An Efficient Regeneration of Singlet Oxygen from 2,5-Diphenylfuran Endoperoxide Produced by a Dye-Sensitized Oxygenation

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The maximum quantum yield of 4.5 was evaluated from the kinetic analysis for the Methylene Blue-sensitized oxygenation of 2,5-diphenylfuran, and the contribution of a chain process to produce the furan endoperoxide was suggested. After the photoreaction, the thermolysis of the endoperoxide occurred to regenerate 2,5-diphenylfuran and singlet oxygen and to produce *cis*-1,2-dibenzoylethylene simultaneously. The activation energy of singlet oxygen recovery was estimated to be 18.5 kcal mol^{-1}. The reversible conversion of singlet oxygen took place efficiently with thiazine and xanthene dyes. A concerted dissociation of singlet oxygen from the endoperoxide was supposed from the negative value of activation enthropy (−9.8 e.u.) for the reaction.

Singlet oxygen($^1O_2$) is one of the active oxygen species which are utilized for synthetic chemistry with oxidative reactions and which affect the photodynamic action in the field of photobiology and photomedecine.[1] Since these active species of $^1O_2$, $O_2^{-}\cdot$, $OH\cdot$, H_2O_2, etc., are of a high-energy compound thermodynamically and are interconvertible with each other through the respective oxidation and reduction processes, the photochemical formation of $^1O_2$ is significant in the performance on various reactions of the up-hill type upon free energy change.

Provided that the $^1O_2$ formed with a photosensitized reaction is once trapped and stored, and is then regenerated in the dark, such a phenomena of $^1O_2$ formation will show a fascinating feature of the reversible conversion with light energy; visible light can be efficiently used for $^1O_2$ formation by means of an energy transfer from the triplet organic dyes without the decomposition of sensitizers. Choosing 2,5-diphenylfuran (DPF) as an efficient acceptor for the $^1O_2$ formed photochemically, we found the quantum yields on the DPF oxygenation which exceeded the intersystem crossing probability of the triplet sensitizers.

In the present paper, the reaction mechanism of the efficient oxygenation of DPF has been discussed. Then, the decomposition of the product of DPF endoperoxide, resulting in the regeneration of $^1O_2$ has been kinetically investigated.

Experimental

Materials. All the organic dyes (G.R. grade) of Methylene Blue ($C_{16}H_{18}N_3SCl$; MB), Thionine ($C_{12}H_{20}N_3SCl$; Th), Eosine Y ($C_{20}H_6O_5Br_4Na_2$; EY), Erythrosine B ($C_{20}H_6O_5I_4Na_2$; Ery), and Rose Bengal ($C_{20}H_2O_5I_4Cl_4Na_2$; RB) were recrystallized twice from ethanol. The 2,5-diphenylfuran(Tokyo Kasei Co., G.R.) and 1,3-diphenylisobenzofuran(Aldrich Co., G.R; DPBF) and all the solvents (Kanto Kagaku Co., G.R.) of acetonitrile, methanol, chloroform, 1,1,2,2-tetrachloroethane, etc. were used as received.

Procedures. An iodometry reported for the similar compounds was used to determine the amount of DPF-peroxide.[2,3] The extinction coefficient of I_3^- in acetonitrile was 2.55×10^4 M^{-1} cm^{-1} (1 M=1 mol dm^{-3}) at the peak of 363 nm. The sensitized oxidation of DPF and DPBF was monitored with an usual cross-illumination apparatus, as has been reported previously.[4] After the irradiation within a few minutes, the recovery of DPF was also monitored by means of the same apparatus for several tens of minutes in the dark. The photobleaching of MB in an air-saturated aqueous solution was used as a chemical actinometer (the quantum yield: 4.5×10^{-5}) to obtain the light intensity from a 300W tungsten lamp and to estimate the quantum yield of DPF oxidation (Φ).[5] For the spectral and kinetical analyses of the reactions, a system composed of a spectrophotometer (Hitachi, 200-10), a microcomputer(NEC, PC8801), and a digitizer(Mitablet) was used.

