Photosensitized Oxidation of Leuco-uranine. II. Kinetics of an Acridine-sensitized Photoöxidation in the Deaerated Solution

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As has been reported in a preceding paper[1], leuco-uranine is oxidized to the colored form when its deaerated aqueous solution is irradiated by 365 mμ in the presence of acridine. There was some ambiguity as to the role which acridine plays in this reaction, since, although its quantity remained almost constant in most cases, in a few experiments it decreased a little, as judged from its spectra. In spite of this finding, preliminary experiments showed that the rate of restoration of the dye is quite reproducible under given conditions, suggesting that the process in question does not essentially affect the overall rate of the reaction.

As described in the preceding paper, acridine is a suitable sensitizer for a quantitative study of the reaction; the objective of the present paper is to report on investigations into the influence of various factors upon this reaction. They may be summarized as follows. The triplet state of acridine reacts with leuco-uranine, producing perhaps the semi-hydrogenated form of both species. The various ionic forms of leuco-uranine (mono-, di- and tri-valent anions) have different reactivities towards the triplet state of acridine, which can be evaluated quantitatively from the pH dependence of the overall rate constant. The rate constants of various steps have been obtained with moderate accuracy.

1) K. Uchida and M. Koizumi, This Bulletin, 35, 1871 (1962).

Apparatus and Procedure

The apparatus is shown in Fig. 1.

The light source, L, is a high-pressure mercury lamp (Mazuda SHL 100 UV) operating at 100 V. The power was supplied through a voltage stabilizer, Volco H. T. A remarkable feature is that the same light source, L, was made use of in a specific manner both for inducing the reaction (excitation) and for tracing the reaction (measurement). This technique, which was suggested by Dr. Kato, is described below.

F_1 is an aqueous solution of copper sulfate designed to remove the thermal radiation. F_2 is a specially-designed interference filter (manufactured by the Shonan Komaku Co.), the second order interference of which is 727 mμ; accordingly, the

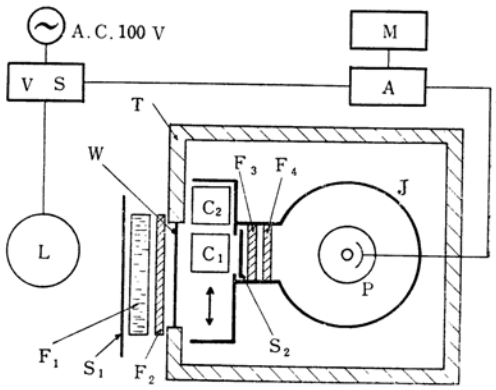

Fig. 1. Apparatus for the reaction.

V. S.: Voltage stabilizer A: Amplifier
M: Micro-ammeter W: Glass window

third and the fourth interference are, respectively, 490 and 375 mμ (half width 18 mμ), transmitted light being chiefly limited in the region near the above three wavelengths. The 365 mμ of the mercury lamp can pass through the above filter with a transmission of about 19%. 490 mμ corresponds just to the absorption maximum of the aqueous uranine solution and, since the present mercury lamp has a weak continuous emission, the light in the region of 490 mμ passing through F_2 can be utilized for measuring the quantity of uranine produced. The light of 490 mμ passing through the solution is received by a photocell, P (Mazuda No. 7211). The optical density of the solution at this wave length can easily be evaluated. The fact that its intensity is very weak does not affect the reaction. Between the sample-solution and the photocell are inserted an opaque glass, F_3, and a cut-off filter, F_4 (>450 mμ), in order to remove the light of 365 mμ.

C_1 and C_2 are, respectively, the reaction cell and the reference cell for optical density. Both are set tightly in a movable cell-holder. They are made from Terex, are 1×1×4 cm, and are fitted with a side tube for evacuation. The reading of the meter, M, was calibrated by the use of a Hitachi spectrophotometer (EPU-2A). J is a brass tube with an air-tight glass window, F_3; it contains a photocell and a part of circuit for multiplication, C_1, C_2 and J being immersed in a water-thermostat, T. S_1 and S_2 are shutters. The reaction temperature is 30°C unless otherwise denoted.

