triplet state.5) Sometimes other weak absorption bands were observed which might also be attributed to the triplet acridine. In the presence of $\sim10^{-3}$ M oxygen, no transient spectra appear. At $3.2\text{—}5.7\times10^{-6}$ M of oxygen, weak absorption spectra due to T-T transition were observed.

[*1] Present address: Institute of Physical and Chemical Research, Bunkyo-ku, Tokyo.

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

2) A. V. Buettner and R. Livingston, International Congress on Photochemistry, Rochester, 1963.

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

4) G. Jackson and G. Porter, *Proc. Roy. Soc.*, **A260**, 13 (1961).

5) G. Porter and M. W. Windsor, *ibid.*, **A245**, 238 (1958).

The extinction coefficients of the T-T absorption spectra were determined by comparing the decrease in the optical density at the peak of the absorption of acridine,[*2] 358 mμ, with the increase at 440 mμ, which lies in the non-absorbing region of acridine. The former, immediately after flashing, is only 0.038, whereas the latter reaches 0.27. Using the ε_{358} value of acridine (1.1×10^4 $\text{M}^{-1}\text{cm}^{-1}$), $\varepsilon_{440}{}^{\text{T}}$ was evaluated to be 8×10^4 $\text{M}^{-1}\text{cm}^{-1}$. This is compared with the value of the anthracene triplet at the absorption peak, 7×10^4 $\text{M}^{-1}\text{cm}^{-1}$. The absorption spectra of triplet acridine are shown in Fig. 1. The concentration of triplet acridine immediately after the flash was evaluated to be 8.9×10^{-7} for the acridine concentration of 3×10^{-5} under the usual conditions.

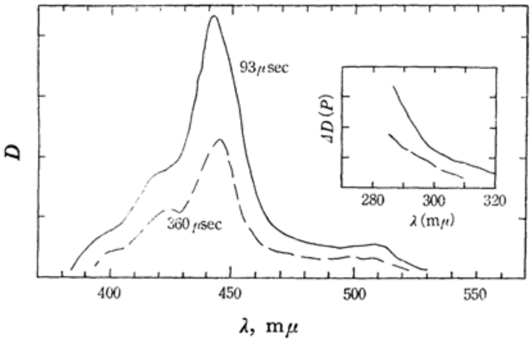

Fig. 1. T-T absorption spectra of acridine in the degassed benzene solution.
[acridine]$=3\times10^{-5}$M.

Decay of Triplet Acridine. Figures 2 and 3 give, respectively, the first-order plot and the second-order plot of the decay of triplet acridine in the degassed benzene solution.

The characteristic features of the curves are similar, independent of the wavelength, showing that the decay is a superposition of the first- and the second- order processes. They are:

$$\text{A}^{\text{T}} \xrightarrow{k_1} \text{A} \qquad [1]$$

$$\text{A}^{\text{T}} + \text{A}^{\text{T}} \xrightarrow{2k_2} (\text{A} + \text{A}) \qquad [2]^{*3}$$

The identical slope in the later stage (Fig. 2) for different concentrations of acridine rules out an appreciable contribution of the $\text{A}^{\text{T}}+\text{A}\rightarrow2\text{A}$ process.

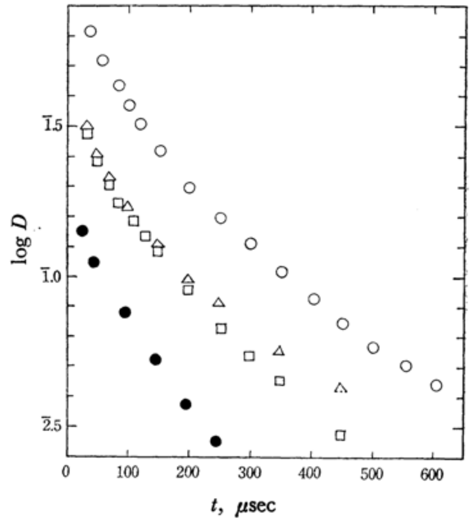

Fig. 2. First order decay plots of the triplet acridine in benzene.
○, 440 mμ □, 420 mμ
△, 460 mμ ●, 290 mμ