In the kinetical analysis of the present photochemical reaction, the rapid irradiation with a higher intensity has to be performed at low temperatures in order to avoid the influence of the thermal decomposition during irradiation.

Results and Discussion

DPF Concentration Effect on the Quantum Yield, Φ. The singlet oxygen($^1O_2$) which is produced by the energy transfer from the triplet sensitizer(^{3}Sens) decays to the ground state molecule($^3O_2$) in a solution or reacts with the added DPF to produce the endoperoxide(DPFO$_2$) competetively. The scheme for such reactions has already been reported to be as follows:[4,6–10]

$$^3\text{Sens} \longrightarrow {}^1\text{Sens} \qquad (1)$$

$$^3\text{Sens} + {}^3O_2 \longrightarrow {}^1\text{Sens} + {}^1O_2 \qquad (2)$$

$$^1O_2 \longrightarrow {}^3O_2 \qquad k_d \qquad (3)$$

$$^1O_2 + \text{DPF} \longrightarrow \text{DPFO}_2 \qquad k_q \qquad (4)$$

Scheme 1.

According to the above essential scheme, the initial quantum yield of DPF oxygenation(Φ) is expressed as Eq. 5:

$$\Phi = \Phi_{\mathrm{so}}\frac{[\mathrm{DPF}]}{\beta_{\mathrm{DPF}}+[\mathrm{DPF}]} \qquad (5)$$

where Φ_{so} and β_{DPF} stand for the $^1O_2$ formation yield from ^{3}Sens and the rate parameter of k_d/k_q respectively. From the linear relationship between $1/\Phi$ and $1/[\mathrm{DPF}]$, the reactivity index, β_{DPF}, can be estimated.[4,6] The experimental results for the DPF concentration effect on Φ is shown in Fig. 1. Although the Φ_{so} value for the sensitizer of MB is 0.52, the Φ value at higher concentrations of DPF exceeds Φ_{so}, and its limitation goes up to about eight times of the Φ_{so} value.[11] The amounts of peroxide produced photochemically were determined by means of iodometry; they are listed in Table 1. Although the thermal decomposition of the unstable endoperoxide occurred during irradiation, and thus the amounts of the peroxide decreased at higher temperatures (>25 °C), it was shown that the added DPF changed completely to the peroxide, as is shown in Fig. 1. These results suggest that Eq. 5 cannot be adopted and that DPF might be oxygenated through a chain-reaction process. Since the effect of temperature (0—55 °C) on Φ values was not observed under the present experimental conditions, it seems that the chain cycles for DPF oxygenation proceed rapidly without an activation energy and that the thermal decomposition of the product can also be neglected at the initial stage of irradiation.

Thus we can tentatively introduce a mechanism in which the thermically activated state or intermediate ($DPFO_2^*$) reacts with DPF, competing with its own deactivation. The activated state, DPF*, is oxygenated by dissolved oxygen via Eqs. 7—9. This chain mechanism is shown as Scheme 2:

$$\begin{array}{rcllr}
{}^3\mathrm{Sens} & \longrightarrow & {}^1\mathrm{Sens} & & (1)\\
{}^3\mathrm{Sens} + {}^3O_2 & \longrightarrow & {}^1\mathrm{Sens} + {}^1O_2 & \Phi_{\mathrm{so}} & (2)\\
{}^1O_2 & \longrightarrow & {}^3O_2 & k_d & (3)\\
{}^1O_2 + \mathrm{DPF} & \longrightarrow & \mathrm{DPFO_2^*} & k_q & (4)\\
\mathrm{DPFO_2^*} & \longrightarrow & \mathrm{DPFO_2} & k_1 & (6)\\
\mathrm{DPFO_2^*} + \mathrm{DPF} & \longrightarrow & \mathrm{DPFO_2'} + \mathrm{DPF^*} & k_2 & (7)\\
\mathrm{DPF^*} & \longrightarrow & \mathrm{DPF} & k_3 & (8)\\
\mathrm{DPF^*} + {}^3O_2 & \longrightarrow & \mathrm{DPFO_2^*} & k_4 & (9)
\end{array}$$

Scheme 2.