The intensity of the irradiating light was controlled by changing the distance between the light source and the cell, or by the use of neutral density filters (manufactured by the Hoya Co.), and it was measured each time by means of a potassium ferrioxalate actinometer.

Results

Rate Formula for a Run. — Under certain experimental conditions, i. e., when the intensity of light, I_0, the concentration of acridine, [A], the initial concentration of leuco-uranine, $[L]_0$, and the temperature, T, are in proper range, the reaction proceeds as of first order with regard to [L]:

$$\frac{d[U]}{dt}=k'[L] \qquad (1)$$

Hence,

$$\ln\frac{[L]_0}{[L]}=k't \qquad (2)$$

Equation 2 fits the experimental results quite satisfactorily, and the reproducibility is moderately good. Typical examples are shown in Fig. 2. The conditions of the reaction for these examples are $[A]=1.3\times10^{-4}$ M, $[L]_0=9.5\times10^{-6}$ M, $I_0\sim5.5\times10^{-8}$ mol. min^{-1} cm^{-2}, and temperature, 30°C. When [A] becomes less and $[L]_0$ larger than the above values, the applicability of the first order rate formula becomes gradually less satisfactory (see below).

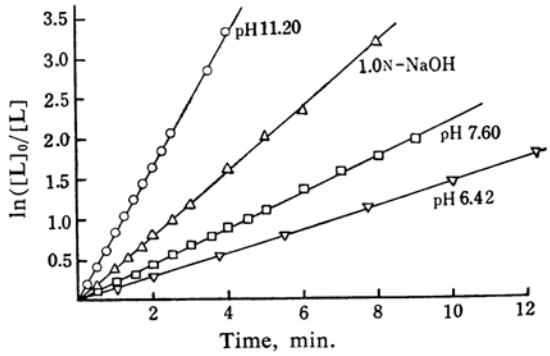

Fig. 2. Plots of $\ln([L]_0/[L])$ against time for typical examples.
$[L]_0=9.5\times10^{-6}$ M, $[A]=1.3\times10^{-4}$ M

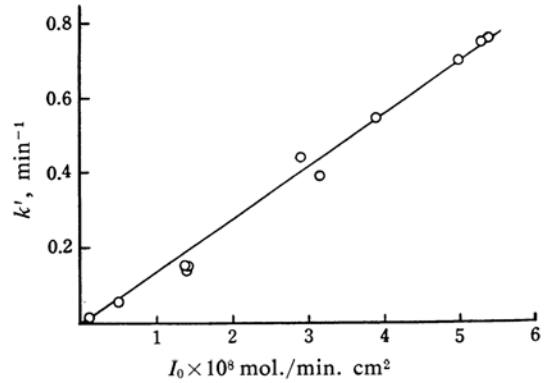

Fig. 3. Dependence of k' on the light intensity.
pH=11.1, $[A]=1.7\times10^{-4}$ M, $[L]_0=9.5\times10^{-6}$ M

In this paper, most of the experiments were performed under the above conditions.

The Effect of Light Intensity.—The results are shown in Fig. 3. k' increases proportionally to the light intensity.

The Effect of the Concentration of Acridine. —The values of k' for various [A]-values are listed in Table I.

In this table, D is the optical density at 365 mμ; hence, $1-10^{-D}$ is a fraction of the light absorbed by acridine. The concentration of acridine was calculated from the optical density of the solution at 365 mμ using the value of $\varepsilon_{365}=0.455\times10^4$.

