Fluorescein-photosensitized Furan Oxidation in Methanolic and Reversed Micellar Solutions, Part II

Kinetic Analysis

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The 1,3-diphenylisobenzofuran oxidation was investigated in methanolic and dodecylammonium propionate reversed micellar solutions using fluorescein sodium as photosensitizer. The furan oxidation was caused by the singlet oxygen mechanism (Type II). Aniline enhanced remarkably the furan oxidation in methanolic solutions, but inhibited highly this oxidation in the reversed micellar solutions. This enhancement of the furan oxidation was considered to be brought about by the occurrence of a radical mechanism (Type I) besides Type II mechanism. No Type I reaction occurred in the micellar solutions. The rate constants concerning with both reaction processes were evaluated by kinetic analysis, employing various aryl- and alkyl-amines. The reaction mechanism of Type I and the quenching mechanism of singlet oxygen by amines were discussed from the relationship between the rate constants, and the ionization potential of amines and the solvent polarity.

Introduction

In the previous paper [1], we have found that the DF oxidation reaction employing F as photosensitizer was markedly enhanced by aniline in methanolic solutions, whereas it was inhibited in DAP reversed micellar solutions, and proposed that two reaction mechanisms, radical (I) and singlet oxygen mechanisms (II), were involved in the F-photosensitized DF oxidation in methanolic solutions in the presence of aniline. In the present investigation, the DF oxidation in the above reaction system was kinematically analyzed and the main rate constants in the two reaction paths were evaluated. Some rate constants obtained were discussed in relation to the ionization potential of various amines (aryl- and alkylamines). Further, the effect of the solvent polarity on these rate constants was examined in MeOH–H₂O mixed solutions. The reaction control by DAP micelles was also discussed from the results obtained.

Materials and Methods

Alkylamines obtained from Katayama Co. were guaranteed or extra pure reagents. The other chemicals, sample preparations and experimental methods used were described in the previous papers [1].

Results and Discussion

In the previous paper [1], a reaction scheme which is reproduced in Fig. 1 was proposed for the F-photosensitized DF oxidation in methanolic solutions containing F, DF and A, 1F, 1F* and 3F, ground, excited singlet and triplet F’s, respectively; 3O₂ and 1O₂, triplet (ground) and singlet oxygens, respectively; DF(ox), oxidized DF; [F•⁻•A⁺], charge-transfer intermediate; k₁A, rate constant for formation of charge-transfer intermediate between F and A, and DF oxidation by singlet oxygen, respectively; kDF, overall rate constant for DF oxidation by A⁺; k₁, k₂ and k₅, rate constants for quenching of triplet F by A, quenching of triplet F through charge transfer complex, singlet oxygen quenching by A and physical decay of singlet oxygen, respectively; k₅, rate constant for generation of singlet oxygen from triplet oxygen. A, amines; I and II, radical and singlet oxygen mechanisms, respectively.

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Abbreviations: F, fluorescein sodium; DF, 1,3-diphenylisobenzofuran; DAP, dodecylammonium propionate, A, aniline and its derivatives or alkylamines.
photosensitized DF oxidation in methanolic solutions in the presence of amines. This reaction scheme gives the ratio of quantum yields of the DF oxidation in the presence (Φ_A) and absence (Φ) of amines as follows.

\[
\Phi_A = \frac{k_{DF}[DF] + k_d}{\Phi} \quad \frac{k_0[O_2] + (k_{A^R} + k_q)[A]}{k_{DF}(k_{DF}[DF] + k_q)^R + k_{O_2}[O_2] + k_{A}[A] + k_d}
\]

(1)

where \(k_{DF}, k_{A^R}, k_{DF}^R, k_{O_2}, k_A, k_q, k_q^R\) and \(k_d\) are illustrated in the legend of Fig. 1.