The activated intermediates of $DPFO_2^*$ and DPF* act as chain carriers, and the chain cycle is involved by means of Eqs. 7 and 9 as long as sufficient DPF exists. $DPFO_2^*$ produces the endoperoxide($DPFO_2$), competing with the reverse reaction of Eq. 4. $DPFO_2'$ is tentatively assumed to be the peroxide which produces *cis*-1,2-dibenzoylethylene(DBE) via a thermal decomposition as will be described below. In the studies of the reactivity of $^1O_2$ for endoperoxide formation, the existence of such intermediates as an addition complex or a π complex between $^1O_2$ and an acceptor was frequently assumed.[6,12,13] These complexes can be assigned to the $DPFO_2^*$ and $DPFO_2'$ in Scheme 2. Although $DPFO_2$ regenerated $^1O_2$ and DPF thermically after the irradiation, the degree of DBE formation against the thermal recovery of DPF became small, after irradiation when the initial concentration of DPF was low ([DPF]<20 μM). When the irradiation procedures after the thermal recovery of DPF from $DPFO_2$ were repeated, the added DPF changed to DBE quantitatively. These results are consistent with Scheme 2.

Table 1. Temperature Effect on the Amounts of DPF-Peroxide

Temperature	Concentration(/10^{-4} M) of	
°C	reacted DPF	produced $DPFO_2$
55	1.18	0.344
35	1.18	0.639
25	1.06	0.831
15	1.18	1.01
5	1.18	1.05
−2	1.06	0.92
−7	1.06	1.03
−11	1.06	1.03

$[\mathrm{MB}]=10\,\mu\mathrm{M}$, $[\mathrm{DPF}]_0=120\,\mu\mathrm{M}$, in CH_3CN.

The quantum yield of DPF disappearance, Φ_C, which is derived by applying the stationary-state method to ^{3}Sens, $^1O_2$, and these activated intermediates in Scheme 2, can be expressed as in Eq. 10:

$$\Phi_C = \Phi_{\mathrm{so}}\frac{[\mathrm{DPF}]}{\beta_{\mathrm{DPF}}+[\mathrm{DPF}]}\left(1+(1-r)\frac{k_2[\mathrm{DPF}]}{k_1+rk_2[\mathrm{DPF}]}\right) \qquad (10)$$

where $r=k_3/(k_3+k_4[O_2])$; i.e., r means the degree of DPF* deactivation of Eq. 8 in competition with the process of Eq. 9. Under the conditions of $k_1/k_2 \gg [\mathrm{DPF}]$, the expression of Φ_C coincides with Eq. 5, which is the equation of Φ without the chain process. Further, the rate of the photochemical oxygenation of DPF was analyzed as a first-order reaction under the approximate condition of $\beta_{\mathrm{DPF}} \gg [\mathrm{DPF}]$, and the rate constant was found to be inversely proportional to β_{DPF}. In the case of the DPBF oxygenation, β_{BF} in acetonitrile, which stands for the rate parameter of k_d/k_q' for the reactions, was similarly obtained as 1.26×10^{-5} M at 20 °C. From the comparison of the rate constants for the DPF and DPBF oxygenations, the β_{DPF} value for DPF in acetonitrile (8.3×10^{-5} M) can be estimated.[4] By substituting the k_d value ($=3\times10^4\ \mathrm{s}^{-1}$ in acetonitrile) into the β_{DPF}, k_q was obtained as $3.7\times10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.[4,6,9,14]