If the rate is proportional to the absorbed light, Eq. 1 can be rewritten as follows with a new constant, k;

$$\frac{d[U]}{dt}=-\frac{d[L]}{dt}=k'[L]$$
$$=10^3\frac{k}{d}I_{abs}[L]$$
$$=10^3\frac{k}{d}I_0(1-10^{-D})[L] \qquad (3)$$

TABLE I. THE EFFECT OF THE CONCENTRATION OF ACRIDINE

0.010 N NaOH $[L]_0=9.5\times10^{-6}$ M

Exp. No.	$[A]\times10^4$ M	$I_0\times10^8$ mol. cm^{-2} min^{-1}	$1-10^{-D}$	k' min^{-1}	$k'/(I_0\times10^7)$ cm^2 mol^{-1}	$\frac{10^{-3}k'\cdot d}{(1-10^{-D})I_0}\times10^{-4}$
145	1.92	6.08	0.867	0.749	1.23	1.42
146	1.46	6.08	0.784	0.75	1.23	1.57
154	1.05	6.70	0.667	0.835	1.25	1.88
147	0.835	6.90	0.583	0.898	1.30	2.23
162	0.651	6.25	0.494	0.617	0.988	2.00
155	0.525	6.54	0.425	0.576	0.882	2.07
148	0.319	6.90	0.284	0.456	0.662	2.33
158	0.233	6.35	0.217	0.293	0.462	2.12
150	0.132	6.2	0.129	0.161	0.260	2.01

TABLE II. THE EFFECT OF THE INITIAL CONCENTRATION OF LEUCO-URANINE

$[A]\sim0.6\times10^{-4}$ M, $[NaOH]=0.010$ N

Exp. No.	$[L]_0\times10^5$ M	$(1/[L]_0)\times10^{-5}$ M^{-1}	$I_0\times10^8$ mol. cm^{-2} min^{-1}	$1-10^{-D}$	Init. rate $\times10^6$ min^{-1} M	$\frac{10^3I_0(1-10^{-D})}{\text{Initial rate}}$	k' min^{-1}
157	0.475	2.11	6.52	0.462	3.56	8.46	0.968
161	0.713	1.40	6.35	0.457	4.33	6.70	0.738
155	0.950	1.05	6.54	0.425	4.70	5.91	0.576
162	0.950	1.05	6.25	0.494	4.82	6.40	0.617
156	1.90	0.526	6.52	0.435	5.42	5.23	0.339
159	6.89	0.145	6.35	0.480	6.34	4.81	—
160	23.8	0.042	6.35	0.504	8.17	3.92	—

where I_{abs} is the number of photons (in the mole) absorbed ($cm^{-2}.min^{-1}$), d is the light path length (=1 cm.), and D is the optical density at 365 mμ. $k[L]_0$ gives the quantum yield at the initial stage.

As may be seen from Table I, $k'd/10^3I_0(1-10^{-D})=k$ begins to decrease beyond about 0.8×10^{-4} M of acridine. This is most plausibly due to the self-quenching of the singlet or triplet excited state of acridine.

It can be said from the above results that the rate is proportional to the absorbed light up to ca. 0.8×10^{-4} M, whence the self-deactivation of the excited acridine molecule becomes appreciable.

The Effect of the Initial Concentration of Leuco-uranine. — Equation 1—3 hold when $[L]_0\leqq10^{-5}$ M and $[A]\geqq10^{-4}$ M. To examine the general applicability of the first order rate formula, $[L]_0$ was increased from 0.475×10^{-5} to 2.38×10^{-4} M, keeping [A] constant (0.6×10^{-4} M, about half of the usual value). The results are listed in Table II.

As may be seen from Table II, the initial rate increases with the rise of $[L]_0$. Each run can be approximately treated as of the first order with respect to [L] up about 1×10^{-5} M. However, it is evident that k' decreases appreciably with the increase in $[L]_0$. For the highest concentrations of $[L]_0$ (6.89 and 23.8 $\times10^{-5}$ M), the zeroth order rate formula is rather better than that of the first order.

All these facts suggest that the order of the reaction is generally between zero and one, the first order rate formula holding only for the limited conditions under which most of the experiments happen to have been performed. The interpretation of this will be given in the discussion of the 7th column, $10^3\ I_0(1-10^{-D})/$ (initial rate), of the table.

The Effect of the pH Value.—When the pH value of the solution was changed from ca. 6.4 to 14 by the use, for example, of the phosphate buffer, $[L]_0$ and [A] being given the values of 9.5×10^{-6} M and 1.3×10^{-4} M respectively, it was found that the rate changes in a curious manner.

