The Photoreduction of Acridine in Deaerated and Aerated Alcohol Solutions.[1] *II.*

By Shigeya NIIZUMA and Masao KOIZUMI

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In the preceding paper,[1] Kato, Minagawa and one of the present authors (M. K.) studied the photoreduction of acridine in ethanol and observed the following facts:

i) A solution of aridine, 1×10^{-4} M, in ethanol free from oxygen, when illuminated by 365 mμ, produces acridan, the quantum yield being about 0.13, independent of the temperature.

ii) In an air-saturated solution, the photoreduction goes on at the rate of about one-third of the evacuated solution.

iii) For both cases, the rate is simply proportional to the absorption of light.

iv) When the concentration of oxygen is varied, the reaction proceeds at the same rate as that of the air-saturated solution so long as the oxygen concentration is much larger than that of acridine. However, when the oxygen concentration becomes of the order of the acridine concentration, then the earlier part of the reaction proceeds at a rate approximately equal to that of the air-saturated solution, although at a certain point the rate increases rather suddenly to that of the oxygen-free solution.

The forth finding above was interpreted by assuming that, in the presence of oxygen, the acridan-producing reaction (with no consumption of oxygen) and the oxygen-consuming reaction (with no production of acridan) proceed simultaneously and that, when the existent oxygen is exhausted, only the former reaction survives. On this basis, the rate of oxygen consumption was calculated to be about twice as large as that of the reduction of acridine. A tentative scheme was proposed which can interpret the above results.

Now, in the present paper we will extend the study to the reaction in methanol and isopropanol and discuss all the results so far obtained, including those for ethanol, on the basis of the same scheme.

Experimental

Sample.—Acridine was purified by the method described in the previous paper. The concentration of acridine is always 1×10^{-4} M, while ε at 365 mμ is 1.12×10^4, 1.14×10^4, 1.19×10^4 for methanol, ethanol and isopropanol solutions respectively.

Methanol.—Iwai Kasei's methanol (G. R.) was used without further purification.

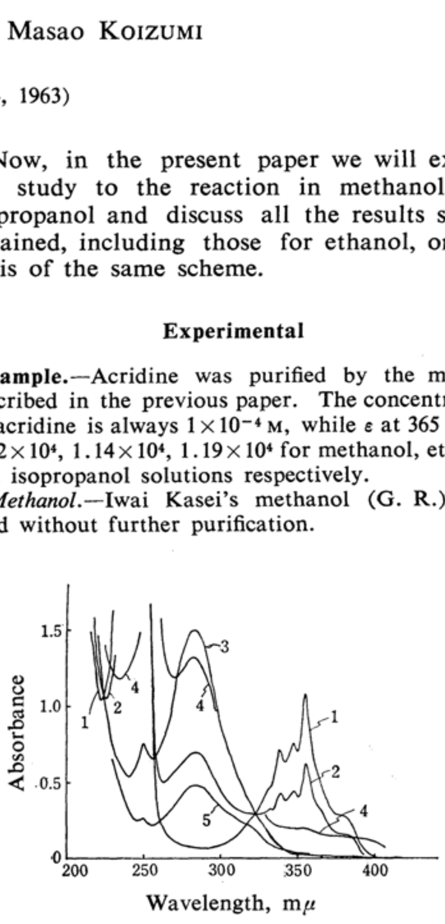

Fig. 1. The absorption spectra of acridine and the photoproducts in methanol solution. $[A]=1\times10^{-4}$ M

1 Before illumination (initial)
2 Short time illumination
3 30 min. illumination (photoproduct)
4 Long time illumination
(1–4: air-saturated solution)
5 Long time illumination; degassed solution

A large decrease in the optical density of curve 5 is due to the precipitation of the photoproduct (see text).

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[1] S. Kato, S. Minagawa and M. Koizumi, This Bulletin, 34, 1026 (1961). This paper shoud be numbered I.

Isopropanol. — Wako Junyaku's isopropanol was twice distilled. (B. p. 81.9∼82.1°C) An impurity causing a slight absorption near 240 mμ was eliminated by the purification.