On the other hand, at the higher concentration of DPF ($[\mathrm{DPF}] \gg k_1/k_2$), Φ_C can be approximately written as in the following equation:

$$\Phi_C = \Phi_{so}\frac{[DPF]}{\beta_{DPF}+[DPF]}\frac{1}{r}$$
$$= \Phi_{so}\frac{1}{r} = \Phi_{max}\ (\beta_{DPF}\ll[DPF]) \qquad (11)$$

Therefore, a linear relationship between $1/\Phi$ and 1/[DPBF] was derived from Eq. 11 over the DPF concentration of 20 μM, as is shown in Fig. 1: i.e, the reciprocal plot holds approximately with Eq. 11, but with Eq. 5. From the interception in Fig. 1 a maximum value of Φ_C(Φ_{max}) was obtained as 4.5. The β_{DPF} value of 6.9×10^{-5} M was obtained from the interception and the slope. By substituting the Φ_{max} value into Eq. 11, the r value of 0.116 is obtained. This suggests that DPF* reacts with $^3O_2$ as an efficient chain carrier in Eq. 9.

Incidentally, the following numerical equation is shown as a dotted line in Fig. 1:

$$\Phi_C(\text{calcd}) = \frac{0.52[DPF]}{6.9\times10^{-5}+[DPF]} \times\left(1+\frac{0.884[DPF]}{1.7\times10^{-6}+0.116[DPF]}\right) \qquad (12)$$

From this equation, which is drawn to coincide with the experimental data, the ratio of the rate constants ($k_1/k_2=1.67\times10^{-6}$ M^{-1}) was obtaind using the r value of 0.116. Thus, at the higher concentrations of DPF$\gg k_1/k_2$($=1.67\times10^{-6}$ M), it seems that DPFO$_2$* reacts with DPF predominantly and that the chain reaction occurs efficiently.

Recovery Process of DPF from the Endoperoxide. It has been reported that the endoperoxides are unstable and that the thermal decomposition occurs easily.[2,15,16] In order to clarify the reaction mechanism of the decomposition from the point of view of $^1O_2$ regeneration, a kinetic investigation was carried out. By measuring the UV-spectral change of the sample immediately after irradiation, it was confirmed that the regeneration of DPF occurred by means of the DPFO$_2$ decomposition in the dark. Simultaneously, *cis*-1,2-dibenzoylethylene(DBE) with the absorption maximum at 265 nm was produced as is shown in Fig. 2.[2] After irradiation at a higher concentration of DPF (10—300 μM) and at a lower temperature (0—20 °C), the percentage recoveries of DPF and DBE to the added DPF concentration were 55 and 40% in acetonitrile respectively. At lower concentrations of DPF(<10 μM), the percentage recovery of DPF increased, but that of DBE decreased to some extent.

The rate of DPF recovery could be apparently analyzed as first-order with the peroxide concentration, which was estimated as the value of [DPF]$_{max}$−[DPF] from the maximal recovery of DPF, ([DPF]$_{max}$):

$$\ln([DPF]_{max}-[DPF]) = \ln[DPF]_{max}-k_rt \qquad (13)$$

Similarly, the DBE formation was also analyzed as a first-order reaction. The rate constants were $7.0(\pm0.2)\times10^{-4}$ s^{-1} for DPF (k_r) and $6.9(\pm0.2)\times10^{-4}$ s^{-1} for DBE respectively at 25 °C. The initial rates for the recovery were not influenced by the DPF concentration. Provided that the back reaction of Eq. 14 occurred, the kinetic treatment on DPF should deviate from the first order analysis of Eq. 13:

$$DPFO_2 \longrightarrow DPF + {}^1O_2 \qquad k_r \qquad (14)$$
$${}^1O_2 \longrightarrow {}^3O_2 \qquad (15)$$