Figure 4 shows the plot of k against the pH value, where k is the constant introduced in Eq. 3. Equations 1 to 3 hold satisfactorily throughout the whole pH region. It is evident that the rate constant has a maximum near the pH value of 11∼12. The full line represents the calculated values, which will be described in the discussion below.

It is to be noted that below a pH value of 6, the oxidized form of uranine exists as a neutral molecule, of which the absorption in the visible region at 490 mμ is quite small.

Under the present experimental conditions, no coloration could be perceived in situation below a pH value of 6.0, but preliminary experiments showed that the solution, after being irradiated, becomes colored when made alkaline. As to the higher alkaline solution, the solubility of acridine decreases with the

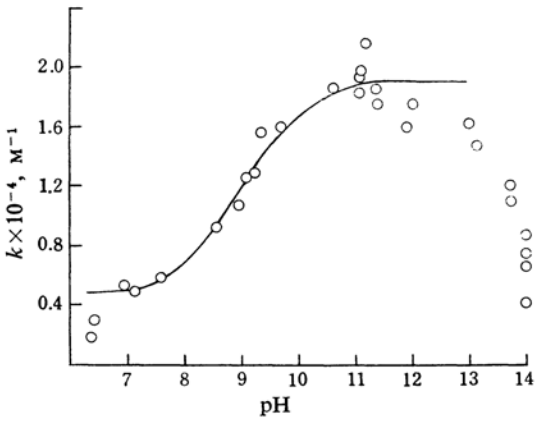

Fig. 4. Dependence of k on pH. The line corresponds to the calculated values.
$I_0=5.5\sim7.0\times10^{-8}$ mol./cm^2 min.
$[A]=1.3\times10^{-4}$ M, $[L]_0=9.5\times10^{-6}$ M

alkalinity, and the experiments could not be carried out beyond 1.5 N.

The Effect of Temperature.—The rate was measured from 10° to 52°C. The results are listed in Table III.

These data are not very accurate, and the following Arrhenius formula only serves to show an approximate relation between k and T:

$$k=8.1\times109\exp(-8000/RT)$$

TABLE III. THE EFFECT OF TEMPERATURE

pH=11.0, $[A]=1.5\times10^{-4}$ M, $[L]_0=9.5\times10^{-6}$ M
$I_0\simeq6\times10^{-8}$ mol. cm^{-2} min^{-1}

Exp. No.	Temp., °C	k' min^{-1}	k l./mol.$\times10^{-4}$
79	10.0	0.270	0.546
80	20.0	0.336	0.680
81	30.0	0.766	1.55
82	40.0	1.00	2.03
83	51.0	1.01	2.04
19*	25.0	0.933	1.07
37*	52.	1.85	3.83

* pH=13.14, $[A]=1.3\times10^{-4}$ M

Discussion

The first problem to be solved is the exact determination of the excited species of acridine (singlet or triplet) which actually reacts with leuco-uranine. This can be judged from the experiment concerning the effect of leuco-uranine on the fluorescence of acridine. The fluorescence intensity of the aqueous solution of acridine (1.3×10^{-4} M) was measured by a fluorescence accessory attached to a Hitachi spectrophotometer. The addition of leuco-uranine (9.5×10^{-6} M) to the above solution scarcely affected the intensity of the fluorescence, showing that the quenching effect of the former is within the range of experimental error.

From this result, it can be inferred that leuco-uranine does not appreciably attack the singlet excited state, because the opposite assumption leads, as is shown below, to a relation contradicting the experimental result.

Let the quantum yield of the fluorescence be designated as η_E and η_E', in the absence and in the presence of leuco-uranine respectively. If leuco-uranine attacks the singlet excited state as the first step of the reaction, η_E and η_E' can be expressed as follows:

$$\eta_E=\frac{v_E}{v_E+v_Q} \qquad \eta_E'=\frac{v_E}{v_E+v_Q+v_R} \tag{4}$$

where v_E, v_Q and v_R are, respectively, the rate of emission, the inner quenching, and the process leading to the reaction.

