Photoreduction of Acridine in Deaerated and Aerated Ethanol Solutions

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Photochemical reaction of acridine was studied recently by several workers[1-6]. According to Zanker, the solution of acridine in ethanol when irradiated by ultraviolet light, yields diacridane in case when the concentration is above 10^{-3} M; this was confirmed by means of infrared spectrum and polarography. Zanker's result was reconfirmed by Kellman[4]. Zanker further found that when the concentration of acridine is below 10^{-3} M, the photoproduct consists mainly of acridane.

Zanker's remark that he studied the reaction under the presence of dissolved oxygen attracted much of our attention, because we formerly found that the photochemical reduction of eosine dissolved in ethanol is completely suppressed by the presence of a very small quantity of oxygen[7]. Nothing, however, is described in Zanker's paper about the effect of oxygen on the reaction. We made some preliminary investigations on this problem.

Although our experiments were done only under the limited condition, the results obtained are so specific that they seem to be very important for elucidating the mechanism of the reaction. At least the results must be taken into account in order to give a correct description of the photochemical behavior of acridine in ethanol. Therefore, it is worth while to report, as we believe, the results obtained and some deductions based on them.

Experimental

Sample.—Tokyo Kasei's acridine was recrystallized twice from the water-ethanol mixture (3 : 2 in volume ratio). Wako Junyaku's ethanol (G. R.) was used without further purification.

Procedure of Degassing. — In order to exclude the air from the solution, the following procedure was employed. The sample solution was put into B (Fig. 1) and was evacuated by a diffusion pump through a trap A dipped in liquid air. Most of the dissolved air was eliminated during the distilla-

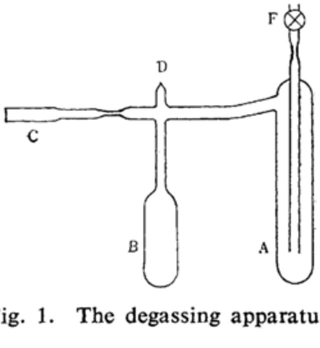

Fig. 1. The degassing apparatus.

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[1] V. Zanker and P. Schmid, *Z. physik. Chem.*, **17**, 11 (1958).
[2] V. Zanker and P. Schmid, *Ber.* **92**, 2210 (1959).
[3] A. Kellman, *J. de Chemie phys.*, **56**, 574 (1959).
[4] A. Kellman, ibid., **57**, 1 (1960).
[5] N. Ivanoff, ibid., **55**, 786 (1958).
[6] V. Zanker and F. Mader, *Ber.*, **93**, 850 (1960).
[7] M. Imamura and Koizumi, This Bulletin, **29**, 899 (1956).

tion of the solvent from B to A. When all the solvent went to A, tap F was closed and the solvent was distilled back from A to B, dipping B in liquid air. The above procedure was repeated.

In Fig. 1, C is the reaction cell (1×1×4 cm.) and D is the inlet of sample solution.

The above procedure is superior to repeated distillation in a closed system since it requires far less time for the satisfactory degassing. The loss of the solvent is negligible.

Apparatus.—The apparatus is shown in Fig. 2.

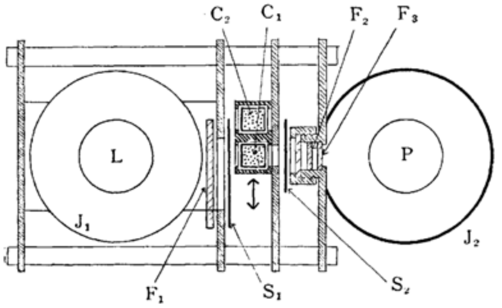

Fig. 2. Diagram of the apparatus of the reaction.

