# *The Photosensitized Oxidation of Leuco-uranine. III. The Kinetics of an Acridine-sensitized Photoöxidation in an Aerated Solution*

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In previous papers[1-3] the author and his co-workers have studied some properties of leuco-uranine and the kinetics of the acridine-sensitized photoöxidation of leuco-uranine in a deaerated solution. Leuco-uranine prepared by reducing uranine with sodium amalgam was photoöxidized to the colored form by adding some suitable sensitizer to the solution and then by irradiating it with the light appropriate to the sensitizer. In the case of the deaerated solution, leuco-uranine attacked by the triplet state of a sensitizer, i. e., acridine, was transformed into the oxidized form via semiquinone and perhaps with the evolution of molecular hydrogen. The evolved hydrogen, however, could not be successfully detected because of its small quantity.

Now in an aerated solution the rate of the photosensitized oxidation of leuco-uranine is more than ten times slower and the recovery of uranine is less quantitative than in a deaerated solution under suitable conditions. The purpose of the present report is to clarify kinetically the mechanism of this sensitized oxidation in the aerated solution by investigating quantitatively the concentration effect of the dissolved oxygen. The conclusions may be summarized as follows: oxygen rapidly reacts with the triplet state of acridine and produces between them perhaps a molecular complex, which may be similar to that proposed by Schenck.[4] It decomposes mostly into oxygen and acridine, only a little portion participating in the oxidation of leuco-uranine. Therfore, when the concentration of dissolved oxygen is low, oxygen prohibits the formation of uranine, while in the high concentration, the oxidation of leuco-uranine takes place via a different mechanism from that of the deaerated solution which has been elucidated before.[3]

## Experimental

**Material.** — *Leuco-uranine.* — The method of preparation has already been reported in detail.[1] Uranine was reduced with sodium amalgam in an aqueous alkaline solution and recrystallized from ethanol a few times. The crystal was desiccated in a high vacuum.

*Acridine.*—Tokyo Kasei's acridine was recrystallized twice from a water-ethanol mixture.

*Sodium Hydroxide.* — The saturated solution was prepared from a G. R. reagent of the Wako Junyaku Co., and the supernatant solution was diluted to the desired concentration.

*Disodium Hydrogen Phosphate and Potassium Dihydrogen Phosphate.*—G. R. Reagents of the Wako Junyaku Co. were recrystallized three times from an aqueous solution.

*Oxygen.* — Air was used, and it was purified by removing moisture and carbon dioxide by the use of soda lime, calcium chloride and a trap cooled with dry ice.

**Procedure.**—Usually the stock solution of leuco-uranine $9.5\times10^{-5}$ M was diluted ten times. In most experiments, the concentration of the acridine used as a sensitizer was about $1.5\times10^{-4}$ M. For the control of the pH value of the solution, a phosphate buffer (about M/30) and sodium hydroxide (for the region of the higher pH values) were used. The pH value was measured with a Hitachi pH meter (model EHP-1).

The concentration of oxygen was controlled in the following way: the sample solution was sufficiently evacuated, repeatedly melted and refrozen in vacuo, and then saturated with oxygen of a definite pressure at 30°C. The oxygen concentration in the solution was calculated with a Bunsen-coefficient, 0.026 at 30°C.[5]

The reaction apparatus was described in detail in the previous paper.[3] The light source was a high-pressure mercury lamp (Matsuda SHL-100 UV), and a specially-designed interference filter transmitting near 490 and 375 m$\mu$ was used. This mercury lamp was used as the exciting light (at 365 m$\mu$) and also as the monitoring light (at 490 m$\mu$) with which the absorbance of the solution was measured. From the change of absorbance, the rate of the formation of uranine may easily be evaluated. The reaction cell made of Terex glass is $1\times1\times4$ cm. and has a side arm for evacuation along the long axis. To change the light intensity, the distance between the lamp and the reaction cell was changed, and each time the intensity was measured with a potassium ferrioxalate actinometer.[6] All experiments were performed at 30°C.

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[1] K. Uchida, S. Kato and M. Koizumi, This Bulletin, **35**, 16 (1962).

[2] K. Uchida and M. Koizumi, ibid., **35**, 1871 (1962).

[3] K. Uchida and M. Koizumi, ibid., **35**, 1875 (1962).

[4] E. g., G. O. Schenck, *Naturwissenschaften*, **40**, 205, 212 (1953).

[5] An interporated value in a 0.1N sodium hydroxide aqueous solution ; Chemical Society of Japan (ed.), "Handbook of Chemistry (Kagaku Benran)", Maruzen, Tokyo (1958), p. 571.

[6] C. A. Parker, *Proc. Roy. Soc.(London)*, **A220**, 104 (1953) ; C. G. Hatchard and C. A. Parker, ibid., **A235**, 518 (1956).

## Results

**Determination of the Order of the Reaction with Respect to Leuco-uranine.** — The initial rate of the formation of uranine as a function of the initial concentration of leuco-uranine, $[L]_0$, was investigated. A slight variation in the concention of acridine, [A], and in the light intensity, $I_0$, was standardized by dividing the initial rate by the quantity of absorbed light, since, as will be described later, the rate is proportional to the absorbed light. The results are shown in Fig. 1. It is apparent that the rate is proportional to $[L]_0$. Thus, the rate may be represented as follows:

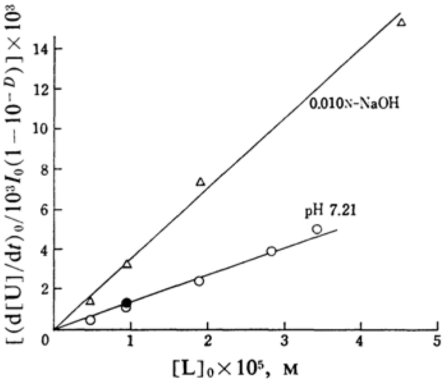

Fig. 1. Dependence of the initial rate on $[L]_0$.
$I_0 \sim 8\times10^{-8}$ mol. cm$^{-2}$ min$^{-1}$
$[A] \sim 1.3\times10^{-4}$ M
●: Uranine is beforehand added to $5\times10^{-6}$ M (pH 7.21).

$$\left(\frac{d[U]}{dt}\right)_0 = k_0'[L]_0 \tag{1}$$

$$\frac{(d[U]/dt)_0}{10^3 I_{abs}} = \frac{(d[U]/dt)_0}{10^3 I_0(1-10^{-D})} = k_0[L]_0 \tag{2}$$

where $(d[U]/dt)_0$, [U] and $k_0$ are the initial rate of the formation of uranine, the concentration of uranine, and the rate constant respectively. $I_{abs}$ is the number of photons (in mol.) absorbed (cm$^{-2}$ min$^{-1}$) and is represented as $I_0(1-10^{-D})$, where $I_0$ is the incident light intensity and $D$, the absorbance of acridine at 365 mμ.