The quantum yield of the reaction, on the other hand, can be written as follows:

$$\eta_R=\frac{v_R}{v_E+v_Q+v_R}\cdot\alpha \tag{5}$$

where $\alpha<1$. Equations 4 and 5 lead to the following relation:

$$\frac{\eta_E-\eta_E'}{\eta_E}=\frac{\eta_R}{\alpha} \tag{6}$$

Now, since the addition of leuco-uranine does not affect the intensity of fluorescence beyond the range of experimental error, the left side of the above equation can safely be said to be smaller than 1/10, perhaps, a few hundredths or so. Thus, $1/10>\eta_R/\alpha$ must hold. The quantum yield of the reaction being in favorable conditions, ~0.2, η_R must >0.2; hence, $\alpha>2$, which never holds in any case. Thus one can safely conclude that leuco-uranine does not appreciably react with the singlet state, its contribution to the entire reaction, even if it exists, being less than 10%.

In the following, we assume that the entire reaction proceeds via the triplet state of acridine, which attacks leuco-uranine.

In general, it must be taken into account that the triplet state returns to the ground state, dissipating its excess energy. Therefore, $k[L]$ in Eq. 3 must be represented as follows:

$$k[L]=\varphi\frac{k_r[L]}{k_d+k_r[L]}^{*} \tag{7}$$

where φ gives the fraction of the singlet excited state that goes to the triplet, and k_d and k_r are, respectively, the rate constant of deactivation and the reaction with leuco-uranine. The rate formula should be of the first order or zeroth order according as $k_r[L]\ll k_d$ or $k_r[L]\gg k_d$. The general applicability of Eq.

* The mere deactivation by leuco-uranine in this case may be ignored.

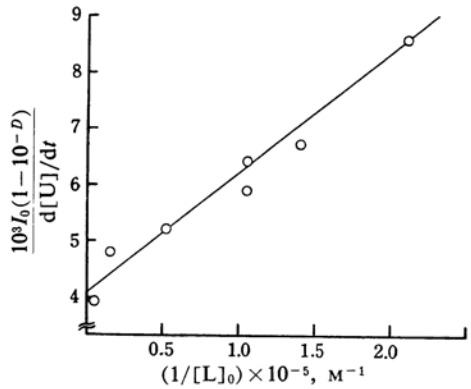

Fig. 5. Plot of $10^3 I_0(1-10^{-D})/(\mathrm{d[U]/d}t)$ against $1/[\mathrm{L}]_0$.

7 can be tested from the data in Table II. Based on Eqs. 3 and 7, the initial rate can be written as follows:

$$\frac{\mathrm{d[U]}}{\mathrm{d}t}=10^3 I_0(1-10^{-D})\varphi\frac{k_r[\mathrm{L}]_0}{k_r[\mathrm{L}]_0+k_d} \qquad (8)$$

whence

$$\frac{10^3 I_0(1-10^{-D})}{\mathrm{d[U]/d}t}=\frac{1}{\varphi}+\frac{1}{\varphi}\times\frac{k_d}{k_r[\mathrm{L}]_0}$$

As is shown in Fig. 5, the plot of $10^3 I_0(1-10^{-D})/(\mathrm{d[U]/d}t)$ against $1/[\mathrm{L}]_0$ gives a satisfactory straight line. From the slope and the intercept, the values of φ and k_d/k_r can be set at 0.24 and 0.51×10^{-5} mol./l. φ gives the intersystem crossing probability ($S'\rightarrow T$); this value reconfirms that the reaction involves the triplet state of acridine.

In most experiments the initial concentration of leuco-uranine is $\sim1\times10^{-5}$ M; hence, $k_d/k_r[\mathrm{L}]_0\sim0.51$. Thus, the rate of deactivation is rather smaller than that of the reaction. Integrating Eq. 8, one gets an exact rate formula as follows:

$$\frac{k_r}{k_d}\{[\mathrm{L}]_0-[\mathrm{L}]\}+\ln\frac{[\mathrm{L}]_0}{[\mathrm{L}]}=10^3\frac{k_r}{k_d}I_0(1-10^{-D})\varphi t \qquad (9)$$

Equation 9 can reproduce quite satisfactorily most of the runs for which the first order rate formula fails. Examples are shown in Fig. 6.