L :	Mazda super-high-press. Hg lamp SHL-100 UV
J_1 :	Glass cylinder
J_2 :	Brass cylinder which contains a photoelectric cell and an amplifier set up in a unit
P :	Photoelectric cell of Mazda #7211
F_1, F_3 :	Filter of Hoya U-2, transmitting chiefly the light near 360 mμ
F_2 :	Frosted glass
C_1 :	Reaction cell
C_2 :	Cell containing pure solvent as a reference
S_1, S_2 :	Shutter

The illuminating light is comparatively pure monochromatic light of 365 mμ. The electric source is supplied from VOLCO-HT high-grade automatic voltage stabilizer.

The reaction is followed by the change of optical density at 365 mμ, the reading of the meter being carried out during the course of the reaction.

Quantum Yield.—Quantum yield was determined by potassium ferri-oxalate actinometer.

Results

Comparison of Aerated and Deaerated Solutions.—The experiments were done with the solution of acridine 1×10^{-4} M in ethanol dissolving various amounts of oxygen from air-saturation to complete degassing. In order to check the effect of a small quantity of water contained in alcohol, the reaction was tried with the solution containing various amounts of water and it was established that a small amount of water does not affect essentially the rate of the reaction. Hence the alcohol employed was not particularly dehydrated by any chemical method.

In case the rate of the disappearance of acridine is proportional to the light absorption, the relation

$$-\frac{dc}{dt}=\frac{kI_0}{d}(1-e^{-E})\times1000 \qquad \text{(a)}$$

must hold, where $E=\alpha cd$, c is the concentration of acridine, α the absorption coefficient at 365 mμ. Integrating, one obtains

$$\ln(e^{-E}-1)=\ln(e^{E_0}-1)-1000\,k\alpha I_0 t \qquad \text{(b)}$$

Hence $\ln(e^E-1)$, when plotted against t, must give a straight line with the inclination of $1000k\alpha I_0$, which gives the relative rate of the reaction. The experimental results satisfy the above relation very satisfactorily as shown in Fig. 3, for both the air-saturated and the deaerated solution. It is seen from these results that the rate in the aerated solution is about one-third of that in the deaerated solution.

The absorption spectra of the solution were examined immediately after the reaction, and it was found that there is no difference in the two cases, aerated and deaerated, and they are quite the same as the one reported by Zanker. Thus it can safely be concluded that the reductive photochemical reaction can occur even in the presence of oxygen. This is somewhat surprising and is in sharp contrast to the case of eosine in ethanol solution.

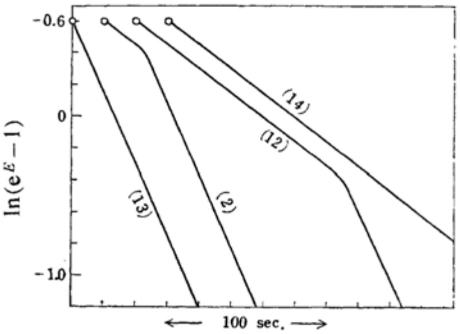

Fig. 3. Plots of $\ln(e^E-1)$ vs. time for typical decay. The numbers in the figure point out the experimental number in Table I.

The Effect of Oxygen Concentration.—When the concentration of the dissolved oxygen is below a certain value, $\ln(e^E-1)\sim t$ relation shows quite a sharp breaking point at a certain point and the inclination of the line preceeding the breaking point is almost equal to that of the air-saturated solution, while the one after the breaking point is approximately equal to that for the evacuated solution. It was found that the length of the initial part with smaller inclination becomes shortened with the decrease of oxygen concentration and yet the inclination itself remains practically constant irrespective of the oxygen concentration. Typical results are shown in Fig. 3 and the complete data are given in Table I.