As the initial rates are obtained from the tangent of the plot [U] vs. time $t$, some error may be inevitable and $k_0$ may not be entirely accurate. The values of $k_0$ obtained are 353 l. mol$^{-1}$ for a 0.010 N aqueous alkaline solution and 136 l. mol$^{-1}$ at pH 7.21.

**The Effect of the Concentration of Oxygen.** —The oxidation of leuco-uranine in a deaerated solution proceeds about ten times faster than in an air-saturated solution. In order to investigate how oxygen behaves in the reaction, the concentration effect of oxygen on the reaction rate was examined. The results are shown in Fig. 2, in which the initial rate is plotted against the concentration of oxygen, $[O_2]$. In the lower concentration region, the rate decreases rapidly with the concentration of oxygen, but the slope of the curve lessens near $[O_2] \sim 5\times10^{-5}$ M, and from this concentration up to $[O_2] \sim 24\times10^{-5}$ M (air-saturated solution) the rate declines very slowly. From the above results, it is obvious that oxygen suppresses the oxidation, which takes place in vacuo. Judging from a very large retarding effect at the low concentration of oxygen, the rate ought to be negligible in a concentration as high as that in the air saturated solution. However, the fact is that the reaction actually proceeds at an appreciable rate, even in the air-saturated solution. This leads to the conclusion that oxidation of a different mechanism, involving oxygen, is taking place. The percentage of the recovery of uranine after the reaction also decreases with the concentration of oxygen. The results are shown in Fig. 2 with a dashed line.

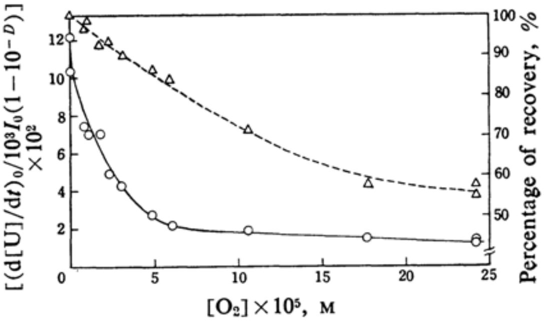

Fig. 2. Effects of $[O_2]$.
0.11 N-NaOH
$I_0 = (4.9\sim5.5)\times10^{-8}$ mol. cm$^{-2}$ min$^{-1}$
$[A] = (1.8\sim2.0)\times10^{-4}$ M
○: $\dfrac{(d[U]/dt)_0}{10^3 I_0(1-10^{-D})}$
△: Percentage of the recovery of uranine

**The Rate Formula.** — Let us now discuss a rate formula for each run in the air-saturated solution. Although the total reaction consists of the formation of uranine and the decomposition of the dye, the rate formula for only the former will be considered. It was found that the next equation holds satisfactorily. The interpretation of this equation will be given in the discussion.

$$\frac{d[U]}{dt} = k'([U]_\infty - [U]) \tag{3}$$

From this,

$$\ln [U]_\infty - \ln([U]_\infty - [U]) = k't \tag{4}$$

where $[U]_\infty$ is the concentration of uranine at

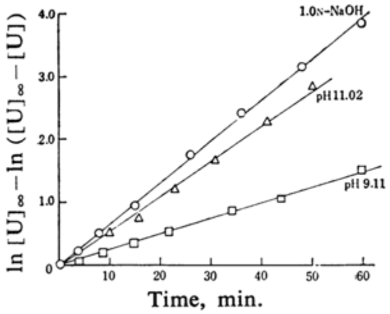

Fig. 3. Plots of $\{\ln [U]_\infty - \ln ([U]_\infty - [U])\}$ against time for typical examples.
$[L]_0 = 9.5 \times 10^{-6}$ M, $[A] \sim 1.4 \times 10^{-4}$ M
$I_0 \sim 5.5 \times 10^{-8}$ mol. cm$^{-2}$ min$^{-1}$

the end of the reaction and $k'$ is a rate constant. Some examples are shown in Fig. 3.

In the range of lower pH values, however, this equation fails, and when the pH value is lower than 8, the reaction at the initial stage appears to be rather of approximately the zeroth order with respect to the concentration of leuco-uranine. Examples in the range of lower pH values are shown in Fig. 4. Thus the order of the reaction obtained from each run is quite different from that which is obtained from the dependence of the initial rate on the concentration of leuco-uranine, which maintains the first order, as has been mentioned already. This discrepancy suggests that the reaction might be promoted by some reaction products. The problems will be considered in the discussion.

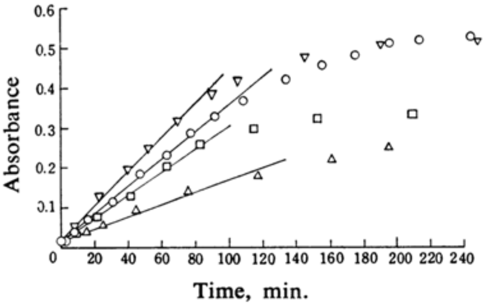

Fig. 4. Dependence of absorbance on the irradiation time.
$[L]_0 = 9.5 \times 10^{-6}$ M, $[A] = 1.4 \times 10^{-4}$ M
○: pH 7.2, ▽: pH 6.9, □: pH 6.2,
△: pH 7.2 ($[L]_0 = 4.75 \times 10^{-6}$ M)

Next, the effects of various factors upon the $k'$ values of the air-saturated solution were examined.