Procedure.—The procedures for degassing and the apparatus are almost the same as in the previous paper. The exciting light was 365 mμ from a high-pressure mercury lamp, and the reaction was followed by the change in the optical density of the sample at 365 mμ in a reaction cell (1×1×4 cm.). The intensity of the exciting light was measured by a potassium ferri-oxalate actinometer and found to be ca. 0.21×10^{-7} and 0.65×10^{-8} M $\text{sec}^{-1}\text{cm}^{-2}$ for methanol and isopropanol respectively.

Results

The Absorption Spectra of Products. — The absorption spectra of the products in each solvent are shown in Figs. 1, 2 and 3. As can be seen in Figs. 1, 2 and 3 the main product in the case of methanol and ethanol is acridan, irrespective of the presence or absence of oxygen. The differences in the absorbance in the 230∼300 mμ region for the aerated and deaerated solutions might be partially due to different by-products or to the small contribution of accompanied side reactions. The latter is plausible in view of the fact that prolonged illumination, after the depression of the optical density down to practically zero in the 350 mμ region, causes a gradual rise in the same region (cf. curve 4 in Fig. 1). When the ethanol solution of the product is kept for a long time, a white precipitate[2] is produced which may be attributed to acridan. In the case of isopropanol, the products in the degassed solution and in the air-saturated solution are different. In the former case, the product is judged to be acridan, while in the latter case the spectra with the peaks at 250, 345, 355 mμ resemble those of diacridan.[3] It is to be added that there is a clear isosbestic point in the change of acridine into acridan.

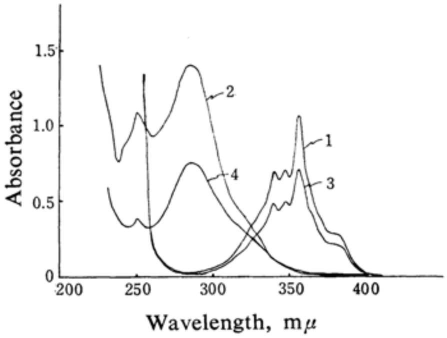

Fig. 2. The absorption spectra of acridine and the photoproducts in ethanol solution.
$[A]_{\text{air-sat}}=1\times10^{-4}$ M
$[A]_{\text{degassed}}=0.7\times10^{-4}$ M

1	Before illumination	air-saturated solution
2	After illumination	
3	Before illumination	degassed solution
4	After illumination	

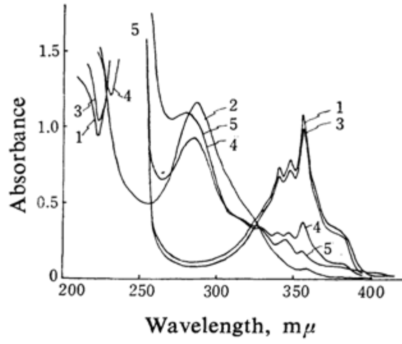

Fig. 3. The absorption spectra of acridine and the photoproducts in isopropanol solution.
$[A]\approx1\times10^{-4}$ M

1	Before illumination	degassed solution
2	After illumination	
3	Before illumination (initial)	air-saturated solution
4	Short time illumination	
5	After illumination (photoproduct)	

A Comparison of Aerated and Deaerated Solutions.—When the reaction is proportional to the absorption of light, the relation

$$-\frac{\mathrm{d}c}{\mathrm{d}t}=\frac{kI_0}{d}(1-\mathrm{e}^{-\alpha cd})\times10^3 \qquad (1)$$

must hold, where c, t, I_0, d and α are respectively the concentration of acridine (M), the time of reaction, the quantum yield, the light intensity (M/sec. cm²), the thickness of the cell (1 cm.), and the absorption coefficient at 365 mμ. The integration of Eq. 1 leads to

$$\ln(\mathrm{e}^{\alpha cd}-1)=\ln(\mathrm{e}^{\alpha c_0 d}-1)-1000k\alpha I_0 t \qquad (2)$$

Equation 2 can represent very well the results in methanol and isopropanol and for both the air-saturated and oxygen-free solutions. From the linear plot of $\ln(\mathrm{e}^{\alpha cd}-1)\sim t$ one gets $1000k\alpha I_0$, and so the value of k (quantum yield) can be calcurated using the values of α and I_0. A few examples of the plots are shown in Fig. 4. The values of k are summarized in Table I.