TABLE I. THE EFFECT OF OXYGEN CONCENTRATION UPON THE RATE OF THE PHOTOCHEMICAL REACTION OF ACRIDINE
[Acridine] $=1\times10^{-4}$ M

Exp. No.	$[O_2]$ $\times10^4$ M	Temp. °C	$k\alpha I_0\times10^5$ sec^{-1}	
13	0	13.3		2.28
19	0	25.0		2.16
20	0	25.0		2.38
21	3.63	18.8	0.78	
22	7.75	14.5	0.86	
14	air-saturation	13.0	0.73	
18	〃	25.0	0.70	
Average			0.77	2.27
			Before breaking point	After breaking point
1	0.336	16.3	1.02	1.99
9	0.340	19.3	0.83	2.06
2	0.465	19.3	0.83	2.16
8	0.460	21.4	0.78	1.82
10	0.600	17.0	0.96	1.91
3	0.656	20.7	0.86	2.12
15	0.720	13.2	0.78	1.76
11	0.740	18.3	0.73	2.06
4	0.919	18.6	0.83	1.76
12	0.920	22.9	0.78	2.01
17	0.985	13.7	0.78	1.76
Average			0.85	1.95

Although the reproducibility is not so good, it is apparent that the rate before the breaking point is, on the average, about one third of that for the deaerated solution and that the rate after breaking point is approximately equal to that of the deaerated solution.

Further, the results in Table I seem to indicate that the rate of reaction is not so much dependent upon temperature, whether oxygen is present or not. To confirm this, the reaction rate of the evacuated solution was investigated in the wider range of temperature. The results shown in Table II establish quite definitely the temperature independence of the rate in the degassed solution.

TABLE II. THE EFFECT OF TEMPERATURE ON THE RATE FOR THE DEGASSED SOLUTION OF ACRIDINE
[Acridine] $=0.7\times10^{-4}$ M

Temp., °C	$k\alpha I_0\times10^5$ sec^{-1}	Average
25	2.28	
	1.90	2.09
35	2.16	
	2.13	2.14
45	2.27	
	1.93	2.10

From the above results, it can be said that the rate is about one third of the deaerated solution as long as a very small amount of oxygen is present in the solution and that the oxygen is exhausted near the crossing point of the two linear parts, whence the rate gets the value of the degassed solution.

To confirm this further, the following experiment was performed using a special reaction cell. The volume of the upper part, i. e. the gaseous part of the cell was increased about three times to that of the liquid part. The area of the liquid surface was so small that the dissolution of oxygen during the course of the reaction, would be neglected in view of a rather rapid rate of the reaction. Now, if the solution of acridine in ethanol containing a proper amount of oxygen is irradiated in such a cell, one would expect the breaking point to appear after a certain time interval when the oxygen in the liquid phase is consumed. Furthermore one would expect that if one shakes the cell at this stage in order to bring on a new equilibrium of dissolution between gaseous and liquid phase, and then continue to irradiate the solution again, the rate would fall down to the original value and another breaking point would once more appear after a certain time. These expectations were in fact realized as shown in Fig. 4.

Thus one can conclude with much confidence that in the presence of oxygen the reduction of acridine and the consumption of oxygen takes place simultaneously and that the latter process is intimately connected with the recovery of acridine from a certain transient intermediate.

The decrease of acridine concentration during the consumption of dissolved oxygen can easily

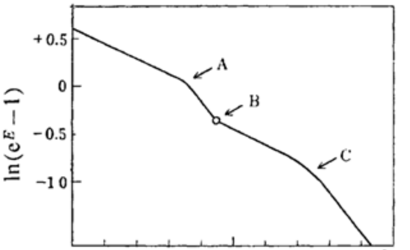

Fig. 4. A decay curve in the special cell. At the time A, dissolved oxygen would exhausted. At B, the cell was shaken and oxygen was introduced into the liquid phase, then at C it would be exhausted again.
$[O_2]=0.912\times10^{-4}$ M (35.0 mmHg), 18°C, $C_0=1\times10^{-4}$ M