**The Effect of Light Intensity.** — The results are shown in Fig. 5. As the concentration of acridine differs slightly from sample to sample, the quantity of the absorbed light is used as an abscissa instead of the incident light intensity, $I_0$. It is calculated from $10^3 I_0(1-10^{-D})$. Figure 5 shows the plot of $k'$ against this quantity. It is apparent that $k'$ increases in proportion to the light intensity.

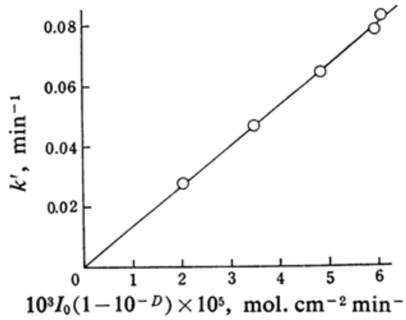

Fig. 5. Plot of $k'$ against $I_0$.
$[L]_0 = 9.5 \times 10^{-6}$ M, $[A] = (1.27 \sim 1.42) \times 10^{-4}$ M
$[\mathrm{NaOH}] = 0.010$ N

**The Effect of the Concentration of Acridine.** —The results obtained in region [A] from 0 to $2.06 \times 10^{-4}$ M are listed in Table I. Since the quantity of the absorbed light is given by $I_0(1-10^{-D})$ and since the $k'$ values are proportional to $I_0$, as has been mentioned above, it is convenient to plot the value of $k'/I_0$ against $(1-10^{-D})$ as in Fig. 6. From Fig. 6 it is certain that the values of $k'$ are proportional to the absorbed light under these conditions. Thus, Eq. 3 can be written as follows:

$$\frac{d[U]}{dt} = 10^3 k I_0 (1-10^{-D})([U]_\infty - [U]) \qquad (5)$$

where $k$ is a new rate constant. The value of

TABLE I. THE EFFECT OF THE CONCENTRATION OF ACRIDINE
$[L]_0 = 9.5 \times 10^{-6}$ M, $[\mathrm{NaOH}] = 0.122$ N

| $[A] \times 10^4$ M | $k'$ min$^{-1}$ | $I_0 \times 10^8$ mol. cm$^{-2}$ min$^{-1}$ | $k'/I_0 \times 10^{-5}$ cm$^2$ mol$^{-1}$ | $1-10^{-D}$ | $k \times 10^{-3}$ l. mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 0.00067 | 7.48 | 0.0896 | 0 | — |
| 0.160 | 0.0145 | 7.48 | 1.94 | 0.155 | 1.25 |
| 0.308 | 0.0265 | 7.48 | 3.54 | 0.276 | 1.28 |
| 0.903 | 0.0552 | 7.48 | 7.38 | 0.612 | 1.21 |
| 1.42 | 0.0667 | 6.73 | 9.91 | 0.775 | 1.28 |
| 2.04 | 0.0845 | 7.48 | 11.3 | 0.881 | 1.28 |
| 2.06 | 0.0612 | 5.48 | 11.2 | 0.885 | 1.26 |

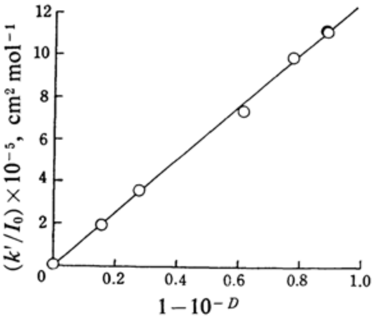

Fig. 6. Plot of $k'/I_0$ against $(1-10^{-D})$.

$k([U]_\infty-[U])$ gives the quantum yield for the formation of uranine. This is not affected by the concentration of acridine, as Table I shows.

**The Effect of the pH Value.** — The rate of the formation of uranine varies with the pH value of the solution. The results are listed in Table II. Mention will be made later of the column under $\varphi k_8/k_7$ and $\varphi k_9/k_7$ in Table II. Above a 2 N sodium hydroxide solution, the solubility of acridine is less than $1.5\times10^{-4}$ M, at which value the usual experiments were performed. In the region between pH values of 14 and 11, the $k$ values are almost constant. Below pH 11, they begin to decrease, and at pH∼8, Eq. 4 fails; thus the reaction proceeds approximately in the zeroth order respect to the concentration of leuco-uranine at the initial stage. The further decrease of pH seems to increase the rate. The relation between pH values and $k$ values is shown in Fig. 7 by a solid line. It is to be added that the $k$ values in a lower pH region are tentative, since they were obtained from the tangent at time zero on the plot of the left side of Eq. 4, $\{\ln[U]_\infty-\ln([U]_\infty-[U])\}$, against time. Although the quantity of the produced uranine at the end of the reaction seems to be affected by a very small difference in the experimental conditions and although the reproducibility is not very good, the recovery of uranine at the end of the reaction is about 40∼55% at the higher pH values. The percentage begins to increase near pH∼11 and approaches 100% at pH∼6. The results are shown in Fig. 7 with a dashed line.