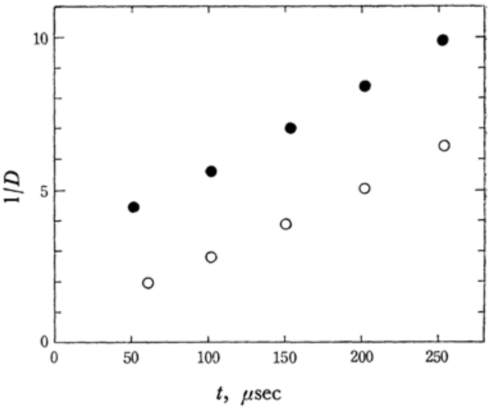

Fig. 3. Second order decay plots of the triplet acridine in benzene.
●, 290 mμ ○, 440 mμ

The second-order plot in Fig. 3 is written in terms of the rate constant, k_2 as:

$$\frac{1}{D} = \frac{2k_2}{\varepsilon_{\text{T}}{}^{\lambda} l} + \text{const} \qquad (1)$$

where $\varepsilon_{\text{T}}{}^{\lambda}$ and l are, respectively, the extinction coefficient at a wavelength, λ, and the legnth of the optical path. From (1) the k_2-value was evaluated as 7.6×10^9 $\text{M}^{-1}\text{sec}^{-1}$.

Another method, which is more reliable, was used to evaluate k_1 in addition to k_2. Since the values of the tangents, k', at any points of the curves in Fig. 2 are written as:

$$k' = k_1 + (2k_2/l\varepsilon_{\text{T}}{}^{\lambda})D \qquad (2)$$

k' should be linear against D. This really holds, as may be seen in Fig. 4. The values of k_1 and k_2

[*2] It is tentatively assumed that no T-T absorption exists in this region. This assumption seems to be correct, at least approximately, in view of the results of Porter *et al.* (Refs. 4 and 5). However, according to a private communication from Dr. E. J. Land (Paterson Lab., Manchester), the ε-value at 4325 Å (peak position) in cyclohexane is $\sim3.1\times10^4$, which is about one third of our value. Reexamination is desirable.

[*3] It is unknown whether the reaction is a) $\text{A}^{\text{T}}+\text{A}^{\text{T}}\rightarrow2\text{A}$ or b) $\text{A}^{\text{T}}+\text{A}^{\text{T}}\rightarrow\text{A}^{\text{T}}+\text{A}$. We tentatively assume a); in the case of b), $2k_2$ should be replaced by k_2 throughout the present paper.

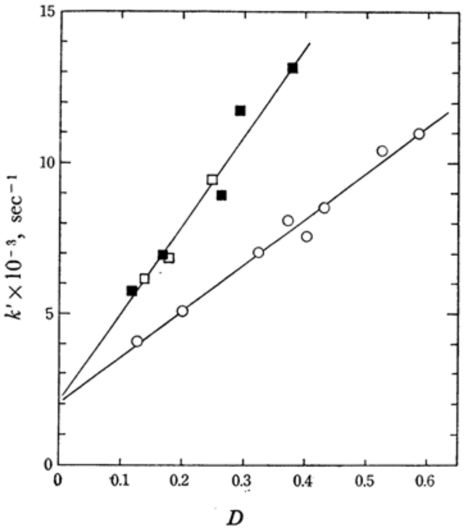

Fig. 4. Plots of k' (values of the tangents at various points of the curves in Fig. 2) against [D] (*cf.* Eq. (2)). $[A]_0 = 5 \times 10^{-5}$ M
○, 440 mμ
□, 420 mμ
■, 420 mμ (intensity is 1.5 times as above.)

thus evaluated are $k_1 = 1—2 \times 10^3$ sec^{-1} and $k_2 = 6.0 \pm 0.1 \times 10^9$ M^{-1}sec^{-1}. Livingston's value for k_2 is 3×10^9 M^{-1}sec^{-1}.[2)]

Decay of Triplet Acridine in the Presence of Oxygen. When a small quantity of oxygen is dissolved, the decay curves of triplet acridine satisfactorily obey the first order, as may be seen from Fig. 5. Figure 6 gives the plot of the apparent first-order rate constant, k_{ob}, against the oxygen concentration.