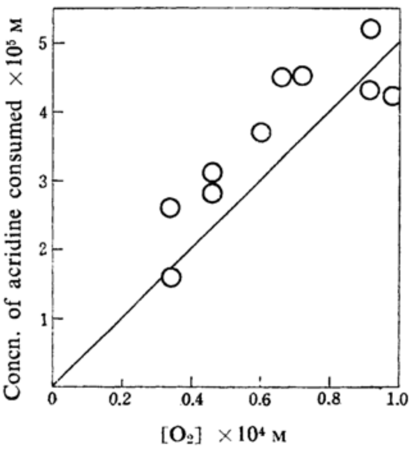

Fig. 5. Plots of the decrease of acridine concentration before the breaking point of the decay curve, vs. the initial concentration of dissolved oxygen.

be evaluated and this is plotted in Fig. 5 against the concentration of oxygen dissolved in the solution. Since the initial concentration of acridine obtained from the optical density is always a little less than 1×10^{-4} M, the concentration of the prepared solution, the latter was used, though somewhat arbitarily, instead of the former.

There is an appreciable scattering of the points, but it is evident that the ratio (consumed oxygen): (reduced acridine) lies near 2:1.

Quantum Yield.—The light intensity entering into the solution was measured to be 0.156×10^{-7} M sec^{-1} cm^{-2}. Since α is 1.14×10^4 at 365 mμ, from the value of $k\alpha I_0$, the quantum yield for the deaerated solution was found to be about 0.13.

Discussion

The plausible scheme for the deaerated solution may be pictured as follows

$$\left.\begin{aligned}&A+h\nu \rightarrow A^*\\&A^*+RH_2 \rightarrow AH\cdot+RH\cdot\end{aligned}\right\} \quad (0)$$

$$AH\cdot+RH\cdot \rightarrow AH_2+R \quad (1)$$

$$AH\cdot+RH\cdot \rightarrow A+RH_2 \quad (2)$$

$$AH\cdot+AH\cdot \rightarrow AH_2+A \quad (3)$$

$$RH\cdot+RH\cdot \rightarrow HR\text{-}RH \text{ or } R+RH_2 \quad (4)$$

where A, RH_2, R are acridine, ethanol, acetaldehyde respectively and A* denotes the excited singlet or triplet state as the case may be.

The above scheme is essentially the same as that of Kellman⁴⁾ except that it involves the recovery of A and RH_2 (process 2).

At first, let us consider the molecular species X which oxygen attacks. Since the rate of the reaction is independent of the concentration of oxygen unless it is too low, the rate with which oxygen attacks X should be much faster than the rate with which X disappears in the deaerated solution. Supposing that the diffusion of oxygen is the rate-determining step of the reaction between O_2 and X, as is plausible, the experimental result that the rate is independent of oxygen concentration above 10^{-5} M leads to the conclusion that the life of X in the deaerated condition is $\sim10^{-5}$ sec. or more. Hence X can not be the singlet excited state. We have found that the fluorescence of acridine is not quenched appreciably by oxygen and this discovery also supports the above conclusion.

If X is triplet, then the formation of molecular associate $X\cdots O_2$ analogous to the intermediate of the Schenck's scheme⁸⁾ might be conceivable, but it is difficult to interpret the reductive reaction on this basis.

The possibility that T-state is quenched partially by oxygen depending on its concentration can of course be rejected on the ground that the rate is independent on the concentration of oxygen. Thus it is most plausible to assume that oxygen attacks the semi-reduced form of A produced by the process 0. In case of reductive photobleaching of eosine in ethanol, this process really takes place very rapidly*. In that case, however, the reaction was completely suppressed by a very small quantity of oxygen and the following scheme could account for the experimental results⁷⁾.

$$DH\cdot+O_2 \rightarrow D+HO_2\cdot$$

$$RH\cdot+O_2 \rightarrow RH\cdots O_2$$

$$HO_2\cdot+HO_2\cdot \rightarrow H_2O_2+O_2$$

$$RH\cdots O_2+RH\cdots O_2 \rightarrow 2\ \text{Acid}+H_2O_2$$

$$RH\cdots O_2+HO_2\cdot \rightarrow H_2O_2+\text{aldehyde}+O_2$$

But in the present case where acridine is reduced even in high oxygen concentration, one can not interpret the formation of acridan in any way by a single process in which oxygen attacks $AH\cdot$. This leads to the assumption that some other intermediate such as $AH\cdots O_2$ be produced and some of them go back to A and the remainder turns into AH_2 through a bimolecular reaction. Perhaps $AH\cdots O_2$ may have its hydrogen attached to nitrogen, and the oxygen loosely combined with 9-carbon.