TABLE II. THE EFFECT OF THE pH VALUE
$[L]_0=9.5\times10^{-6}$ M, $[A]=(1.4\sim1.5)\times10^{-4}$M
$I_0\sim5.5\times10^{-8}$ mol. cm$^{-2}$ min$^{-1}$

| pH | $k'$, min$^{-1}$ | $k\times10^{-3}$ l. mol$^{-1}$ | Percentage of the recovery % | $\varphi k_8/k_7$ | $\varphi k_9/k_7$ |
|---|---|---|---|---|---|
| 14.0 | 0.0552 | 1.28 | 60.2 | 770 | 509 |
| 13.09 | 0.0524 | 1.22 | 54.7 | 667 | 553 |
| 12.46 | 0.0558 | 1.29 | 55.3 | 713 | 577 |
| 12.42 | 0.0417 | 0.948 | 56.2 | 533 | 415 |
| 11.02 | 0.0540 | 1.25 | 59.5 | 744 | 506 |
| 10.88 | 0.0527 | 1.22 | 59.8 | 730 | 490 |
| 10.14 | 0.0408 | 1.03 | 62.5 | 644 | 386 |
| 9.53 | 0.0300 | 0.664 | 68.2 | 453 | 211 |
| 9.11 | 0.0254 | 0.588 | 70.7 | 416 | 172 |
| 8.6 | 0.0120 | 0.278 | 79.7 | 221 | 56 |
| 8.5 | 0.00980 | 0.227 | 81.0 | 184 | 43 |
| 7.86 | 0.00646 | 0.148 | 88.1 | 130 | 18 |
| 6.90 | 0.0115 | 0.268 | 96 | 257 | 11 |
| 6.28 | 0.0152 | 0.358 | 100 | 358 | 0 |

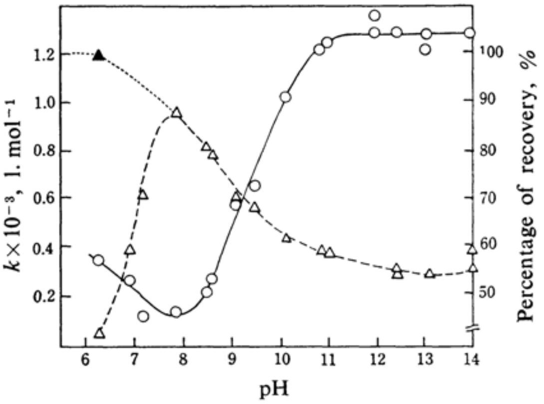

Fig. 7. Effects of the pH value.
○ : $k$
△ : Percentage of the recovery of uranine
(▲ : after addition of alkali)

In order to make clear why the recovery of the dye is incomplete in high alkalinity, the solution after the reaction was evacuated and again irradiated, but no recovery of uranine was observed. Since the recovery of uranine should take place perfectly in a deaerated solution, the above results show that uranine is partially decomposed irreversibly. The absence of leuco-uranine in the thoroughly irradiated solution was further substantiated by means of paper chromatography.[1] From these results, it is obvious that photolysis of the dye takes place, accompanied by the formation of uranine. This decomposition reaction decreases in magnitude below pH 11.

Since uranine has a p$K$ value of about 7 for the dissociation of univalent into divalent anions,[7] the concentration of univalent anions becomes appreciable below pH 8. As the univalent anions of uranine have absorption maxima at 455 and 475 mμ and as the molar extinction coefficient at 490 mμ is smaller than that of dianions, it is naturally expected that the rise of absorbance at 490 mμ is far less than that in high alkalinity, even when the recovery of the dye really occurs to the same

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[7] V. Zanker and W. Peter, *Chem. Ber.*, **91**, 572 (1958); L. Lindqvist, *Arkiv. Kemi.*, **16**, 79 (1960).

extent. The recovery of the dye in this pH region was definitely confirmed, however, by adding one drop of an alkaline solution to the thoroughly irradiated solution. Below pH 6, moreover, the neutral molecule of uranine exists in the solution, which has an absorption maximum at 437 m$\mu$, but its extinction coefficient (particularly at 490 m$\mu$) is so much smaller that the absorption can not be recognized at the concentration of $10^{-5}$ M. Therefore, the experiment below pH 6 cannot be performed for the usual concentration used in the present experiment. However, it was qualitatively confirmed, by a test analogous to that mentioned above, that even with such low pH values uranine is photochemically recovered.

## Discussion

In the case of the deaerated solution, leuco-uranine reacts with the triplet state of acridine and becomes an oxidized form via a semiquinone form. The details of this mechanism have been reported on in a previous papers.[2,3] In the case of the aerated solution, it is clear from the effect of dissolved oxygen that oxygen retards the oxidation reaction. However, if oxygen were to behave only as a retarder, it would be expected that the reaction should be completely suppressed at such a high oxygen concentration as in an air-saturated solution. The experimental results are contrary to the above expectation. Thus, although the rate decreases rapidly with the concentration of oxygen in the lowest region, the decrease becomes less and less near $[O_2] \sim 5\times10^{-5}$ M, and even in the air-saturated solution the reaction proceeds at an appreciable rate. These results would imply that the oxidation of leuco-uranine of another type, one involving oxygen, also occurs in addition to the oxidation which involves no oxygen.

From spectroscopic and paper-chromatographic analyses, there is no doubt that the photoöxidized product in the air-saturated solution is uranine[1] and that the acridine acting as a sensitizer does not change at all.

Next, the retardation of the reaction by oxygen will be considered. It is plausible that oxygen attacks and chiefly deactivates the triplet state of acridine. This was confirmed by the following supplementary experiments.

When acridine in an aqueous solution ($10^{-4}$ M in a phosphate buffer of pH 7.3) was irradiated by the light of 365 m$\mu$ from a mercury lamp, acridine was photolysed; the quantum yield of the photolysis is $2\times10^{-4}$ in the aerated solution. From the fact that the quantum yield is very small, it is certain that most of the excited state of acridine is deactivated, only a small portion of it being decomposed by the oxygen. When the concentration of oxygen is decreased, the rate of decomposition begins to fall at about $[O_2] \sim 3\times10^{-5}$ M. If one assumes that the reaction between an excited molecule and oxygen takes place so fast that the diffusion is the rate-determining process, the above finding implies that oxygen attacks a fairly long-lived excited species, since the dependence of the rate on the concentration of oxygen becomes apparent at such a low concentration. Thus, it is probable that oxygen attacks the triplet state of acridine rather than the singlet excited state. The existence of leuco-uranine in the system would not alter the situation essentially. Now, however, the triplet state of acridine reacts with not only oxygen but also with leuco-uranine at similar rates in this case. Hence it is expected that the concentration effect of oxygen will appear in a somewhat higher concentration. This expectation conforms well to the experimental results, confirming again that oxygen reacts with the triplet state of acridine and not with the excited singlet state. Besides, this is supported by the fact that no quenching of the fluorescence of acridine by oxygen is observed. As for the reaction between oxygen and the triplet state, Schenck[4] has studied many examples of photosensitized oxidation and has proposed that a loosely-bound molecular complex between oxygen and a triplet state of a sensitizer is formed in the course of the photosensitized oxidation. On the basis of Schenck's scheme, it can be considered that the intermediate between oxygen and the triplet state of acridine, $(A^t\cdots O_2)$, is formed during the photosensitized oxidation when acridine is used as a sensitizer, and that most of it may decompose into the original acridine and oxygen and only a little part participate in the recovery of uranine or the irreversible decomposition of the dye.