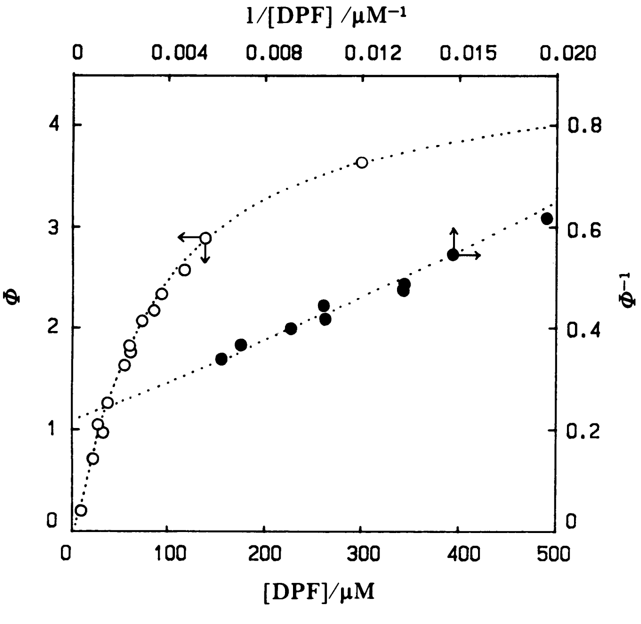


Fig. 1. DPF concentration effect on the oxidation yield, Φ in acetonitrile. (Dotted line: Eq. 12 in text) [MB]: 5 μM; 5 °C.

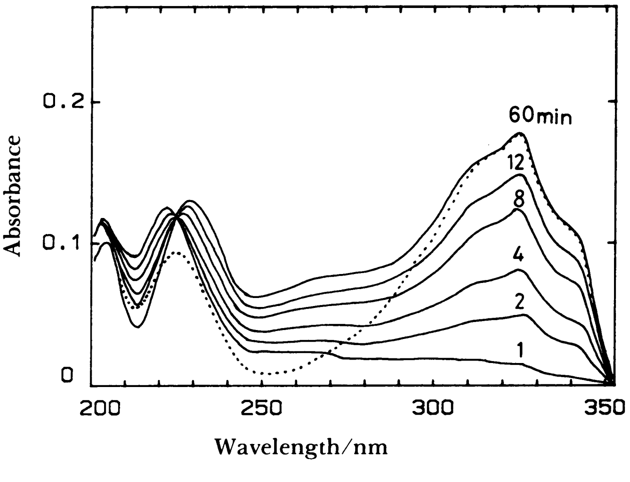


Fig. 2. UV-spectral change for DPF-recovery and DBE formation processes after irradiation in acetonitrile. (Dotted line: Spectrum of DPF in which the absorption was normalized at a peak after 60 min-recovery) [MB]: 5 μM; [DPF]: 10 μM; 50 °C.

However, when the stationary concentration of $^1O_2$ is low (about 30% for the $DPFO_2$ concentration), Eq. 13 approximately holds in a computer simulation for the concentration change in each component, even if both the equilibrium for Eq. 14 and the competitive reactions of Eq. 15 are involved. Since $^1O_2$ is deactivated by acetonitrile, it seems that a first order reaction of Eq. 13 was practically observed under the present conditions.

From the temperature effect on the rate constants of DPF recovery and DBE formation, the apparent activation energies (EA) were obtained as 18.5±0.5 kcal mol^{-1}(DPF) and 17.0±0.5 kcal mol^{-1}(DBE) respectively. These values are smaller than those in the cases of the endoperoxides of anthracene derivatives(for example; 9,10-diphenylanthracene endoperoxide: 27.8 kcal mol^{-1}, rubrene endoperoxide: 32.6 kcal mol^{-1}).[17-19] By reference to the behavior of the endoperoxide of 3-(4-methyl-1-naphthyl)propionic acid, which has been reported to have the EA value of 17 kcal mol^{-1}, DPF recovery was actually observed even at room temperature.[20]