In most of the experiments, [A] was chosen as $\geqq1.3\times10^{-4}$ M, where the deactivation of the triplet state is rather large (see Table I); hence, k_d becomes more than twice as large as the above value. Thus, the situation in this case is more favorable for the first order rate formula; yet it is unlikely that the $k_r[\mathrm{L}]$ term is negligible in comparison with the k_d term. Therefore, the possibility of the quenching action of uranine (produced) on the triplet state of acridine was examined. Thus, if

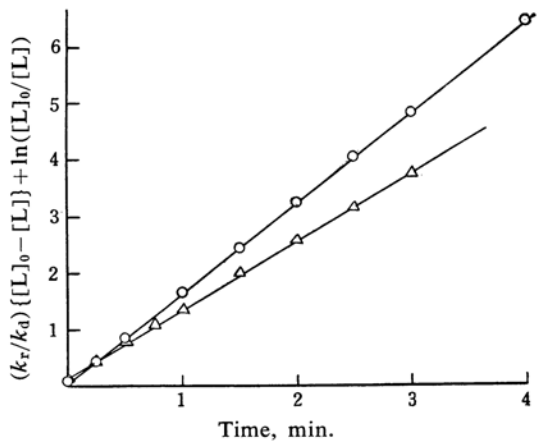

Fig. 6. Plots of $(k_r/k_d)\{[\mathrm{L}]_0-[\mathrm{L}]\}+\ln([\mathrm{L}]_0/[\mathrm{L}])$ against t.
○: [A] $=0.6\times10^{-4}$ M, [L] $=0.95\times10^{-5}$ M, [NaOH] $=0.01$ N
△: [A] $=0.6\times10^{-4}$ M, [L] $=1.9\times10^{-5}$ M, [NaOH] $=0.01$ N

uranine were to deactivate the triplet of acridine about a rate constant equal to that with which leuco-uranine attacks the triplet state of acridine, then the denominator of Eq. 7 would be expected to be approximately constant during the course of the reaction. In this case, Eq. 7 can be replaced by:

$$k[\mathrm{L}]=\varphi\frac{k_r[\mathrm{L}]}{k_d+k_r[\mathrm{L}]_0} \qquad (7a)$$

and the run is to proceed as of the first order in [L]. However, it was found that the addition of uranine up to 8×10^{-6} M never affects the rate beyond the range of experimental error. Taking all the above facts into account, there still remains some question as to the reason why the first order rate formula fits most of the experimental results quite well.

We will next discuss the actual molecular species which participates in the reaction. First, acridine is a base, and in an acidic solution it exists as acridinium cation; it must be determined which species is really involved in the reaction. However, according to Jackson and Porter[2], the pK value of acridine in the triplet state is 5.6 and, in the present pH range, it can be said that acridine exists only as a neutral molecule.

On the other hand, due attention must be paid to the various ionic forms of leuco-uranine. Information as to the reactivity of various species can be obtained from an analysis of the pH effect. In other words, the results depicted in Fig. 4 can be satisfactorily

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

interpreted on the basis of the four species of leuco-uranine, L, L^-, L^{2-} and L^{3-}, having different reactivities and, accordingly, different rate constants.

All the processes to be considered (taking the deactivation process into account) are:

$$A + h\nu \rightarrow A^* \qquad 10^3\varphi I_{abs} \qquad \text{(i)}$$

$$A^* + L^{3-} \rightarrow AH + UH^{3-} \qquad k_1 \qquad \text{(ii)}$$

$$A^* + L^{2-} \rightarrow AH + UH^{2-} \qquad k_2 \qquad \text{(iii)}$$

$$A^* + L^- \rightarrow AH + UH^- \qquad k_3 \qquad \text{(iv)}$$

$$A^* + L \rightarrow AH + UH \qquad k_4 \qquad \text{(v)}$$

$$A^* \rightarrow A \qquad k_q \qquad \text{(vi)}$$

$$A^* + OH^- \rightarrow A + OH^- \qquad k_{OH} \qquad \text{(vii)}$$

In this scheme, A* is the triplet state of acridine. ii~v are tentatively expressed as formations of the semi-reduced forms of acridine and uranine. This is plausible, as has been described in the preceding paper, but it has not yet been decided definitely. vii was added for the sake of completeness (see below).