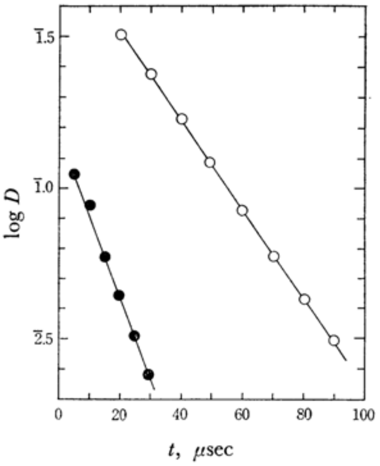

Fig. 5. Decay of the absorbance at 440 mμ in the presence of oxygen. $[A]_0 = 3 \times 10^{-5}$M
○, $[O_2] = 4.1 \times 10^{-6}$ M
●, $[O_2] = 8.8 \times 10^{-6}$ M

The rate constant for:

$$A^T + O_2 \rightarrow (A + O_2^*) \qquad [3]$$

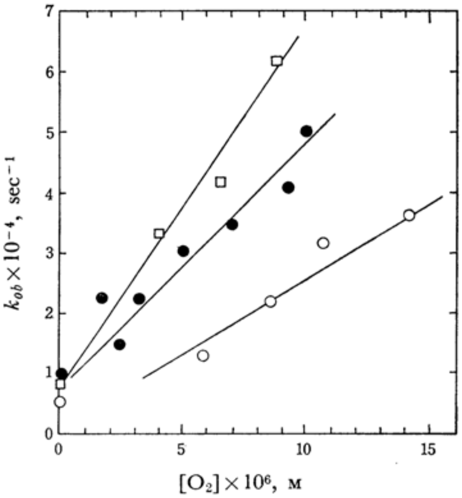

Fig. 6. Dependence of the apparent first-order rate constant on the oxygen concentration.
□, benzene ○, ethanol ● methanol

TABLE 1.

	Benzene	Ethanol	Methanol*
k_1	2×10^3	2×10^2	2×10^2
k_2	6.0×10^9	$\sim 4 \times 10^9$	$\sim 9 \times 10^9$
k_3	6×10^9	2.5×10^9	3.8×10^9

* To be published.

was evaluated from this plot as $k_3 = 6 \times 10^9$ M^{-1}sec^{-1}. Table 1 gives the values of the rate constants for the similar processes in benzene, methanol, and ethanol solutions.

The values of k_2 approach being diffusion-controlled, but they do not seem to depend only on the viscosity.[6)] The smaller k_1-values for methanol and ethanol, as compared with that for benzene, are consistent with the fact that the lowest triplet is not a reactive state in alcohols.[7)]

Intermediates in the Solution Containing Acridine and Acridan. *Transient Absorption Spectra.* Figure 7 shows the transient absorption spectra at 93 and 360 μsec after flashing. It was confirmed that no absorption is perceived when a solution containing only acridan is flashed under otherwise similar conditions. The spectra at 93 μsec after flashing may have a contribution from the triplet acridine, but those for 360 μsec may safely be ascribed only to half-reduced acridine. Hereafter, we will assume that this species is a half-reduced form and denote it by AH, although

---

6) The specific viscosities for benzene, ethanol, and methanol are, respectively, 0.60, 1.1, and 0.60 cp. *Cf.* G. Porter and M. R. Wright, *Discussions Faraday Soc.*, **27**, 18 (1959); G. Jackson, R. Livingston and A. C. Pugh, *Trans. Faraday Soc.*, **56**, 1635 (1960).

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

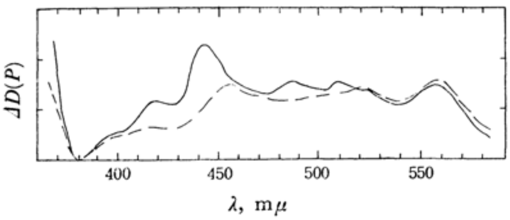

Fig. 7. Transient absorption spectra produced in the degassed benzene solution containing acridine and acridan.
$[A]_0=3\times10^{-5}$ M, $[AH_2]_0=3.6\times10^{-5}$ M
—— 93 μsec after flashing
- - - 360 μsec after flashing

this is not altogether conclusive.*4 AH has an appreciable absorption around 350 mμ where the absorption of acridine is also prominent. Plate 1, which gives the time dependence of the optical density at 350 mμ after flashing, clearly indicates that ε_{AH} is larger than ε_A at this wavelength.