It has been reported that the decomposition mechanism of the furan endoperoxides was dependent on the solvent.[16] In alcohol, the addition of a solvent to $DPFO_2$ produces the hydroperoxide. Hardly no DPF recovery was observed in methanol, ethanol, and 1-propanol, etc. In the mixture of acetonitrile and heptane or ethyl acetate, a good DPF recovery was observed, since the reaction of Eq. 14 occurs successively as a result of the rapid deactivation of $^1O_2$ in these solvents. However, in the solvent mixture of acetonitrile and 1,1,2,2-tetrachloroethane, though the rate of DPF recovery was increased to some extent, the amount of recovery was decreased, as is shown in Table 2. This means that the back reaction in Eq. 14 was not neglected during the recovery, since the lifetime of $^1O_2$ is longer in 1,1,2,2-tetrachloroethane or carbon tetrachloride.[8,21-23]

Regeneration of Singlet Oxygen. DPBF reacts rapidly and specifically with $^1O_2$, without being complicated by any side reactions. In order to check experimentally whether or not $^1O_2$ was produced in the DPF recovery process, DPBF was added to the sample immediately after the irradiation. For the kinetical treatment to $^1O_2$ and the DPBF reaction, the following scheme can be introduced:

$$
\begin{array}{rcllr}
DPFO_2 & \longrightarrow & DPF + {}^1O_2 & k_r & (14)\\
{}^1O_2 & \longrightarrow & {}^3O_2 \text{ (in } CH_3CN) & k_d & (15)\\
{}^1O_2 + DPBF & \longrightarrow & DPBFO_2 & k_q' & (16)
\end{array}
$$

Scheme 3.

Since $^1O_2$ is easily deactivated in acetonitrile, and also since DPBF traps $^1O_2$ in competition with the deactivation, the reaction rate of DPBF in Scheme 3 can be analyzed as in Eqs. 17 and 18 under the assumption of the stationary state method for [$^1O_2$], using the relation of $[DPFO_2]=[DPFO_2]_0\exp(-k_rt)$. The reaction probability between DPBF and $^1O_2$ was assumed to be unity.[8,9] The β_{BF} value($=k_d/k'_q$) and the k_r value for the DPF recovery reaction in acetonitrile were used in Eq. 18, which was the integrated equation to Eq. 17:

$$-\frac{d[DPBF]}{dt} = k'_q[{}^1O_2][DPBF] \tag{17}$$

$$\begin{aligned}\beta_{BF}\ln[DPBF] + [DPBF]\\ &= \beta_{BF}\ln[DPBF]_0 + [DPBF]_0\\ &\quad - [DPFO_2]_0(1-\exp(-k_rt))\end{aligned} \tag{18}$$

The linear relationship in Eq. 18 is shown in Fig. 3. Since the slope in Fig. 3 was equal to $[DPFO_2]_0$, the initial concentration of $DPFO_2$ which produced $^1O_2$ was calculated to be 60 μM under the present conditions; the amount was approximately equal to the recovered DPF concentration. Accordingly, it can be suggested that the $^1O_2$ regenerated in Eq. 14 was

Table 2. Solvent Effect on the Recovery Rate and Amounts of DPF (25°C)[a]

Solvent χ_{TeCE}[b]	$k_r/10^{-4}$ s^{-1}	Recovered [DPF]/μM (percent recovery)
0	7.01	15.3 (54.9)
0.048	6.5	13.7 (49.0)
0.13	10.1	10.6 (37.1)
0.20	10.4	10.0 (36.0)
0.30	12.0	7.6 (27.1)

a) [MB]=5 μM, [DPF]=27.9 μM. b) Molar fraction of 1,1,2,2-tetrachloroethane.