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

$$\frac{d[U]}{dt} = 10^3\varphi I_{abs} \times \frac{k_1[L^{3-}]+k_2[L^{2-}]+k_3[L^-]+k_4[L]}{k_1[L^{3-}]+k_2[L^{2-}]+k_3[L^-]+k_4[L]+k_q+k_{OH}[OH^-]} \qquad (10)$$

As long as the first order rate formula holds, $k_1[L^{3-}]+k_2[L^{2-}]+k_3[L^-]+k_4[L]+k_q$ may be put approximately as

$$k_r[L]_m + k_q = k_t$$

in which $[L]_m$ is the mean value of [L] during the course of the reaction and k_r depends on the pH value. Furthermore, one may assume that:

$$k_t \gg k_{OH}[OH^-]$$

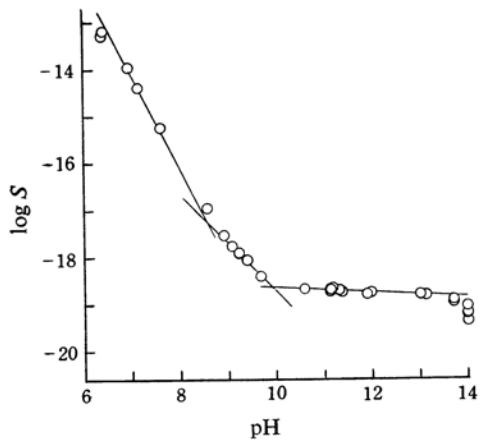

Fig. 7. Plot of log S against the pH value.

so long as $[OH^-]$ is not very great.

By the use of the successive dissociation constants of leuco-uranine (K_1, K_2 and K_3), Eq. 8 can be rewritten as follows:

$$\frac{d[U]}{dt} = 10^3\frac{\varphi}{k_t}I_{abs} \times \frac{k_4[H^+]^3+k_3K_1[H^+]^2+k_2K_1K_2[H^+]+k_1K_1K_2K_3}{[H^+]^3+K_1[H^+]^2+K_1K_2[H^+]+K_1K_2K_3}[L]_s \qquad (11)$$

where $[L]_s$ is the analytical concentration of leuco-uranine.

Thus, the experimentally-obtained k-value in Eq. 3 can be related to the rate constants of various species in the following way:

$$k\{[H^+]^3+K_1[H^+]^2+K_1K_2[H^+]+K_1K_2K_3\}(=S) = \frac{\varphi}{k_t}\{k_4[H^+]^3+k_3K_1[H^+]^2+k_2K_1K_2[H^+] + k_1K_1K_2K_3\} \qquad (12)$$

The left side of this equation is experimentally determined, since K_1, K_2 and K_3 have already been evaluated as $pK_1=3.8$, $pK_2\approx$, and $pK_3=9.6$[3].

Plotting log S against the pH value, 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 should be a straight line with a slope of -3. As the pH value increases, the straight line gradually curves and connects with another straight part having a slope of -2, then further to a part with slopes of -1 and of 0.

The results obtained by the use of the above K-values and the experimentally determined k-values are shown in Fig. 7. It is seen that the curve really consists of three linear sections with slopes of -2, -1 and approximately 0, although the second range is very short and is not quite clear. The most plausible values of k_1 to reproduce the experimental curve are $\varphi k_1/k_t = 1.9\times10^4$, $\varphi k_2/k_t = 1.4\times10^4$ and $\varphi k_3/k_t = 0.48\times10^4$ (l./mol.)*. The calculated values of k at various pH values are compared with the experimental values in Fig. 4. The line with a slope of -3 having not been obtained, $\varphi k_4/k_t$ can not be obtained under the present experimental conditions.