From Table I we can say that k-values are generally independent of the temperature, and that the ratio of k_d (for an oxygen-free solution) and k_a (for an air-saturated solution) is ca. 4, ca. 3 and ca. 2.8 for methanol, ethanol and isopropanol. It is worth mentioning that, for the degassed solutions, k is practically the same for methanol and for ethanol, while it is much smaller for isopropanol.

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[2] V. Zanker and H. Schnith, *Chem., Ber.*, **92**, 2210 (1959).

[3] V. Zanker and P. Schmid, *Z. physik. Chem.*, **17**, 11 (1958).

TABLE I. *k*-VALUES OBTAINED

Condition	Solvent: Ethanol	Solvent: Methanol	Solvent: Methanol	Solvent: Isopropanol
Air-saturated solution	0.040_3(25°C)	0.028_4(25°C)	0.038_1(15°C)	0.031_8(25°C)
	0.045_6(25°C)	0.034_4(25°C)	0.028_3(15°C)	0.030_8(25°C)
	0.044_9(25°C)	0.032_7(25°C)	0.031_2(15°C)	0.034_5(25°C)
Average	0.043±0.002	0.032±0.003	0.033±0.003	0.032±0.002
Oxygen free solution	0.12_8(13.3°C)*	0.12_6(25°C)	0.12_3(15°C)	0.087(25°C)
	0.12_1(25°C)*	0.13_6(25°C)	0.13_6(15°C)	0.086(25°C)
	0.13_4(25°C)*	0.12_5(25°C)	0.12_5(15°C)	0.093(25°C)
				0.093(25°C)
Average	0.129±0.003*	0.129±0.004	0.128±0.006	0.090±0.003

* S. Minagawa's data

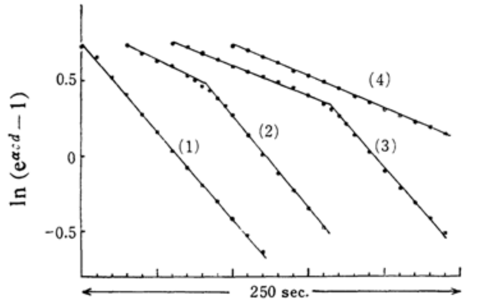

Fig. 4. Plots of $\ln(e^{\alpha cd}-1)$ vs. time for acridine in isopropanol solution.
$[A]=1\times10^{-4}$ M
(1) Degassed soln. (2) $[O_2]=0.6\times10^{-4}$ M
(3) $[O_2]=1.5\times10^{-4}$ M (4) Air-saturated soln.

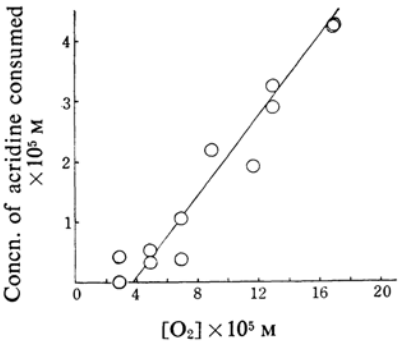

Fig. 5. Plots of the decrease of acridine concentration before the breaking point of the decay curve vs. the initial concentration of dissolved oxygen in methanol solution.

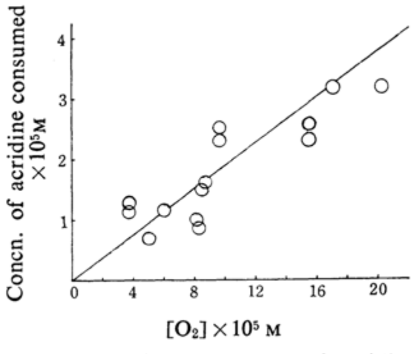

Fig. 6. Plots of the decrease of acridine concentration before the breaking point of the decay curve vs. the initial concentration of dissolved oxygen in isopropanol solution.