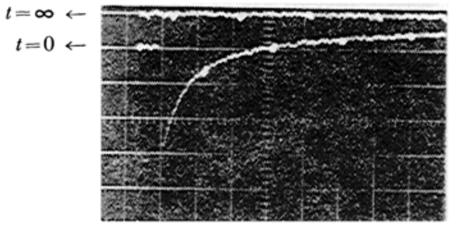

Plate 1. Time dependence of the optical density at 350 mμ after flashing.
$[A]_0=3\times10^{-5}$ M, $[AH_2]_0=6.0\times10^{-5}$ M

Decay of the Triplet State. As Fig. 8 shows, triplet acridine decays according to first-order as long as the concentration of acridan exceeds a certain value. The apparent first-order rate law may partially be due to the occurrence of two processes, $A^T+A^T\rightarrow$ and $A^T+AH\rightarrow$; the former predominates in the early stage, while the latter is dominant in the later stage. The slopes of the curves are independent of the wavelength, but are dependent upon the light intensity. This may also be due to the occurrence of the above two processes. Thus the decay is considered to consist of the following four processes;

$$A^T \xrightarrow{k_1} A \qquad [1]$$

$$A^T + A^T \xrightarrow{k_2} (A + A) \qquad [2]$$

$$A^T + AH_2 \xrightarrow{k_4} 2AH \qquad [4]$$

$$A^T + AH \xrightarrow{k_5} A + AH \qquad [5]$$

The observed rate constant, k_{ob}, is, then, written as:

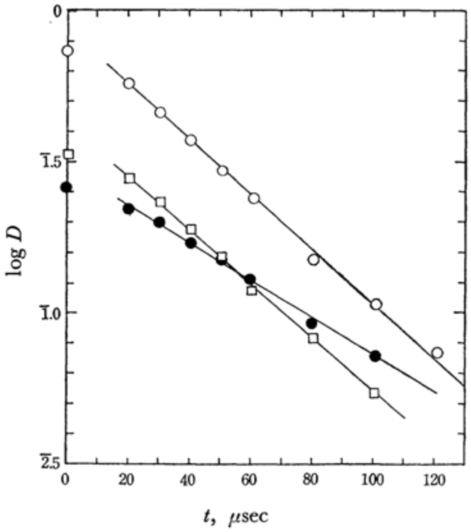

Fig. 8. Decay of triplet acridine in the presence of acridan.
$[A]_0=3\times10^{-5}$ M, $[AH_2]_0=3.0\times10^{-5}$ M
○, 440 mμ (I)
□, 420 mμ (II)
●, 440 mμ (III) (With the usage of a neutral filter, intensity is about one third of (I).)

$$k_{ob} = \{k_1 + 2k_2[A^T]\} + k_4[AH_2] + k_5[AH] \qquad (3)$$

Figure 9 shows the relation between k_{ob} and the concentration of acridan. It may be seen that k_{ob} is linear to the concentration of acridan in the high-concentration region of acridan.

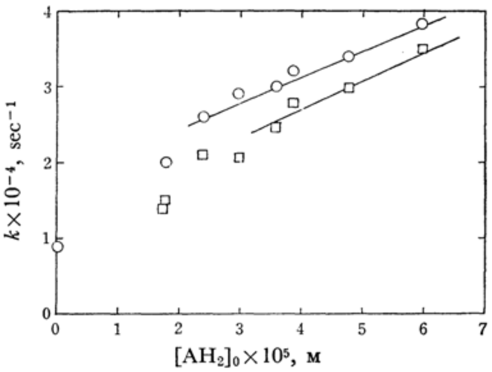

Fig. 9. Dependence of the apparent rate constant of the triplet disappearance, upon the acridan concentration. $[A]_0=3\times10^5$ M
○, with no neutral filter
□, with a neutral filter

From the slopes for the two series of experiments, the value of k_4 is evaluated as 3×10^8 M^{-1}sec^{-1}. Livingston's value is 5×10^8 M^{-1}sec^{-1}. The contribution of the last term in Eq. (3) is thought to be quite a bit smaller than that of the third term in view of the rather large value of k_4.