We will now consider how the decomposition reaction interferes with the recovery of the dye. From the fact that the formation of uranine can be treated satisfactorily with Eqs. 3 and 4, it seems likely that not only is the rate of the formation of uranine (noted below as process [8]) proportional to the concentration of leuco-uranine, as has been shown above, but also the decomposition (noted below as process [9]) is proportional to the concentration of leuco-uranine. Therefore, the relation between the concentration of leuco-uranine and that of uranine may be represented as follows:

$$\{[L]_0-[L]\}\frac{k_8}{k_8+k_9}=[U]$$

$$[\mathrm{L}] = [\mathrm{L}]_0 - \frac{k_8+k_9}{k_8}[\mathrm{U}]$$
$$= \frac{k_8+k_9}{k_8}\{[\mathrm{U}]_\infty - [\mathrm{U}]\} \tag{6}$$

where $k_8$ and $k_9$ are the rate constants of processes [8] and [9] respectively. Thus, the fact that the experimental results are satisfactorily analysed by Eq. 3 implies that the decomposition of the dyes occurs simultaneously with the formation of uranine and at a rate proportional to the concentration of leuco-uranine. The ratio of the quantity of uranine formed to that of the dye decomposed at any time is given by the ratio of $k_8$ to $k_9$.

Such relations, however, seemingly do not hold at a low pH value, perhaps due to the promotion of the oxidation of leuco-uranine by a certain reaction product. To examine if uranine acts as such a product, the effect of the addition of uranine was examined. As Fig. 1 (a solid circle) shows, the result is that the addition of as much as about $5\times10^{-6}$ M of uranine has no effect on the rate beyond the range of experimental error. Another possibility is that hydrogen peroxide which may be formed during the oxidation of leuco-uranine maintains its existence at a lower pH value and oxidizes leuco-uranine to uranine. It is natural to consider that the formation of hydrogen peroxide is accompanied by the oxidation of leuco-uranine, since this has already been confirmed in the case of the oxidation of the leuco form of thiazine dyes.

Summing up all the processes described above, the next scheme can be proposed:

$\mathrm{A} \xrightarrow{h\nu} \mathrm{A}^*$ [0]

$\mathrm{A}^* \rightarrow \mathrm{A}$ [1]

$\mathrm{A}^* + \mathrm{OH}^- \rightarrow \mathrm{A} + \mathrm{OH}^-$ [2]

$\mathrm{A}^* \rightarrow \mathrm{A}^t$ [3]

$\mathrm{A}^t + \mathrm{OH}^- \rightarrow \mathrm{A} + \mathrm{OH}^-$ [2′]

$\mathrm{A}^t \rightarrow \mathrm{A}$ [4]

$\mathrm{A}^t + \mathrm{L} \rightarrow \mathrm{U} + \mathrm{A} + \mathrm{H}_2$ [5]

$\mathrm{A}^t + \mathrm{O}_2 \rightarrow \mathrm{A}^t\cdots\mathrm{O}_2$ [6]

$\mathrm{A}^t\cdots\mathrm{O}_2 \rightarrow \mathrm{A} + \mathrm{O}_2$ [7]

$\mathrm{A}^t\cdots\mathrm{O}_2 + \mathrm{L} \rightarrow \mathrm{U} + \mathrm{A} + (\mathrm{H}_2\mathrm{O}_2)$ [8]

$\mathrm{A}^t\cdots\mathrm{O}_2 + \mathrm{L} \rightarrow$ Decomposition of the dye [9]

where $\mathrm{A}^*$ is the excited singlet state of acridine and $\mathrm{A}^t$, the triplet state of acridine. Processes [2] and [2′] are observed only in very high concentration of hydroxyl ions.

The application of the steady state method leads to the following equation:

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t} = 10^3 I_0(1-10^{-D})\varphi\left\{\frac{k_5[\mathrm{L}]}{k_4+k_5[\mathrm{L}]+k_6[\mathrm{O}_2]} + \frac{k_6[\mathrm{O}_2]}{k_4+k_5[\mathrm{L}]+k_6[\mathrm{O}_2]}\times\frac{k_8[\mathrm{L}]}{k_7+(k_8+k_9)[\mathrm{L}]}\right\} \tag{7}$$

where

$$\varphi = \frac{k_3}{k_1+k_3(+k_2[\mathrm{OH}^-])}$$

when $[\mathrm{O}_2]$ is small, the second term of the right side of this equation can be disregarded. Therefore,

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t} = 10^3 I_0(1-10^{-D})\varphi\frac{k_5}{k_4+k_5[\mathrm{L}]+k_6[\mathrm{O}_2]}[\mathrm{L}] \tag{8}$$

whence

$$\frac{10^3 I_0(1-10^{-D})}{\mathrm{d}[\mathrm{U}]/\mathrm{d}t} = \frac{1}{\varphi}\times\frac{k_4+k_5[\mathrm{L}]}{k_5[\mathrm{L}]} + \frac{1}{\varphi}\times\frac{k_6}{k_5[\mathrm{L}]}[\mathrm{O}_2] \tag{9}$$

In agreement with Eq. 9, the plot of the left side of this equation against $[\mathrm{O}_2]$ gives a straight line in the region of small $[\mathrm{O}_2]$ values, as Fig. 8 shows. From the inclination and the intercept, the values of $k_6/k_5$ and $k_6/k_4$ can be evaluated as 1.3 and $(2.2\pm0.5)\times10^5$ l. mol$^{-1}$ respectively. As the value of $\varphi$ which gives the fraction of the excited singlet state of acridine that goes to the triplet state, the value, 0.24, evaluated in a previous paper[3] was used.