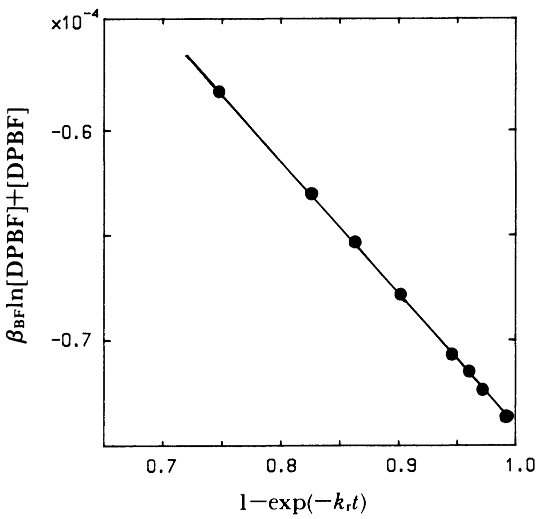


Fig. 3. Kinetic treatment for oxygenation of DPBF with $^1O_2$ regenerated by the thermal decomposition of $DPFO_2$ at 45 °C. (The values for k_r of 1.59×10^{-2} and for β_{BF} of 1.99×10^{-5} are used in Eq. 18.) [MB]: 5 μM; [DPF]: 68 μM; [DPBF]: 49 μM.

reacted with DPBF as is shown in Scheme 3. Provided that DPF and DBE were simultaneously produced from $DPFO_2$, the k_r value in Eq. 18 must be a sum of the rate constants of the formations of DPF and DBE. Putting the sum value into k_r, the plot in Fig. 3 is not expressed as a linear relationship. Thus, as is shown in Scheme 2, it may be supposed that the peroxide which leads to DPF and $^1O_2$ regeneration is not the same as that in the DBE formation.

The possibility of the direct reaction of DPBF with $DPFO_2$ might be considered instead of Eqs. 14—16:

$$DPFO_2 + DPBF \longrightarrow DPF + DPBFO_2 \qquad (19)$$

However, the above reaction was obviated by the facts that the DPF recovery rate was not analyzed as exemplifying the second order kinetics in the case of DPBF addition, and that the reaction rate of DPBF becomes faster in the solvents mixed with the 1,1,2,2-tetrachloroethane or carbon tetrachloride, where the lifetime of $^1O_2$ is longer and where the reaction of Eq. 16 predominates.

Confirming that $^1O_2$ was regenerated as an equivalent molar with DPF, the molar ratio of the reacted DPBF against the recovered DPF was calculated under a higher concentration of DPBF (260 μM). The ratio was 0.65 at 20 °C, but became 0.99 at a temperature higher than 50 °C, where an equimolar production of DPF and $^1O_2$ was confirmed, as is shown in Scheme 3.

A detailed mechanism for the release of $^1O_2$ by the thermal decomposition of the endoperoxides of anthracene derivatives was discussed by Turro et al. They checked the temperature effect on the first-order rate constants, k_r for the recoveries of anthracence derivatives. From the analysis of the Eyring plots for the reaction rate, the activation enthropy, $\Delta S^{\ast}$, and the activation enthalpy, $\Delta H^{\ast}$, were calculated (k: Boltzmann's constant; h: Planck's constant):[24)]

$$\ln k_r - \ln T = \ln(k/h) + (\Delta S^{\ast}/R) + (\Delta H^{\ast}/RT) \qquad (20)$$

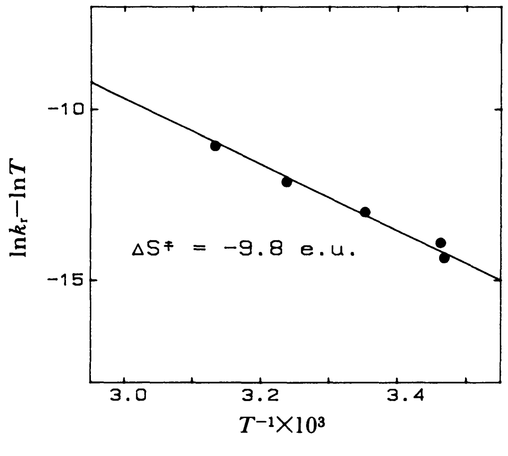
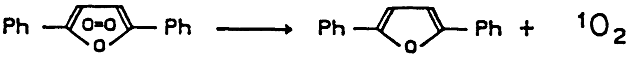


Fig. 4. Estimation of activation entropy for $^1O_2$ formation from $DPFO_2$ in acetonitrile. (Eyring plots) [MB]: 5 μM; [DPF]: 28 μM.