In the absence of A, the reciprocal of the quantum yield of the DF oxidation was proportional to the DF concentration obeying the kinetic relation,

\[
\frac{1}{\Phi} = \frac{k_d}{k_{DF}[DF]} + \frac{k_{A^R}[A]}{k_{DF}[DF] + k_{A^R}[A] + k_d}
\]

In the absence of A, the reciprocal of the quantum yield of the DF oxidation was proportional to the DF concentration obeying the kinetic relation,

\[
\frac{1}{\Phi} = \frac{k_d}{k_{DF}[DF]} + \frac{k_{A^R}[A]}{k_{DF}[DF] + k_{A^R}[A] + k_d}
\]

(2)

From eq. (2), \(Φ_A/Φ\) is proportional to the reciprocal of DF concentrations. This linear relation was held for the experimental values obtained in methanolic solutions as shown in Fig. 2. Dividing the slope (m) of the curve by the intercept (b) with the ordinate, the following relation is obtained.

\[
m = \frac{k_{A^R}}{b[A]} = \frac{k_{A^R}}{k_{DF} \cdot k_{O_2}[O_2]} (k_A[A] + k_d).
\]

(3)

From eq. (3), \(m/b[A]\) is proportional to A concentration, and the experimental values also showed this linear relation. Therefore, \(k_A/k_d\) is obtained from (slope)/(intercept), and the \(k_A\) value is determined using \(k_d = 1.4 \cdot 10^8 \text{ s}^{-1}\) [3]. The \(k_{A^R}\) value is evaluated from the intercept \((k_{A^R} \cdot k_d/k_{DF} \cdot k_{O_2}[O_2])\) using the known values of \(k_d, k_{DF} (7.8 \cdot 10^8 \text{ M}^{-1} \text{s}^{-1})\),

The table below summarizes the rate constants in F-sensitized DF oxidation in the presence of various amines and the ionization potential (IP) of amines. \(k_{A^R}\) and \(k_A\) (MeOH), rate constants in methanolic solutions for charge-transfer complex formation between F and A, and for singlet oxygen quenching by amines, respectively; \(k_A\) (DAP), rate constant in DAP reversed micellar solutions for singlet oxygen quenching by amines; \(k_{DF}\), rate constant for DF oxidation with singlet oxygen.

<table>
<thead>
<tr>
<th>Amines</th>
<th>(k_{A^R}) (10^8 M^{-1} s^{-1})</th>
<th>(k_A) (MeOH) (10^8 M^{-1} s^{-1})</th>
<th>(k_A) (DAP) (10^8 M^{-1} s^{-1})</th>
<th>IP* (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>3.13</td>
<td>19.70</td>
<td>0.39</td>
<td>—</td>
</tr>
<tr>
<td>N-methylaniline</td>
<td>1.71</td>
<td>8.00</td>
<td>0.55</td>
<td>7.30</td>
</tr>
<tr>
<td>Dimethylaniline</td>
<td>4.08</td>
<td>11.98</td>
<td>0.33</td>
<td>7.10</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>2.36</td>
<td>1.68</td>
<td>3.05</td>
<td>8.01</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>2.77</td>
<td>4.01</td>
<td>5.50</td>
<td>7.50</td>
</tr>
<tr>
<td>1,4-Diazabicyclo[2,2,2]octane</td>
<td>6.44</td>
<td>5.43</td>
<td>5.03</td>
<td>7.52</td>
</tr>
<tr>
<td>Pyrrolidine</td>
<td>2.04</td>
<td>0.65</td>
<td>1.93</td>
<td>8.30</td>
</tr>
<tr>
<td>β-Phenethylamine</td>
<td>1.63</td>
<td>0.53</td>
<td>0.40</td>
<td>—</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>0.32</td>
<td>0.29</td>
<td>0.46</td>
<td>8.86</td>
</tr>
</tbody>
</table>

* From Franklin et al. [8].
ko² (1.6 × 10⁹ M⁻¹s⁻¹ [4]) and the oxygen concentration of 2 × 10⁻³ M [5]. The above ko² value is the rate constant for the quenching of the F-triplet state by O₂. But, here it was used as the upper limit of the rate constant for the ¹O₂ production, because no established value for this rate constant is known.