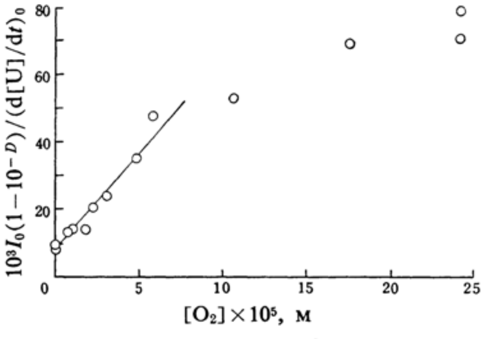

Fig. 8. Plot of $\frac{10^3 I^0(1-10^{-D})}{(\mathrm{d}[\mathrm{U}]/\mathrm{d}t)_0}$ against $[\mathrm{O}_2]$.

When the $[\mathrm{O}_2]$ value is high, the $k_6[\mathrm{O}_2]$ term is so much greater than the $k_5[\mathrm{L}]$ term that the first term of Eq. 7 can be disregarded in favor of the second term. From the fact that the overall rate is proportional to [L] up to $4.5\times10^{-5}$ M, one may assume

$$k_7 \gg (k_8+k_9)[\mathrm{L}] \tag{10}$$

Thus, the rate of the formation of uranine may be approximately represented as follows:

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t}=10^3 I_0(1-10^{-D})\varphi\frac{k_6[\mathrm{O_2}]}{k_4+k_5[\mathrm{L}]+k_6[\mathrm{O_2}]}\times\frac{k_8}{k_7}[\mathrm{L}] \qquad (11)$$

When $[\mathrm{O_2}]$ is great, one may put

$$k_6[\mathrm{O_2}] \gg k_4+k_5[\mathrm{L}] \qquad (12)$$

and Eq. 11 is reduced to

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t}=10^3 I_0(1-10^{-D})\varphi\frac{k_8}{k_7}[\mathrm{L}] \qquad (13)$$

Applying the relation of Eq. 6 to Eq. 13, one gets

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t}=10^3 I_0(1-10^{-D})\varphi\frac{k_8+k_9}{k_7}([\mathrm{U}]_\infty-[\mathrm{U}]) \qquad (14)$$

A comparison of Eq. 14 with Eq. 5 leads to

$$k=\varphi\frac{k_8+k_9}{k_7} \qquad (15)$$

The values of $\varphi k_8/k_7$ and $\varphi k_9/k_7$ can easily be obtained from $[\mathrm{U}]_\infty$, $[\mathrm{L}]_0$, as can the ratio of the quantity of the produced uranine to that of the decomposed dye, i. e., $k_8/k_9$. The values listed in Table II were obtained in this way. Figure 9 gives the plot of $\varphi k_n/k_7$ ($n=8$ or 9) against pH. Alternatively, the values of $\varphi k_8/k_7$ can also be evaluated from the relation between the initial rate and the initial concentration of leuco-uranine. The agreement between them is rather satisfactory in view of some errors in both values due to the poor reproducibility of the fraction of the produced uranine for the former and the rather inexact procedure of drawing the tangent to the absorbance—time curve at the initial time for the latter.

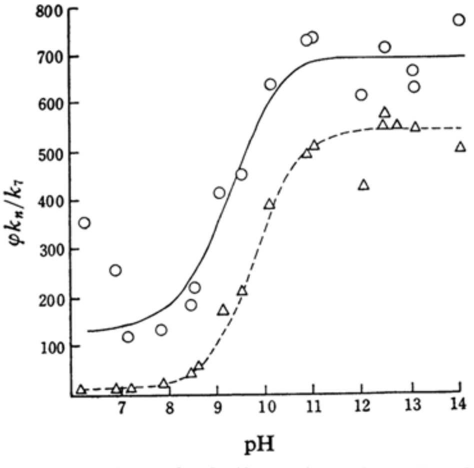

Fig. 9. Plots of $\varphi k_n/k_7$ against the pH value.
○: $\varphi k_8/k_7$ △: $\varphi k_9/k_7$

The pH dependence of the rate in the air-saturated solution is curious at first sight. However, the results can satisfactorily be interpreted in the same way as in the deaerated solution, i. e., on the basis that the various ionic forms of leuco-uranine have different reactivities and, accordingly, have different rate constants. Thus, the next scheme can be written on this basis:

$$\mathrm{A^t\cdots O_2 + L^{3-} \rightarrow U} \qquad [\mathrm{i}]$$

$$\mathrm{A^t\cdots O_2 + L^{2-} \rightarrow U} \qquad [\mathrm{ii}]$$

$$\mathrm{A^t\cdots O_2 + L^{-} \rightarrow U} \qquad [\mathrm{iii}]$$

$$\mathrm{A^t\cdots O_2 + L \rightarrow U} \qquad [\mathrm{iv}]$$

$$\mathrm{A^t\cdots O_2 + L^{3-}} \rightarrow \text{Decomposition of the dye} \qquad [\mathrm{i}']$$

$$\mathrm{A^t\cdots O_2 + L^{2-}} \rightarrow \text{Decomposition of the dye} \qquad [\mathrm{ii}']$$

$$\mathrm{A^t\cdots O_2 + L^{-}} \rightarrow \text{Decomposition of the dye} \qquad [\mathrm{iii}']$$

$$\mathrm{A^t\cdots O_2 + L} \rightarrow \text{Decomposition of the dye} \qquad [\mathrm{iv}']$$

where $k_{\mathrm{i}}$, $k_{\mathrm{ii}}$,$\cdots$, $k_{\mathrm{iv}}'$ are the rate constants for each process.