Now the scheme should further account for the following three experimental results.

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8) G. O. Schenck, *Naturwissenschaften*, **40**, 212 (1953).

* From the results of the flash experiment, it is not proper to say that oxygen attacks only semiquinone. See Ref. 9.

9) S. Kato et al., This Bulletin, **33**, 262 (1960).

[a] The rate of the reaction is proportional to the rate of light absorption for both the aerated and the deaerated condition.

[b] The rate in the aerated solution is about one third of that in the deaerated solution.

[c] The ratio of consumed oxygen to the reduced acridine ($=\gamma$) is about 2.

Now in the deareated condition one can easily derive the following equation by means of steady state method

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=\frac{\mathrm{d}[\mathrm{AH_2}]}{\mathrm{d}t}=\frac{\phi I_{\mathrm{abs}}(k_1+\sqrt{k_3k_4})}{k_1+k_2+2\sqrt{k_3k_4}}=\phi\beta f_{\mathrm{abs}} \qquad \text{(a)}$$

$$\beta=\frac{k_1+\sqrt{k_3k_4}}{k_1+k_2+2\sqrt{k_3k_4}}$$

where ϕ is the quantum yield of the formation of AH· and RH·, and k_1, k_2, k_3 and k_4 are respectively the rate constants of the processes 1, 2, 3 and 4.

Assuming the formation of $\mathrm{AH\cdots O_2}$ and $\mathrm{RH\cdots O_2}$, the following processes may be conceivable for the aerated solution.

$$\mathrm{AH\cdot + O_2 \rightarrow AH\cdots O_2} \qquad (5)$$

$$\mathrm{RH\cdot + O_2 \rightarrow RH\cdots O_2} \qquad (5')$$

$$\mathrm{2AH\cdots O_2 \rightarrow AH_2 + A + 2O_2} \qquad (6)$$

$$\mathrm{AH\cdots O_2 \rightarrow A + HO_2\cdot} \qquad (7a)$$

$$\mathrm{2RH\cdots O_2 \rightarrow 2\ Acid + H_2O_2} \qquad (8)$$

$$\mathrm{AH\cdots O_2 + RH\cdots O_2 \rightarrow AH_2 + R + 2O_2} \qquad (9)$$

$$\mathrm{AH\cdots O_2 + RH\cdots O_2 \rightarrow A + R + H_2O_2 + O_2} \qquad (10)$$

$$\mathrm{AH\cdots O_2 + RH\cdots O_2 \rightarrow A + RH_2 + 2O_2} \qquad (11)$$

In the presence of oxygen the reaction 5 is so fast that the reactions 1, 2 and 3 can be neglected.

To simplify the discussion, only the following two extreme cases will be considered.

Case I. — When $\mathrm{AH\cdots O_2}$ disappears mainly through the reactions 6 and 7a, the reaction 8 must take place accompanied by them. If so, the formation of acridane would not be simply proportional to the rate of light absorption, because the process 7a is a first order reaction concerning $[\mathrm{AH\cdots O_2}]$ while 6 is a second order one. This contradicts the experimental result [a]. Hence, the reaction 7a should be replaced

$$\mathrm{2AH\cdots O_2 \rightarrow 2A + H_2O_2 + O_2} \qquad (7)$$

by a bimolecular reaction and the steady state method leads to the following expression.