The Effect of the Oxygen Concentration.—When the oxygen concentration is of the same order as that of acridine, the rate of the reaction at first is practically the same as that of the air-saturated solution, but after a certain time there appears a sharp break, after which the rate becomes approximately the same as that of the degassed solution. The length before the break is approximately proportional to the concentration of oxygen. This phenomenon is common to both methanol and isopropanol and is quite similar to that already reported in ethanol.[1] There is no doubt that an interpretation similar to that given for ethanol in the previous paper can be applied to methanol and isopropanol. Thus, in such circumstances, the oxygen-consuming reaction (accompanied by the recovery of acridine from some transient intermediate) and the acridan-producing reaction go parallel and that, when the oxygen is exhausted only the latter reaction proceeds by the mechanism prevailing in oxygen-free solution.

The plot of the consumed acridine up to the breaking point against the initial oxygen concentration is given in Figs. 5 and 6. Although the average deviation from the drawn line is rather large especially in the latter case, the ratio between the quantities of acridine and of oxygen consumed before the break is, respectively, about 3 and 5.3 for methanol and isopropanol. The fact that the plot in Fig. 5

cuts the abscissa instead of passing through the origin, might be due to the participation of some other reaction like the following in such a low concentration of oxygen;

$$A^* + RH_2 \rightarrow AH\cdot + RH\cdot$$

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

$$AH\cdot + RH\cdots O_2 \rightarrow A + R + H_2O_2$$

A similar tendency, although much less conspicuous, is observed in the case of ethanol described in the preceding paper (see Fig. 5 in Ref. 1). Table II gives a summary of γ and k_d/k_a values. In the case of ethanol, the reaction rate under the air-saturation could be restored when a small quantity of air was dissolved after the break in Fig. 4. Similar experiments were undertaken for isopropanol, but the results proved to be as shown in Fig. 7.

TABLE II. γ AND k_d/k_a

Solvent	γ	k_d/k_a
Methanol	ca. 3	4
Ethanol	ca. 2	3
Isopropanol	ca. 5.3	2.8

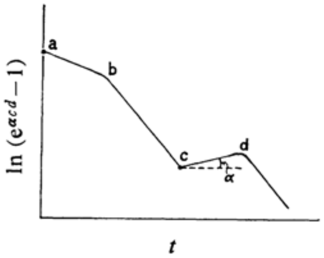

Fig. 7. A typical decay curve for supplementary experiments. At time dissolved oxygen would be exhausted. At c, the cell was shaken and oxygen was introduced into the liquid phase. At d, the oxygen would be exhausted again. The longer the interval bc is, the larger the value of α becomes.

Thus, when 10^{-4} M oxygen is added again after the exhaustion of oxygen (period ab) at c, the optical density does not fall, but rises. It was found that the longer the bc interval (the reaction in the absence of oxygen), the larger the value of α and, so, the larger the increase in the optical density. When bc is extremely short, then the slopes of ab and cd become practically the same. A similar phenomenon was also observed in the case of ethanol, and methanol although to a lesser extent. This is the reason why the phenomenon was overlooked in the preceding paper. At d, oxygen is consumed and the reaction goes on at the rate of the degassed solution.

The rise in the optical density during the cd period seems to be due to the oxidation of acridan to acridine by some unknown process, the extent of this reaction exceeding the usual reduction of acridine to acridan. This view is supported by the following facts. First, as is shown in Fig. 7, the spectra of acridine increase during the cd period while the spectra of the product (280~285 mμ) decrease, and second, this change goes on with an isosbestic point at 325 mμ. The dependence of α on the length of bc strongly suggests that some reaction products during the bc (degassed condition) period play an essential role in the reaction during cd period. To confirm this, the effect of the addition of acridan to various systems was examined. The addition of acridan (0.5×10^{-4} M) to an ethanol solution of acridine (0.5×10^{-4} M) containing 0.7×10^{-4} M of oxygen (P_{air}=27.5 mmHg at 18°C) did not have any effect. No effect was observed either when the same amount of acridan was added to an isopropanol solution of acridine (0.5×10^{-4} M) or when 1×10^{-4} M of acridan was added to an ethanol solution of acridine (1×10^{-5} M), both saturated with air.