---

*4 There is some possibility that AH in benzene is a different species than AH in alcohol (see below).

Production of AH. The finding that a concentration of acridan as low as 10^{-5} M is enough for the formation of AH implies that a reactive state consists mostly of the lowest triplet acridine. This view was further substantiated by the results shown in Fig. 10. It may be seen that the formation of AH continues for several tens of μ seconds after flashing. If one assumes that the build-up curve refers to $A^T + AH_2 \rightarrow 2AH$, the rate constant may be evaluated to be $\sim 9 \times 10^8$ $M^{-1}sec^{-1}$. Although the value is not very reliable, it is in approximate agreement with the value already evaluated.

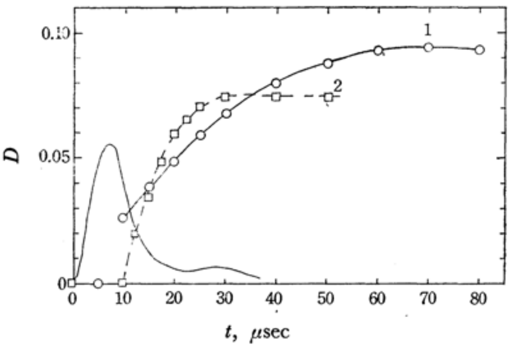

Fig. 10. Increase of the absorbance at 520 mμ.
—○—, $[A]_0 = 3 \times 10^{-5}$ M, $[AH_2] = 6 \times 10^{-5}$ M
———, flash lamp
—□—, increase of the absorbance at 290 mμ in the air saturated ethanol solution of acridine (reference)
(The time-origins for Curves 1 and 2 are somewhat arbitrary.)

Nature and Reaction of AH. Plate 1 indicates that one flash causes a decrease in the concentration of aridine; there is scarcely any doubt that this is due to this reaction:

$$2AH \rightarrow (AH)_2 \qquad [6]$$

However, the dismutation reaction:

$$2AH \rightarrow A + AH_2 \qquad [7]$$

may also occur. Figure 11 shows some examples of the second-order decay of AH in terms of D. At 350 mμ where the absorption of acridine exists, $D - D_\infty$ (D_∞ is the optical density long time after the reaction) is used instead of D.

The slopes of the lines which are $2(k_6+k_7)/\varepsilon_{AH}{}^{\lambda} \cdot l$ are 3.4 ± 0.2, 3.4 ± 0.1, and $0.9 \pm 0.1 \times 10^4$ sec^{-1} respectively at 520, 560, and 350 mμ. The proportion of dismutation and dimerization may be estimated from the quantity of triplets produced and from the decrease in acridine, if one assumes that all the triplets react with AH_2 and produce AH. With $[A] = 3 \times 10^{-5}$ M and $[AH_2] = 4 \times 10^{-5}$ M, the quantity of triplets produced is 1×10^{-6} M and the decrease in acridine is 6×10^{-7} M. Thus about 60% of AH produces diacridan. This is perhaps the lowest possible estimation, since some triplet acridine does not react with AH_2. Assuming that the percentage of the dimerization is 60—100%, the ε-values of the absorption spectra of AH may be evaluated as follows:

$$\varepsilon^{520^{*5}} = 6 \times 10^3 — 10^4 \ M^{-1}cm^{-1}$$

$$\varepsilon^{560} = 5.5 — 9 \times 10^3 \ M^{-1}cm^{-1}$$

$$\varepsilon^{350} = (1.8 \pm 0.6) — (3 \pm 1) \times 10^4 \ M^{-1}cm^{-1}$$

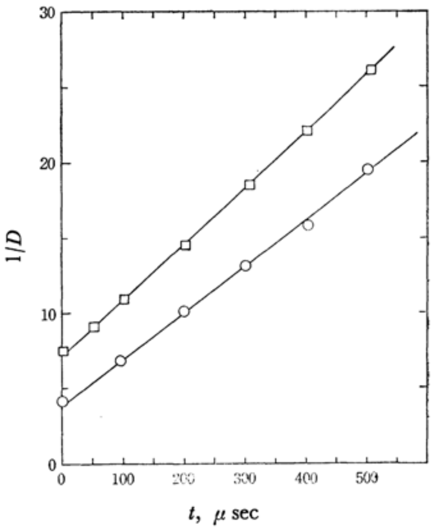

Fig. 11. Second order decay of AH at 520 mμ.
$[A]_0 = 3 \times 10^{-5}$ M
○, $[AH_2]_0 = 6 \times 10^{-5}$ M; $[O_2] = 0$
□, $[AH_2]_0 = 2.5 \times 10^{-4}$ M; $[O_2] = 9.1 \times 10^{-5}$ M

The above values of ε lead to $2(k_6+k_7) = (1.8—3) \times 10^9$ $M^{-1}sec^{-1}$, the values for the three wavelengths being much the same. Livingston's value is 2×10^9 $M^{-1}sec^{-1}$.

The Effect of Oxygen Concentration on the Yield of AH. This was investigated to get information on the interaction between the triplet acridine and oxygen. The relation between the yield of AH and the oxygen concentration is shown in Fig. 12, where the former quantity is approximated by the maximum value in the decay curve of AH. If one assumes that oxygen simply deactivates triplet acridine, then the quantity of AH produced, $[AH]_p$, should be capable of being calculated approximately by the following relation:

$$[AH]_p = \frac{2k_4[AH_2]}{k_{ob} + k_3[O_2]} [A^T]_i \qquad (4)$$

where $[A^T]_i$ is the concentration of triplet acridine immediately after the flash and where k_{ob} and k_4 are the rate constants, all in the absence of oxygen but under otherwise similar conditions. A curve from Eq. (4) is also given in Fig. 12.

---

*5 According to our unpublished results, $\varepsilon_{AH}{}^{520}$ in ethanol and methanol is evaluated to be 4.6×10^3 $M^{-1} \cdot cm^{-1}$ on the assumption that only dimerization occurs.

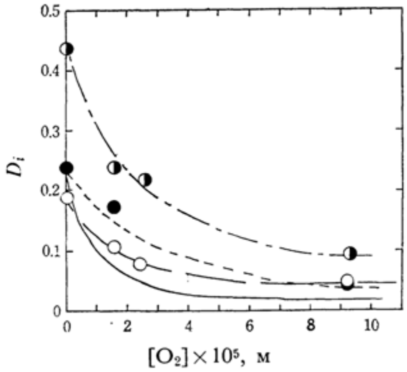

Fig. 12. The effect of oxygen concentration on the yield of AH.
$[A]_0=3\times 10^{-5}$ M, $[AH_2]=6\times 10^{-5}$ M
—◑—, 350 mμ
--●--, 520 mμ
—○—, 560 mμ
———, 520 mμ: calculated from Eq. (4)

Although the above calculation is only approximate in nature, yet it is evident that the quantities of AH really produced are too great to admit the assumption made at the start. Hence, there is scarcely any doubt that the interaction of the triplet acridine with oxygen produces a certain species which in turn leads to the formation of AH. We tentatively assume, as was done in the previous paper,[1] that it is the following process or the like:

$$A^T + O_2 \rightarrow A + O_2^* \qquad [8]$$

$$O_2^* + AH_2 \rightarrow AH + HO_2 \qquad [9]$$

If one assumes that the formation of singlet oxygen is the only reaction between oxygen and triplet acridine, then its rate constant is $6\times 10^9\ \mathrm{M^{-1}sec^{-1}}$, as has already been evaluated. Thus $[O_2^*]_p$ may be approximated by:

$$[O_2^*]_p = \frac{k_8[O_2]}{k_8[O_2]+k_{obs}}[A^T]_i \qquad (5)$$

Putting $[AH_2]\approx 6\times 10^{-5}$ M, $k_{ob}\approx 3.8\times 10^4\ \mathrm{sec^{-1}}$, $k_8=6\times 10^9\ \mathrm{M^{-1}sec^{-1}}$ and $[O_2]=10^{-4}$—10^{-5} M, one may approximately equate $[O_2^*]_p$ with $[A^T]_i$. If only Reaction [9] occurs efficiently, the yield of AH should be constant independent of the oxygen concentration. This contradicts the plot shown in Fig. 12; one must, therefore, take into account the existence of the deactivating process of O_2^* by some unknown substance, M:

$$O_2^* + M \rightarrow O_2 + M \qquad [10]$$

If one assumes that Reactions [9] and [10] compete, then the ratio of k_{10} to k_9 may be estimated on the basis of the following equation, where M is assumed to be oxygen.:

$$[AH]_p = \frac{k_9[AH_2]}{k_9[AH_2]+k_{10}[O_2]}[A^T]_i \qquad (6)$$

This may be rewritten in the following form by replacing $[AH]_p$ with $D_i{}^\lambda/\varepsilon_{AH}{}^\lambda\cdot l$:

$$\frac{1}{D_i{}^\lambda} = \left\{\frac{1}{\varepsilon_{AH}{}^\lambda\cdot l}+\frac{1}{\varepsilon_{AH}{}^\lambda\cdot l}\frac{k_{10}[O_2]}{k_9[AH_2]}\right\}\frac{1}{[A^T]_i} \qquad (7)$$

Thus, $1/D_i{}^\lambda$ should be a linear function of $[O_2]/[AH_2]$ if the concentration of acridine and the intensity of flash are kept constant. The following two relations:

$$\Delta\left(\frac{1}{D_i{}^\lambda}\right) = \frac{1}{\varepsilon_{AH}{}^\lambda\cdot l\cdot[A^T]_i}\frac{1}{[AH_2]}\frac{k_{10}}{k_9}\times\Delta[O_2] \qquad (8)$$

and

$$\Delta\left(\frac{1}{D_i{}^\lambda}\right) = \frac{[O_2]}{\varepsilon_{AH}{}^\lambda\cdot l\cdot[A^T]_i}\frac{k_{10}}{k_9}\Delta\left(\frac{1}{AH_2}\right) \qquad (9)$$

where Δ denotes the change in the respective quantities, enable us to evaluate k_{10}/k_9 from the experimental data. The value from (8) is 0.8—1.8, and that from (9) is 1.1—1.7.

The Effect of Oxygen Concentration on the Decay of AH. All attempts to determine the rate constant for $AH+O_2\rightarrow A+HO_2$ were unsuccessful. The difficulty is perhaps due to the existence of various competing reactions in the concentration region of oxygen where the absorption spectrum of AH is observable. These reactions may be: i) $O_2^*+AH_2\rightarrow HO_2+AH$, ii) $AH+O_2\rightarrow A+HO_2$ and iii) $2AH\rightarrow(AH)_2$ (and in addition, perhaps, $AH_2+HO_2\rightarrow AH+H_2O_2$),*[6] as judged from the following estimation. Assuming the rate constants for the first two reactions as $\sim 10^9\ \mathrm{M^{-1}sec^{-1}}$, and setting $[O_2^*]\lesssim 10^{-6}$ M, $[AH_2]\sim 6\times 10^{-5}$ M, $[AH]\lesssim 10^{-6}$ M and $[O_2]\sim 3\times 10^{-5}$ M, one gets:

the rate of the production of AH by

$$O_2^*+AH_2\rightarrow AH+HO_2 \quad \lesssim 6\times 10^{-2}\ \mathrm{Msec^{-1}}$$

the rate of the disappearance of AH by

$$O_2+AH\rightarrow HO_2 \quad \lesssim 3\times 10^{-2}\ \mathrm{Msec^{-1}}$$

the rate of the removal of AH by

$$2AH\rightarrow(AH)_2 \quad \lesssim 2\text{—}3\times 10^{-3}\ \mathrm{Msec^{-1}}$$

Thus the competing two reactions, i) and ii), are judged to be of the same order. In fact, it was found that the apparent second-order decay constant of AH varies less than two fold upon the addition of $\sim 10^{-4}$ M of oxygen. It was also found that, under similar conditions, one flash causes practically no change in the concentration of acridine. This may be due to the simultaneous occurrence of the $AH+O_2\rightarrow A+HO_2$ and $2AH\rightarrow(AH)_2$ reactions.

---

*[6] According to the previous paper (Ref. 1) it does not seem that the occurrence of this reaction is appreciable.