The rate can be approximately given as follows by the use of Eq. 13:

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t}=10^3 I_0(1-10^{-D})\frac{\varphi}{k_7}\times(k_{\mathrm{i}}[\mathrm{L}^{3-}]+k_{\mathrm{ii}}[\mathrm{L}^{2-}]+k_{\mathrm{iii}}[\mathrm{L}^{-}]+k_{\mathrm{iv}}[\mathrm{L}]) \qquad (16)$$

This equation can be rewritten as follows by using the successive dissociation constants of leuco-uranine ($K_1$, $K_2$ and $K_3$):

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t}=10^3 I_0(1-10^{-D})\frac{\varphi}{k_7}\times\frac{\begin{pmatrix}k_{\mathrm{iv}}[\mathrm{H}^+]^3+k_{\mathrm{iii}}K_1[\mathrm{H}^+]^2+k_{\mathrm{ii}}K_1K_2[\mathrm{H}^+]\\+k_{\mathrm{i}}K_1K_2K_3\end{pmatrix}}{[\mathrm{H}^+]^3+K_1[\mathrm{H}^+]^2+K_1K_2[\mathrm{H}^+]+K_1K_2K_3}[\mathrm{L}]_{\mathrm{s}} \qquad (17)$$

where $[\mathrm{L}]_{\mathrm{s}}$ is the analytical concentration of leuco-uranine. Equation 17 can be changed further as follows by using Eq. 13 again:

$$\frac{\varphi k_8}{k_7}\{[\mathrm{H}^+]^3+K_1[\mathrm{H}^+]^2+K_1K_2[\mathrm{H}^+]+K_1K_2K_3\} \quad (=S)$$

$$=\frac{\varphi}{k_7}\{k_{\mathrm{iv}}[\mathrm{H}^+]^3+k_{\mathrm{iii}}K_1[\mathrm{H}^+]^2+k_{\mathrm{ii}}K_1K_2[\mathrm{H}^+]+k_{\mathrm{i}}K_1K_2K_3\} \qquad (18)$$

The left side of this equation can now be evaluated, since $K_1$, $K_2$ and $K_3$ have already been determined.[1,3]

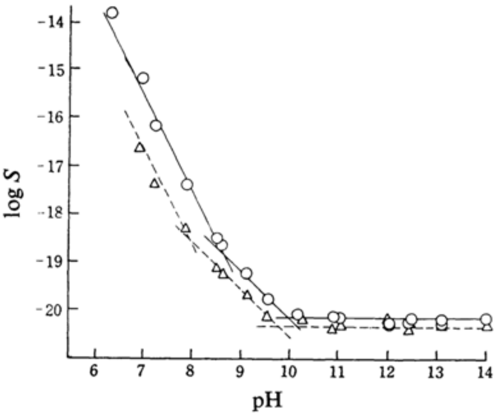

Fig. 10. Plots of log $S$ against the pH value.
○ : Formation of uranine
△ : Decomposition of the dye

Plotting log $S$ against pH, it is expected that in the region where the pH value is so small that the first term of the right side overwhelms the other terms, the curve will be a straight line with a slope of $-3$. As the pH value increases, the straight line gradually curves and joins another straight part having a slope of $-2$ and then one of 0. Extrapolating each straight line to a pH value of zero, $\varphi k_{\text{i}}/k_7$, $\varphi k_{\text{ii}}/k_7$ and $\varphi k_{\text{iii}}/k_7$ can be evaluated. The relations are shown in Fig. 10; the following results were obtained:

$$\varphi k_{\text{i}}/k_7=700 \text{ l. mol}^{-1}$$

$$\varphi k_{\text{ii}}/k_7=400 \text{ l. mol}^{-1}$$

$$\varphi k_{\text{iii}}/k_7=130 \text{ l. mol}^{-1}$$

The value of $\varphi k_{\text{iv}}/k_7$ can not be given in the pH region tested in the present experiment. It is to be noted that below pH 8, a slight deviation from the straight line becomes apparent. The values of $\varphi k_8/k_7$ calculated by the use of these values are plotted in Fig. 9 as a solid line. At pH values lower than 8, a deviation from this line is again observed, the experimental values being appreciably larger than the calculated ones. This deviation may be attributed to a somewhat different scheme in the lower pH region, such as the promoting effect of a product which is marked in this pH region.

The values of $\varphi k_9/k_7$ which are related to the decomposition of the dye have been examined in the same manner as was the value of $\varphi k_8/k_7$. The results obtained are as follows:

$$\varphi k_{\text{i}}'/k_7=550 \text{ l. mol}^{-1}$$

$$\varphi k_{\text{ii}}'/k_7=100 \text{ l. mol}^{-1}$$

$$\varphi k_{\text{iii}}'/k_7=10 \text{ l. mol}^{-1}$$

The values of $\varphi k_9/k_7$ at each pH values were calculated reversely from the above results; the broken curve in Fig. 9 gives the resultant plot. It is seen that this curve fits the experimental values fairly well.

From the above results, it is concluded that the value of $\varphi k_{\text{iii}}'/k_7$ is much smaller than the values of $\varphi k_{\text{i}}'/k_7$ and $\varphi k_{\text{ii}}'/k_7$, in contrast to the case in the deaerated solution, in which the values of $\varphi k_n/k_\iota$ are not very different from each other.[3] In other words, the univalent anions of leuco-uranine are more stable to the oxidation than the di- and trivalent anions. It is remarkable that the values of $\varphi k_n/k_7$ are very much smaller than those corresponding to the deaerated solution. It will be interesting to investigate whether this difference is due to the difference in the rate constants pertaining to the oxidation of leuco-uranine or to that between the rate constants of the deactivation of the triplet state of acridine and that of the molecular complex, $A^t\cdots O_2$; however, this point can not be discussed in the present state of research.