Thus there is no simple sensitized oxidation of acridan by the excited acridine molecule. This is rather natural in view of the finding that ln ($e^{\alpha cd}-1$)~t gives a very satisfactory linear plot until more than a half of the acridine is consumed.

Next, the effect of any other conceivable by-product during bc was examined. Of these, acetaldehyde would be most probable in the case of ethanol. The addition of ~1 M acetaldehyde to an air-saturated ethanol solution of acridine (1×10^{-4} M) does not affect the rate, the rate being practically the same as that of an air-saturated solution of acridine. However, the ultraviolet spectra of the product as shown in Fig. 8 resembles that of diacridan. Using the ethanol solution of acridine (0.1×10^{-4} M) and acridan (0.9×10^{-4} M) to which 1.2 M acetal-

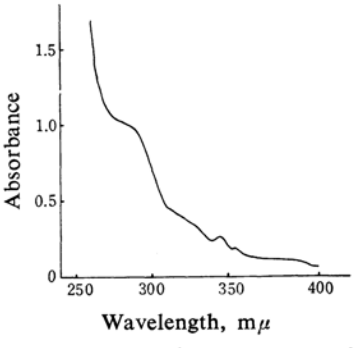

Fig. 8. The Absorption spectrum of photoproduct in air-saturated ethanol solution containing, 0.9×10^{-4} M acridan, 0.1×10^{-4} acridine and ~1 M acetaldehyde.

dehyde had been added, three cases were examined, i.e.; (1) an air-saturated solution; (2) 0.8×10^{-4} M oxygen ($P_{\mathrm{air}}=29.0$ mmHg at 17.5°C), and (3) a completely degassed solution. The results was that for 1 the reduction proceeds at a much slower rate, k being approximately 3×10^{-3}, while for 3 the reaction goes on at just the same rate as when no acridan and acetaldehyde are added, (i.e., $k=0.13$); in case of 2, however, the rise in the optical density occurs first and, at a point where oxygen may be expected to be exhausted, a break appears and the optical density then decreases, but at a slower rate than that for the degassed solution of acridine. When oxygen is introduced again, the back reaction becomes apparent. A similar phenomenon, though to a lesser extent, was observed when acetone (1.0 M) and oxygen (1×10^{-4} M) ($P_{\mathrm{air}}=36.2$ mmHg at 23.0°C) were added to an isopropanol solution containing acridan (0.9×10^{-4} M) and acridine (0.1×10^{-4} M).

Thus one can conclude that a certain quantity of aldehyde or ketone is necessary in order for acridan to be oxidized by the sensitization of acridine. However, there is rather a great possibility that some other oxidative by-products take part in the cd reaction shown in Fig. 7.

Discussion

The scheme presented in the preceding paper for the reaction under the degassed condition is as follows:

$$\left.\begin{array}{l} \mathrm{A} + h\nu \rightarrow \mathrm{A}^* \\ \mathrm{A}^* + \mathrm{RH_2} \rightarrow \mathrm{AH} + \mathrm{RH} \end{array}\right\} \qquad (0)$$

$$\mathrm{AH\cdot} + \mathrm{RH\cdot} \rightarrow \mathrm{AH_2} + \mathrm{R} \qquad (1)$$

$$\mathrm{AH\cdot} + \mathrm{RH\cdot} \rightarrow \mathrm{A} + \mathrm{RH_2} \qquad (2)$$

$$\mathrm{AH\cdot} + \mathrm{AH\cdot} \rightarrow \mathrm{AH_2} + \mathrm{A} \qquad (3)$$

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

where A, $\mathrm{RH_2}$ and R are acridine, ethanol and acetaldehyde respectively. A* is an excited singlet or triplet, but the latter is more plausible since the transient spectra for the degassed solution of acridine observed in our laboratory, perfectly coincides with that reported by Porter[4] and has interpreted to be due to the acridine triplet.