The kₐ₂ and kₐ values in methanolic solutions were obtained in the presence of various amines and are given in Table I. Next, in DAP micellar solutions, the k_DF value was evaluated to be 5.3 × 10⁻⁹ M⁻¹s⁻¹ according to the same procedure as stated above in methanolic solutions, using kₐ = 5.9 × 10⁴ s⁻¹ in cyclohexane [3]. Since the DF concentration used was 1.0 × 10⁻⁵ M, k_DF[DF] < kₐ. Therefore, eq. (2) is obtained with the same assumption stated in methanolic solutions. However, the experimental values of Φₐ/Φ was independent of the reciprocal of DF concentration. This means that kᵣ in eq. (2) was zero or very small. Namely, no Type I reaction occurred in DAP micellar solutions and the DF oxidation was caused by the Type II process. This is also justified from the following consideration. Since the aggregation number of the DAP micelle with the water content of 0.2 M in the present investigation is estimated to be about 8 [6], the micellar concentration was about 1.0 × 10⁻² M [7] (DAP concentration used, 8.0 × 10⁻² M). The concentrations of F and A were 3.6 × 10⁻⁶ and ≤ 7.2 × 10⁻⁶ M, respectively. Accordingly, most of A-bound micelles seem to bind no F. Some A may be present in cyclohexanic phase. Such fractionation of A and F may prohibit the occurrence of the radical process (Type I). Further, even when both F and A are bound to the same micelle and the charge-transfer interaction between them is allowed, it may be difficult for A⁺ to escape from DAP micelle into apolar cyclohexanic phase to react with DF. For these reasons, the Type I reaction may hardly occur, and only the Type II process seems to be responsible for the DF oxidation. Then, the first term in eq. (1) is vanished. Eq. (2) is represented with the assumption of ko²[O₂] ≫ kₐ[A] as follows.

\[
\frac{\Phi_A}{\Phi} = \frac{k_4}{k_A[A] + k_4}
\]

or,

\[
\left(\frac{\Phi_A}{\Phi}\right)^{-1} - 1 = \frac{k_A}{k_4} [A].
\]

The experimental values of [(Φₐ/Φ)^⁻¹ - 1] were plotted against [A] as shown in Fig. 3. The slopes of these curves give kₐ/kₐ. Using the kₐ value described above, kₐ was evaluated. The kₐ values obtained for various amines are given in Table I. The ionization potentials of amines are also given in this Table. These rate constants tend to decrease in the order of tertiary, secondary, primary amines although some exception can be seen. The kₐ values for arylamines are larger in methanolic solutions than in DAP micellar ones, but those for alkyl-
Table II. Comparison of slope values obtained from curves of log $k_{AR}$ or log $k_A$ vs ionization potential (IP) of amines with those estimated in various reaction systems. $k_{AR}$, rate constant for the formation of charge-transfer intermediate between sensitizer and amines; $k_A$, rate constant for singlet oxygen quenching by amines.

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Amine</th>
<th>Solvent</th>
<th>Slope (eV⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescein</td>
<td>Alkyl</td>
<td>Methanol</td>
<td>(From log $k_{AR}$ vs IP curve)</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>Aryl</td>
<td>Methanol</td>
<td>−0.92</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>Alkyl</td>
<td>Benzene, cyclohexane</td>
<td>−1.68</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>Aryl</td>
<td>Benzene, cyclohexane</td>
<td>−1.24* [9]</td>
</tr>
<tr>
<td>Flourenone</td>
<td>Aryl, alkyl</td>
<td>Cyclohexane</td>
<td>−2.45* [9]</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>Alkyl</td>
<td>Methanol</td>
<td>−3.30* [10]</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>Alkyl</td>
<td>DAP cyclohexanic micelle</td>
<td>−1.75 ± 0.11 [11]</td>
</tr>
<tr>
<td>Rubrene</td>
<td>Alkyl, aryl</td>
<td>Chloroform</td>
<td>−1.77* [12]</td>
</tr>
<tr>
<td>Rose bengal</td>
<td>Alkyl, aryl</td>
<td>Methanol</td>
<td>−1.39* [13]</td>
</tr>
<tr>
<td>Photophysically</td>
<td>Alkyl</td>
<td>Freon-113</td>
<td>−1.37* [14]</td>
</tr>
<tr>
<td>Photophysically</td>
<td>Aryl</td>
<td>Freon-113</td>
<td>−1.07* [14]</td>
</tr>
</tbody>
</table>

* Calculated from the curves obtained by authors indicated.