## Summary

The mechanism of an acridine-sensitized photoöxidation of leuco-uranine in an aerated solution has been elucidated. The oxidation takes place in a different manner from that in a deaerated solution. That is, oxygen attacks the triplet state of acridine very rapidly and presumably forms a kind of loosely-bound molecular complex. Most of this decomposes into the original acridine and oxygen, so that oxygen suppresses the oxidation of leuco-uranine occurring in the deaerated solution. Denoting the rate constants of the reactions between the triplet state of acridine and leuco-uranine and oxygen, respectively, as $k_5$ and $k_6$, the value of $k_6/k_5$ is given as 1.3. On the other hand, the oxidation of leuco-uranine by oxygen becomes apparent in a high oxygen concentration, such as an air-saturated solution. Namely, the molecular complex consisting of the triplet state of acridine and oxygen reacts with leuco-uranine, and the oxidation of the latter takes place. If one writes the rate constant of this reaction as $k_8$ and that of the reaction in which the molecular complex decomposes into acridine and oxygen as $k_7$, one can evaluate the ratio of $\varphi k_8/k_7$ from the experimental results, where the value of $\varphi$ is the transition probability in which acridine goes to the triplet state from the excited singlet state. An irreversible decomposition of the dye also competes with the above reactions. Putting its rate constant as $k_9$, the value of $\varphi k_9/k_7$ has been evaluated. The variation of the ratios of $\varphi k_8/k_7$ and $\varphi k_9/k_7$ with the variation in pH values has been interpreted on the basis

that the reactivities of leuco-uranine are different in each ionic species. With the higher values of pH, the quantum yield becomes greater. The quantum yields of the formation of uranine and the irreversible decomposition of the dye have been evaluated as 0.0070 and 0.0055 respectively, yields which are about one thirtieth that in the deaerated solution. In the region of pH values lower than 8, a promoting action of a certain reaction seems to take part in the reaction and the reaction approaches the zeroth order.

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## Appendix

**The Confirmation of the Hydrogen Evolution.**— In Part I of this series, it was tentatively concluded, on the basis of the results of various kinds of scrutinizing experiments, that the evolution of hydrogen would occur, along with the photosensitized oxidation of leuco-uranine, in the deaerated condition. However, in spite of great effort, we could not succeed at that time in gathering and identifiying the evolved gas, and so the most direct evidence for the hydrogen evolution was lacking. Now, by increasing the quantity of the sample to be irradiated to several times the amount used in the previous paper, the author has succeeded in confirming that hydrogen is evolved. Thus, sample solutions which were about twice as concentrated and the volumes of which were two or four times as great as previous ones were prepared, and the gas evolved during the irradiation was gathered and analysed. As a sensitizer, uranine was used because there is no possibility for the sensitizer itself to be reduced by the evolved hydrogen. It is to be noted, however, that the reproducibility in the feature of the reaction seemed to be rather poor, perhaps because of the use of uranine as a sensitizer. 175～200 ml. of the sample solution ($[\mathrm{L}]=9\times10^{-5}$ M, $[\mathrm{U}]=(4\sim13)\times10^{-6}$ M and $[\mathrm{NaOH}]=2\times10^{-3}$ N) was divided into several portions, each 25～50 ml. in volume, and they were evacuated carefully. After irradiation, all the evolved gas non-condensable at the liquid air temperature was gathered by the use of a small mercury diffusion pump and a Toepler pump. Two similar experiments were then performed; the results obtained are shown in Table III.

TABLE III. QUANTITY OF GAS EVOLVED AFTER IRRADIATION

| Exp. no. | Quantity of oxidized leuco-uranine mol. | Volume of gas obtained (reduced to STP*), ml. | Quantity of gas, mol. |
|---|---|---|---|
| I | $5.2\times10^{-6}$ | 0.149 | $6.7\times10^{-6}$ |
| II | $5.1\times10^{-6}$ | 0.049 | $2.2\times10^{-6}$ |

* Standard temperature (0°C) and pressure (1 atm.)

The gas thus obtained was passed through a tube containing copper(II) oxide at 297°C, and the oxidation product was condensed in a trap cooled by liquid air. The volumes of the non-condensable gases at −183°C, −75°C and at room temperature were determined separately. The results are shown in Table IV.

It is concluded that gas C is water vapor, because water-like mist condensed on the wall when the gas was compressed into a small measuring vessel by the use of a Toepler pump; moreover, its vapor pressure was nearly the same as that of water. The quantity of gas A in Exp. no. I is unexpectedly large; this is perhaps due to the leakage of air during the procedure.

Furthermore, 95% of gases B and C in Exp. no. II disappeared when they were passed through a tube containing sodium hydroxide pellets and were condensed in a trap cooled at about −75°C; so gas B must be carbon dioxide. No organic substance which is not captured by liquid air but which is oxidized into water and carbon dioxide over copper oxide at about 300°C is likely to be produced from leuco-uranine in the reaction.

From the above results, most of the gas evolved in the reaction can be concluded to be hydrogen, but there seems to be some possibility that carbon monoxide might also be produced. The production of the latter might be due to the photochemical reduction of carbonate ions by the hydrogen evolved in the oxidation of leuco-uranine. If one assumes that the equimolar hydrogen is consumed in the reduction of carbonate ions, the quantity of hydrogen initially produced corresponds to 95 and 40% of the oxidized leuco-uranine in the above two experiments. Although the quantitative agreement

TABLE IV. QUANTITY OF GAS AFTER PASSING THROUGH A HEATED CuO-TUBE

(Volumes of gases are reduced to STP)

| Exp. no. | Gas A Non-condensable at −183°C Volume, ml. (mol.) | Gas B Non-condensable at −75°C Volume, ml. (mol.) | Gas C Non-condensable at room temperature Volume, ml. |
|---|---|---|---|
| I | $36\ \times10^{-3}$ ($16\ \times10^{-7}$) | $1.9\times10^{-3}$ ($0.9\times10^{-7}$) | ($\sim110\times10^{-3}$) |
| II | $1.9\times10^{-3}$ ( $0.9\times10^{-7}$) | $22\ \times10^{-3}$ ($9.6\times10^{-7}$) | ($\sim 25\times10^{-3}$) |

is rather poor in the two experiments, it can be concluded from the above results that the evolution of the hydrogen gas is the main process in the photoöxidation of leuco-uranine in the deaerated solution. It is interesting that carbon monoxide seems to be produced under some conditions: this is perhaps due to the photochemical reduction of carbonate ions.