From the above scheme, one can easily derive the following rate formula by means of the steady state method:

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

$$=\phi\beta I_{\mathrm{abs}}$$

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

where ϕ is the quantum yield of the formation of AH· and RH·, and k_1, k_2, k_3 and k_4 are the respective rate constants of processes 1, 2, 3 and 4. From the results in Table I, one can discuss the mechanism to some extent. First, the values of k for the degassed solution of methanol, ethanol and isopropanol are not consistent with the well-known fact that the order of ease of α-hydrogen abstraction in an alcohol molecule is isopropanol > ethanol > methanol. This relation was observed to hold[5] in, for instance, the case of the photoreduction of eosine in a degassed alcohol solution, for which the overall quantum yield is very small, of the order of 10^{-4}. Wells[6] also observed the same order for the photoreduction of sodium-anthraquinone-2-sulfonate. Perhaps the tendency of excited acridine to deprive α-hydrogen atom from alcohol is so large that the general ralation does not hold in this case. The small value of isopropanol may perhaps be due to its small number of α-hydrogen atoms (1, while it is 3 or 2 for methanol and ethanol) or to a certain steric factor. The independence of k of the temperature favors the view that the process following (0) goes along a single path, (1) or (3), and not along (1) and (3) both. As to whether (1) or (3) prevails, one cannot give a definite answer at this stage. The separate determination of ϕ and of the quantum yield of the triplet formation is desirable. It is worth mentioning that the triplet is observed in the flash experiment. If the triplet state is very easily reduced by alcohol, as has been mentioned above, then its life-time might be expected to be very small. Perhaps the relative orientation of the alcohol molecule and acridine must be suitable in order for the hydrogen atom transfer to occur, and this will be a chief reason why the life-time of the triplet is not very short.

Next let us consider the reaction in which oxygen takes part. In the preceding paper we tentatively proposed for the case of ethanol that oxygen very efficiently attacks the half-hydrogenated state of acridine on the grounds that the reaction goes on even in the presence of oxygen and that the rate is almost constant as long as the concentration of oxygen is larger than a certain small value ($\sim10^{-4}$ M). Since similar results were obtained for methanol and isopropanol, it can be said that the pro-

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

[5] M. Imamura and M. Koizumi, This Bulletin, **29**, 899 (1956).

[6] C. F. Wells, *Trans. Faraday Soc.*, **57**, 1703 (1961).

posed scheme was largely substantiated. Therefore, we will discuss it on the basis of the analogous mechanism. However, it is to be noted here that the overall reaction will be somewhat different in methanol and isopropanol. In the former case, the final product will be acid, as in the case of ethanol, but for isopropanol, acetone instead of acid is the most plausible product. For methanol the scheme is exactly the same as for ethanol, which runs as follows:

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

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

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

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

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

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

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

$$AH\cdots O_2 + R\cdots HO_2 \rightarrow A + RH_2 + 2O_2 \qquad (11)$$

In the case of isopropanol, the above scheme will be partly altered in the following way; i.e.,. instead of 6,

$$2AH\cdots O_2 \rightarrow AH\text{–}AH + 2O_2 \qquad (6')$$

and instead of 8,

$$2RH\cdots O_2 \rightarrow 2R + H_2O_2 + O_2 \qquad (8')$$

6′ of course corresponds to the formation of diacridan.

In the above scheme we consider that, in the presence of oxygen, reaction 5 proceeds so fast that 1, 2, and 3 do not occur at all. Of course, the above scheme is too simple and the real situation might involve the participation of $HO_2\cdot$; moreover, some chain reaction might also occur. For example, if the following chain reaction occurs:

$$RH\cdots O_2 \rightarrow R + HO_2\cdot$$

$$HO_2\cdot + RH_2 \rightarrow RH\cdot + H_2O_2$$

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

then the oxygen consumption would be much increased. It is to be noted that such a possibility is disregarded in the following discussion because this possibility is very small in view of the consistency of the analysis.