In the highest pH value region, the line has a little negative slope; this can be attributed to the quenching of the triplet state due to the hydroxyl ion.

Thus, one can write in this region:

3) K. Uchida, S. Kato and M. Koizumi, This Bulletin, 35, 16 (1962).

* As pK, the pH values at the points of intersection in Fig. 7 are employed: $pK_1=3.8$, $pK_2=8.6$ and $pK_3=9.9$.

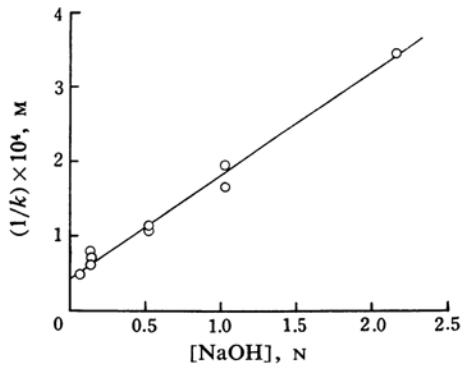

Fig. 8. Plot of $1/k$ against [NaOH].
$[L]_0=9.5\times10^{-6}$ M, $[A]=1.3\times10^{-4}$ M

$$k=\frac{\varphi k_1}{k_t+k_{OH}[OH^-]}$$

or

$$\frac{1}{k}=\frac{k_t}{\varphi k_1}+\frac{k_{OH}}{\varphi k_1}[OH^-] \qquad (13)$$

The plot of $1/k$ against $[OH^-]$ gives a straight line, as is shown in Fig. 8. From the slope and the intercept, one can evaluate k_{OH}/k_t at ~3 l./mol. Furthermore, the value of $\varphi k_1/k_t$ obtained from the intercept is 2.3×10^4 l./mol., with a fair agreement with that obtained from the analysis of Eq. 12.

At this point, it is to be noted that the fluorescence of acridine is also quenched by the hydroxyl ion. The quantitative investigation has shown that the effect is satisfactorily reproduced by Stern-Volmer's equation, the value of the quenching constant K being 0.50 ~0.69 l./mol. K is given by

$$K=\frac{k'_{OH}}{k'_q+k_f}$$

where k_f, k'_q and k'_{OH} are, respectively, the rate constant of emission, of self-quenching and of the reaction between the singlet excited state of acridine and the hydroxyl ion.

In view of the quenching action of the hydroxyl ion on the fluorescence, the above-mentioned value of k_{OH}/k_t ~3 is, of course, an apparent one, pertaining to the action on the singlet excited state as well as on the triplet state. However, the fact that k_{OH}/k_q is much larger than K shows that the latter predominates, reconfirming again that the reaction chiefly takes place via the triplet state of acridine.

In concluding the discussion, it must be added that the absolute value of each rate constant can be estimated with moderate accuracy for a high alkaline region. In this region one may take the value of φ as 0.24; then one can get the value of k_r/k_t as follows:

from the relation between the initial rate and $[L]_0$, 6.6×10^4

from the pH effect on k, 7.9×10^4

from the effect of $[OH^-]$ on k, 9.5×10^4

Perhaps the first value is the most accurate. From this, the value of k_d/k_1 can be evaluated as 0.51×10^{-5} (as has already been described). Although this is not very reliable, chiefly because of the assumption about k_t and φ, it is certain that the reaction between leuco-uranine and the triplet state of acridine occurs quite rapidly, the quantum yield in favorable conditions, being chiefly determined by φ. If one tentatively assumes $k_d=10^4$ sec^{-1}, then k_1 is ca. 2×10^9 sec^{-1} l. mol^{-1}.

Summary

The acridine-sensitized photoöxidation of leuco-uranine in the deareated aqueous solution was studied kinetically. It was established that about 0.24 of the excited acridine molecules goes to the triplet state and then reacts with leuco-uranine. In favorable conditions, the quantum yield is near 0.20, which shows that the genuine reaction rather predominates over the deactivation process of the triplet state.

The pH value dependence of the rate was successfully interpreted from the assumption that each of the different molecular species has a different rate constant.

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