Summary and Concluding Remarks

The elementary processes the rate constants of which have been determined in the present investigation are as follows:

$$A^{T} \longrightarrow A$$

$$k_1 = 1\text{—}2 \times 10^3 \text{sec}^{-1} \qquad [1]$$

$$A^{T} + A^{T} \longrightarrow (2A)$$

$$k_2 = 6.0 \times 10^9 \text{M}^{-1}\text{sec}^{-1} \qquad [2]$$

$$A^{T} + O_2 \longrightarrow (A + O_2^*)$$

$$k_3 = 6 \times 10^9 \text{M}^{-1}\text{sec}^{-1} \qquad [3]$$

$$A^{T} + AH_2 \rightarrow 2AH$$

$$k_4 = 3 \times 10^8 \text{M}^{-1}\text{sec}^{-1} \qquad [4]$$

$$2AH \longrightarrow (AH)_2 \qquad [5]$$

$$ \longrightarrow A + AH_2 \qquad [6]$$

$$k_5 + k_6 = 2\text{—}3 \times 10^9 \text{M}^{-1}\text{sec}^{-1}$$

From the finding that the yield of AH in the presence of 10^{-4}—10^{-5} M of oxygen is too large to be acceptable if oxygen merely deactivates triplet acridine, it may be concluded that the reaction between triplet acridine and oxygen produces a reactive species which induces the oxidation of acridan. This species was tentatively assumed to be singlet oxygen, as is shown in Reaction [3]. However, an increase in the oxygen concentration causes some decrease in the yield of AH. Although this may be interpreted as being due to the partial deactivation of the triplet acridine by oxygen, it is more plausible, in view of the results from the steady-light experiments,1) that there are two competing reactions:

$$O_2^* + AH_2 \rightarrow AH + HO_2 \qquad [9]$$

$$O_2^* + M \rightarrow O_2 + M \qquad [10]$$

where M is some substance contained in the air. The general features of the reaction between acridine and acridan in the benzene solution may now be summarized as follows. In the absence of oxygen, the chief processes are (4), (5), and (6), and the final product is $(AH)_2$. This agrees with the conclusion from the steady-light experiment. In the presence of 10^{-4}—10^{-5} M oxygen, Reaction (3) prevails over Reaction (4) if $[AH_2]$ is 10^{-5}—10^{-4} M. The succeeding reactions are then (10) and (9), the ratio of the rate constants being 1—1.8.

In the steady-light experiment,1) two schemes were tentatively presented; one is the scheme in which oxygen merely deactivates triplet acridine, while the other is similar to the above scheme, consisting of [3], [9], and [10]. After the present investigation the former scheme can now be rejected for the following additional reason. In the latter scheme the value of k_{10}/k_9 was evaluated as 3.3, which agrees rather well with the present results in view of the approximate nature of the present method of evaluation. On the other hand, this value, 3.3, was interpreted, in the former scheme, as the ratio of k_3/k_4, which in the present experiment is 20. In conclusion, one can safely say that the interaction between oxygen and triplet acridine produces O_2^* or some other reactive species, which in turn leads to the formation of AH, and, further, that O_2^* is deactivated by some gaseous substance present in the air.

For the sake of comparison, the rate constants for the corresponding elementary reactions in ethanol and methanol will be added:

Solvent	k_1 sec^{-1}	k_2 $\text{M}^{-1}\text{sec}^{-1}$	k_3 $\text{M}^{-1}\text{sec}^{-1}$	$(k_5+k_6)^*$ $\text{M}^{-1}\text{sec}^{-1}$
Ethanol	2×10^2	$\sim4\times10^9$	2.5×10^9	2.4×10^8
Methanol	2×10^2	$\sim9\times10^9$	3.8×10^9	4.0×10^8

* It was assumed that only Reaction [5] occurs.

The large difference in the rate constant for $2AH \rightarrow (AH)_2$ or $(A+AH_2)$ in benzene and in alcohols is difficult to understand. It may partially be related to the evaluation of ε-values. However, the possibility that AH in benzene is a different species than the one in alcohol is not altogether unconceivable. Further studies are desired in connection with this problem as well as in connection with a reactive species of oxygen and its deactivation process.