Putting k_d/k_a (the ratio of the rate in the deaerated solution to that in the aerated solution) as n, let us now consider which process, 6, 7 and 8 (case I) or 9, 10 and 11 (case II), is more plausible.

As in the previous paper only two extreme cases will be considered.

Case I.—In this case 6 (or 6′ for isopropanol) and 7 occur, and, naturally, 8 (or 8′ for isopropanol) accompanies them. The steady state method gives

$$-\frac{d[A]}{dt}=\begin{cases}\dfrac{k_6\phi I_{abs}}{2(k_6+k_7)} & \text{for methanol}\\[2ex] \dfrac{k_6\phi I_{abs}}{k_6+k_7} & \text{for isopropanol}\end{cases}$$

$$-\frac{d[O_2]}{dt}=\begin{cases}\dfrac{\phi I_{abs}(2k_6+3k_7)}{2(k_6+k_7)} & \text{for methanol}\\[2ex] \dfrac{\phi I_{abs}(k_6+2k_7)}{2(k_6+k_7)} & \text{for isopropanol}\end{cases}$$

Hence,

$$\begin{cases}\dfrac{k_6}{2(k_6+k_7)}=\dfrac{\beta}{n} & \text{for methanol}\\[2ex] \dfrac{k_6}{k_6+k_7}=\dfrac{\beta}{n} & \text{for isopropanol}\end{cases}$$

and

$$\gamma=\frac{d[O_2]/dt}{d[A]/dt}=\begin{cases}2+3\dfrac{k_7}{k_6} & \text{for methanol}\\[2ex] \dfrac{1}{2}+\dfrac{k_7}{k_6} & \text{for isopropanol}\end{cases}$$

From these two equations,

$$\gamma=\begin{cases}\dfrac{3n}{2\beta}-1 & \text{for methanol}\\[2ex] \dfrac{n}{\beta}-\dfrac{1}{2} & \text{for isopropanol}\end{cases}$$

In the case of methanol, $n=4$ and $\gamma=3$; therefore,

$$\gamma=\frac{6}{\beta}-1$$

For γ to be 3, β must be 1.5. This is nonsense, however, because β should be $\leqq 1$. For ethanol, $n=3$, $\gamma=2$ and, from these values, $\beta=1.5$. In the case of isopropanol, $n=2.8$ and $\gamma=5.3$; therefore, $\beta=0.48$.

Case II. — In this case both methanol and isopropanol can be treated in the same way provided that acridan is a main product in the latter case. When 9, 10 and 11 are the main reactions, the steady state method leads to the following equation:

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

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

Hence,

$$k_9/(k_9+k_{10}+k_{11})=\frac{\beta}{n}$$

and

$$\gamma=\frac{k_{10}}{k_9}$$

From these two equations,

$$\frac{k_{11}}{k_9}=\frac{n}{\beta}-(\gamma+1)$$

In the case of methanol, $n=4$ and $\gamma=3$, and for some values of β, k_{11}/k_9 are calculated as follows:

β	1	0.8	0.6	0.5
k_{11}/k_9	0	1	2.6	4

For ethanol, $n=3$, $\gamma=2$, and, as has been reported already:[1)]

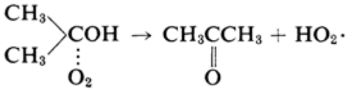
β	1	0.8	0.6	0.5	0.4
k_{11}/k_9	0	0.75	2	3	4.5

In the case of isopropanol, $n=2.8$ and $\gamma=5.3$; therefore,

β	1	0.5	0.45
k_{11}/k_9	-3.5	-0.7	0

From the above analysis it can be said that, with ethanol and methanol, only case II fits the experimental results if alcohol is oxidized to acid. If, on the other hand, the oxidation stops at the stage of aldehyde, case I is also conceivable; the calculation requires that $\beta=1$ for both methanol and ethanol.