Amines are rather smaller in the former solutions than in the latter.

The log of $k_{AR}$ was plotted against the ionization potential (IP) of amines as shown in Fig. 4. The plots fell on two straight lines with the slopes of $-1.68$ eV⁻¹ for arylamines and $-0.92$ eV⁻¹ for alkylamines. Cohen [9] has obtained the linear relation between the log of the quenching rate constant ($k_A$) of amines for triplet benzophenone and fluorenone, and the ionization potential of amines. He proposed the following relation between log $k_A$ and IP.

$$\log k_A = \Delta G_{ET} = IP(D_0) - E(A_c/A_e) - \frac{3}{2}E(A_c) - e_0/\varepsilon a, \quad (7)$$

where $\Delta G_{ET}$, IP($D_0$), $E(A_c/A_e)$, $\frac{3}{2}E(A_c)$, $e_0$, $\varepsilon$ and $a$ are free energy change, ionization potential of amines (donor, $D_0$), oxidation-reduction potential of acceptor ($A_c$), triplet energy of acceptor, electron charge, solvent dielectric constant and encounter distance, respectively. The slope values obtained by us are compared with those calculated from the data obtained by various authors in Table II. The slope value for the complete electron transfer from donor to acceptor is known to be very large such as $-17$ eV⁻¹ [15]. The low absolute values in Table II suggest the occurrence of partial charge-transfer between triplet F and amines. The slope for arylamines is greater than that for alkylamines (Table II). This means that arylamines are more sensitive to the ionization potential. Further, the ionization potential of arylamines is smaller than that of alkylamines. From these points, the ability for the formation of charge-transfer intermediate between F and A is presumed to be higher in arylamines than in alkylamines. However, the $k_{AR}$ values for the former amines were higher than those for the latter as seen in Table I. This may be due to the degree of the overlapping of the filled orbital of the electron donor and the unoccupied orbital of the electron acceptor, and the lifetime of the charge-transfer intermediate which depends on the donor and acceptor species. Cohen et al. [9] and Kayser and Young [11] have discussed about the relation between the rate constant for the formation of charge transfer complex and the ionization potential of amines in benzophenone- or methylene blue-sensitized photooxidation.

The linear relation between the $k_A$ values and the ionization potential of amines, and the low slope values of the curves were also observed in methanolic solutions (Table I and Fig. 4), suggesting that the quenching of singlet oxygen by amines may proceed through a partial charge-transfer intermediate such as $[1^0O_2 \cdots \cdot A^-]$. The $k_A$ values in DAP solutions were higher than those in methanolic solutions in high ionization potential range, but they deviated largely from the straight line of log $k_A$ vs ionization potential relation in low ionization potential range. This might be due to the state of existence of amines in the heterogeneous reaction mixtures. As shown in eq. (7), the rate constants ($k_{AR}$, $k_A$ and $k_{DP}$) depend on the solvent polarity. These rate constants...
were determined in MeOH–H₂O mixed solutions, changing the mole % of H₂O. The plot of log kₐ, log kₐ or log kₐD against the reciprocal of the dielectric constant [16] of the solvent showed a straight line as expected in eq. (7).

In the previous paper [1], we reported that the DF oxidation rate in the presence of aniline was larger in N₂-bubbled methanolic solutions than that in air-bubbled ones. Namely, the DF oxidation in the presence of aniline proceeded more effectively under the circumstance of lower oxygen concentrations. This is understood from the proportionality of \( \Phi_A \) in eq. (1) to the reciprocal of the \( O_2 \) concentration, when \( k_{O_2}[O_2] > (k_{AR} + k_\Phi)[A] \).

In conclusion, the F-sensitized photooxidation of DF oxidation was driven with Type I and II mechanisms in methanolic solutions. However, in DAP reversed micellar solutions, DAP micelles controlled this photooxidation to inhibit Type I reaction, possibly due to the fractionation of reactant molecules in micellar systems. Such reaction control by micelles may give a clue to understand various reaction mechanisms held in the heterogeneous systems such as biological ones.