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=\frac{\mathrm{d}[\mathrm{AH_2}]}{\mathrm{d}t}=\frac{k_6\phi I_{\mathrm{abs}}}{2(k_6+k_7)} \qquad \text{(b)}$$

$$-\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t}=\frac{\phi I_{\mathrm{abs}}(2k_6+3k_7)}{2(k_6+k_7)} \qquad \text{(c)}$$

Thus the result [b] requires

$$\frac{k_6}{2(k_6+k_7)}=\beta/3 \qquad \text{(d)}$$

while γ can be expressed as,

$$\gamma=\frac{\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t}{\mathrm{d}[\mathrm{A}]/\mathrm{d}t}=\frac{(2k_6+3k_7)}{k_6}=2+3k_7/k_6 \qquad \text{(e)}$$

From d and e the following relation holds,

$$\gamma=4.5/\beta-1$$

Since β is smaller than unit, γ should be greater than 3.5. Thus γ does not satisfy the result [c] and we can safely reject this case.

Case II.—When 9, 10 and 11 are the main reactions, the steady state method leads to the following expression

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t=\mathrm{d}[\mathrm{AH_2}]/\mathrm{d}t=\phi I_{\mathrm{abs}}k_9/(k_9+k_{10}+k_{11})$$

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t=\phi I_{\mathrm{abs}}k_{10}/(k_9+k_{10}+k_{11})$$

The result [b] requires that

$$k_9/(k_9+k_{10}+k_{11})=\beta/3 \qquad \text{(f)}$$

and γ is given as follows from the result [c]

$$\gamma=k_{10}/k_9=2 \qquad \text{(g)}$$

From f and g

$$k_{11}/k_9=3/\beta-3 \qquad \text{(h)}$$

Then, this ratio is shown for some values of β,

β	1	0.8	0.6	0.5	0.4	0.3
k_{11}/k_9	0	0.75	2	3	4.5	7

The independence of ϕ and β on temperature in the deaerated solution strongly suggests that the process 1 or 3 only prevails and the process 2 does not occur appreciably. If one excludes 2, then the value of β is limited from 1 to 1/2. The higher limit corresponds to the case in which reaction 1 prevails and the lower to the case in which reaction 3 is a chief one. In view of the fact that dimerization does not occur in diluted solution, reaction 1 seems to be more desirable than 3. Then the only possible case will be the Case II in which $\beta=1$, $k_{11}=0$. In connection with this scheme, it is to be added that there is another possibility in which a certain type of radical complex $\mathrm{AH\cdots RH}$ with an appreciable life is formed and it is attacked by oxygen decomposing in three different ways;

1) $\mathrm{AH\cdots RH + O_2 \rightarrow A + RH_2 + O_2}$
2) $\mathrm{AH\cdots RH + O_2 \rightarrow A + R + H_2O_2}$
3) $\mathrm{AH\cdots RH + O_2 \rightarrow AH_2 + R + O_2}$

This case is quite analogous to the above case at least kinetically.

Of course further investigations are needed to substantiate the above deduction and to decide the scheme unequivocally. Perhaps the flash technique will be most helpfull.

Summary

1. The deaerated solution of acridine 1×10^{-4} M in ethanol, when irradiated by 365 mμ produces acridane with a quantum yield of about 0.13. This reductive reaction can proceed even in the air-saturated solution with the rate about one third of that of the deaerated solution. For both cases the rate is simply proportional to the absorption of light.

2. When the concentration of dissolved oxygen is more than about twice that of acridine concentration, the rate of the reaction is approximately equal to that of the air-saturated solution independent of the oxygen concentration, and at the same time oxygen is consumed at the rate about twice as great as that of the reduction of acridine. Hence, when the existent oxygen is exhausted, the rate gains the value of the deaerated solution.

3. All the above results are almost entirely independent of temperature.

4. A possible scheme was proposed in which a certain type of intermediate is formed between semireduced acridine and oxygen and, from this intermediate acridine is partially recovered accompanied with the consumption of oxygen and, in competition with this, acridane is poduced, both by a bimolecular process.

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