Since the $\Delta S^{\ast}$ values obtained for the endoperoxides of 1,4-dimethyl-9,10-diphenylanthracene and of 1,4-dimethoxy-9,10-diphenylanthracene were comparatively small(i.e., zero or negative), they reported that the $^1O_2$ production from these endoperoxide occurs in the manner of the concerted dissociation of the coupled C–O bonds. For such anthracene endoperoxides as 9,10-diphenylanthracene, which provided the positive values of $\Delta S^{\ast}$, C–O bonds dissociate in a step-by-step fashion, and the peroxide radicals are produced. If the parallel spin-state is involved in the process of the positive $\Delta S^{\ast}$, $^3O_2$ will be produced, and then the yield of $^1O_2$ will decrease.

In the present case of DPF formation, the kinetical results were similar to these for anthracene endoperoxides with a negative $\Delta S^{\ast}$. The $\Delta S^{\ast}$ and $\Delta H^{\ast}$ values from the Eyring plots for the reaction were −9.8 e.u. and 18.9 kcal mol^{-1} respectively, as is shown in Fig. 4. According to Turro's model, it may be considered that the following concerted dissociation on $DPFO_2$ operates for the $^1O_2$ formation:



Quantum Efficiency for Single Oxygen Conversion. At higher concentrations of DPF, about 55 percent of the DPF was recovered and an equimolar amount of $^1O_2$ was regenerated at 50 °C in the dark. If significant reactions with regenerated $^1O_2$ occur successively, the recovery reaction can be utilized as a chemical storage of $^1O_2$ from the sensitization by the use of solar-light energy, since $DPFO_2$ is stable at a lower temperature(<0 °C). In order to increase the efficiency of $^1O_2$-trapping and the conversion of light energy, the following conditions are required practically: (1) The initital concentration of DPF must be larger than the β value in order to trap the $^1O_2$ completely at the photochemical stage. (2) The sensitized reaction should be performed at a lower temperature (<0 °C) and with a higher light intensity to avoid the decomposition of the $DPFO_2$ produced during irradiation.

The conversion efficiency, γ, of $^1O_2$ reproduced in the dark can be defined as the ratio of the total amount of the $^1O_2$ reproduced, $[^1O_2]_\infty$, estimated by means of the amount of recovered DPF, to the total light quantities absorbed in the sample($I_{ab}t$), i.e., $\gamma=[^1O_2]_\infty/I_{ab}t$. In Table 3, the γ values which were obtained by the use of various sensitizers are listed at a constant DPF concentration (150 μM). Higher values were obtained for the sensitizers of MB and Th, which did not bleach durring the irradiation and which were usefully utilized at longer wavelengths. The lower values for xanthene dyes were obtained in spite of the large intersystem crossing probability. Although

Table 3. Quantum Efficiency, γ for the Conversion to $^1O_2$[a)]

Sensitizer	λ_{max}/nm[b)]	Φ_{so}[c)]	γ/%[d)]
Methylene blue	655	0.52	61.5
Thionine	592	0.58	88.9
Eosine Y	538	0.57	11.6
Erythrosine	543	0.68	43.1
Rose Bengal	559	0.83	45.0

a) [DPF]=150 μM. b) Absorption maximum of sensitizer. c) Quantum yield for $^1O_2$ formation. d) $\gamma=[^1O_2]/I_{ab}t$.

these results might be due to the quenching of the dye triplet by DPF, the detailed reason will be investigated in further works.

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