As for the case of isopropanol, one can not decide from the above analysis whether case I or case II is suitable. However, in this case the product contains a considerable quantity of diacridan, and so case I seems to be more plausible. This would perhaps be because $RH\cdots O_2$ has a great tendency to decompose in the following way:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!\underset{\overset{\vdots}{O_2}}{COH} \rightarrow CH_3\underset{\overset{\|}{O}}{C}CH_3 + HO_2\cdot$$

At any rate, in the case of isopropanol the above analysis requires that $\beta\doteqdot 0.5$, whether case I or case II holds. This implies that, in the case of the degassed solution of isopropanol, (3) and (4) prevail instead of (1). On the other hand, in the cases of ethanol and methanol, case I requires that $\beta=1$ (on the condition that the product is aldehyde and not acid); $\beta=1$ holds also in case II if it is assumed that reaction 11 does not occur. Thus, in either case reaction 1 is more favorable.

The above discussion is of itself rather speculative, and we have aimed only at the plausible scheme. For example, the deduction would not hold if the chain reaction participates. However, as to the participation of the chain process, this can be safely denied on the basis of the rather small consumption of oxygen and also from the consistency of the above analysis. Moreover, very recently, it has definitely been established from the pulse radiolysis of ethanol that recombination and disproportionation are the only processes possible for ethanol radicals and that these occur as diffusion rate-determining processes.[7)]

This makes our deduction very reasonable. It seems certain that, in the cases of ethanol and methanol, $AH\cdot + RH\cdot \rightarrow AH_2 + R$ occurs, while in the case of isopropanol, $AH\cdot + AH\cdot \rightarrow AH_2 + A$ and $RH\cdot + RH\cdot \rightarrow$ proceed. If such is the case, the existence of different values of k for methanol and ethanol on the one hand and for isopropanol on the other, is at least partly due to the different processes following (0). Wilkinson[8)] proposed, for the photoreduction of isopropanol by quinone, the following process:

$$(CH_3)_2\dot{C}OH + Q \rightarrow QH\cdot + (CH_3)_2CO$$

However, such a process is not applicable in our case probably because of a rather small tendency of reduction for acidine. At any rate, the complete analysis of the products is desirable in order to obtain a definite answer. Lastly, it should be added that the experimental evidence for the formation of $AH\cdots O_2$ is lacking, but that the present deduction is not altered if $AH\cdots RH$ is formed and reacts with oxygen in any of three different ways, as has been mentioned in the preceding paper.[1)]

As to the sensitized oxidation of acridan into acridine in the presence of aldehyde or acetone and a small quantity of oxygen, the discussion of this will be postponed until much more data have been accumulated.

Summary

The photoreduction of acridine in methanol and isopropanol has been studied and the following results obtained:

1) The quantum yield for the photoreduction in the dagassed solution is, for methanol, 0.13 and, for isopropanol, 0.09. The photoreduction can take place even in an air-saturated solution with quantum yields of 0.032 for methanol) and of 0.032 (for isopropanol).

2) In case of a degassed solution, the product is acridan for both isopropanol and methanol, while in an aerated solution the product is acridan in the case of methanol and mainly diacridan in the case of isopropanol.

3) When the concentration of oxygen is of the order of that of acridine, the reaction proceeds at first at a rate equal to that of an air-saturated solution and then, from the point at which the oxygen is exhausted, the rate

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[7)] I. A. Taube and L. M. Dorfman, *J. Am. Chem. Soc.*, **84**, 4053 (1962).

[8)] F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962).

increases up to the value of a degassed solution.

4) The ratio of the quantities of oxygen and of acridine consumed before the break is, for methanol, about 3 and, for isopropanol, 5.3.

5) By the sensitizing action of acridine, acridan is oxidized to acridine in the presence of aldehyde (or acetone) and a small quantity of oxygen.

6) On the basis of the scheme proposed in the preceding paper and from the reaction product, some tentative discussion of the scheme has been undertaken. It seems plausible that, in the case of ethanol and methanol, $AH\cdot + RH\cdot \rightarrow AH_2 + R$ occurs, while in the case of isopropanol, $AH\cdot + AH\cdot \rightarrow AH_2 + A$ and $RH\cdot + RH\cdot \rightarrow$ take place (for a degassed solution).

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