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Mechanism on the Efficient Formation of Singlet Oxygen by Energy Transfer from Excited Singlet and Triplet States of Aromatic Hydrocarbons

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The formation efficiencies of singlet oxygen for the oxygen quenching in excited singlet of aromatic hydrocarbons; A and for the quenching in the triplet T_1; B were estimated. The hydrocarbons were classified into three types: (i) $A=1$ and $B=1$ for dicyanoanthracene i.e., total 200% efficiency, (ii) $A\approx 0.3$ and $B=1$ for anthracene, (iii) $A\approx 0$ and $B=1$ for pyrene, as examples. It is suggested that the energy levels of T_2 and a dissociative exciplex; $(T_1{}^1\Delta_g)$ correlated to A and B values from the energetic considerations.

Singlet oxygen as well as superoxide ion and hydroxyl radicals are the reactive-oxygen species in the oxidation process of biological system. A large number of investigations have been devoted to the study of the singlet oxygen reactivity toward organic substrates and the quantum yield of singlet oxygen formation, Φ_{SO} from different sensitizers, has been obtained from the investigations of the mechanism of the sensitized reaction.[1—8] The maximum quantum yield for some aromatic hydrocarbon sensitizers (M) in which the S_1-T_1 energy gap is larger than 7880 cm^{-1}, was evaluated to be 1—2 and it was suggested that molecular singlet oxygen ($^1\Delta_g$) generated both in the quenching of excited singlet state ($^1M^*$) and triplet state (^3M) of the molecule, i.e., the mechanism could be expressed as follows: [8,9]

$$^1M^* \rightarrow {}^1M + h\nu_F \qquad k_{FO} \qquad (1)$$

$$^1M^* \rightarrow {}^3M \qquad k_{isc} \qquad (2)$$

$$^1M^* + {}^3O_2 \rightarrow {}^3M + {}^1O_2 \text{ (or } {}^3O_2) \qquad k_{SO} \qquad \langle A \rangle \qquad (3)$$

$$^3M \rightarrow {}^1M \qquad k_T \qquad (4)$$

$$^3M + {}^3O_2 \rightarrow {}^1M + {}^1O_2 \text{ (or } {}^3O_2) \qquad k_{TO} \qquad \langle B \rangle \qquad (5)$$

The Φ_{SO} value depends on oxygen concentration since the deactivation processes of $^1M^*$ and ^3M are competitive with the reactions (3) and (5). The maximum value of Φ_{SO} equals to $A+B$ under a sufficiently high concentration of oxygen, where A and B correspond to the formation efficiencies of singlet oxygen in reactions (3) and (5), respectively. In the quenching processes by oxygen, it has been suggested that the exciplexes-intermediate, $(MO_2)^*$ are involved.[10,11] The present paper deals with the estimation of the respective efficiencies A and B, and with the relaxation mechanism of the exciplexes in the processes (2) to (5). It is proposed that the A value is possibly affected by the value of the energy level of the second excited triplet, T_2 of these sensitizers.

Experimental

Materials. Pyrene(Py), 9,10-dicyanoanthracene (DCA), and 1,2,5,6-dibenz[*a,h*]anthracene (DBA) were purified by recrystallization. Anthracene (AN) (Tokyo Kasei(TK), zone-refined), 9,10-dimethylanthracene (DMA) (TK, GR), 1,2-benz[*a*]anthracene (BA) (TK, GR), neoalloocimene (NA) (TK, GR), chrysene (Chr) (Aldrich, GR), rubrene (Rub) (Aldrich, GR), 1,3-diphenylisobenzfuran (DPBF) (Sigma, GR), iodine and cyclohexane (Kanto, GR) were used as received.

Procedures. A fresh sample of sensitizer/O_2/DPBF in cyclohexane was irradiated by a cross-illumination apparatus with a 75 W high-pressure Hg-lamp ($\lambda_{ex}=313$ nm for Py and Chr) and a 150 W Xe-lamp ($\lambda_{ex}=373$ nm for anthracene derivatives) at 25 °C, using interference filters. The incident light intensity was measured by potassium trioxalatoferrate(III) actinometry as $I_0=5.5\times10^{-9}$ for Xe-lamp and 1.0×10^{-9} for Hg-lamp (mol cm^{-2} s^{-1}). The wavelength band for excitation, λ_{ex} as well as the concentration ratio of DPBF to sensitizer were selected in order to avoid the light absorption by DPBF. Under the experimental conditions for the concentrations of Py (50 μM) and DPBF (5 μM), the ratio of the DPBF absorbance to that of Py was one-tenth at the excitation wavelength of 313 nm, for example. The disappearance rate of DPBF through self-sensitized oxygenation was negligibly slower than that for the sensitized reaction and the small effect of light absorption by DPBF was corrected on the determinations of the quantum yields on sensitized photooxygenation of DPBF, considering the inner-filter effects for the absorption of sensitizer and DPBF.

The quantum yield of photooxygenation of $^1O_2$ acceptor; DPBF, Φ_{BF} ($=-(d[\text{DPBF}]/dt)/I_{ab}$, no deactivation between $^1O_2$ and DPBF occurs) was expressed as Eq. 6 from the measurement of the DPBF disapperance rate, where I_{ab} is the light quantity absorbed by the sensitizer.

$$\Phi_{BF} = \Phi_{SO}[\text{DPBF}]/(\beta + [\text{DPBF}]). \qquad (6)$$

A β value of 5.7×10^{-5} (1M=1 mol dm^{-3}) was obtained from the analysis of the linear plot between $1/\Phi_{BF}$ vs. 1/[DPBF] in cyclohexane, using Rub as sensitizer. Substituting β and the measured Φ_{BF} values in Eq. 6, Φ_{SO} values were obtained for several sensitizer/O_2/DPBF systems.[9,12—14] By means of a fluorescence-quenching experiment, the rate constants, k_q of the reaction between $^1M^*$ and the quenchers (O_2, NA, and I_2) were estimated from the Stern–Volmer constant, K_{SV} and the relation of $K_{SV}=k_q\tau_f$, where the fluorescence lifetime, τ_f was taken from the literature. The interference caused by the ground state complex of M with the quenchers was negligible regarding the dynamic quenching on $^1M^*$.

Results and Discussion

Oxygen Concentration Effect on Φ_{SO}. According to the reaction scheme (1) to (5), Φ_{SO} is related as follows;

$$\Phi_{SO} = \frac{Ak_{SO}[O_2]}{k_F + k_{SO}[O_2]} + \frac{k_{isc} + k_{SO}[O_2]}{k_F + k_{SO}[O_2]}\,\frac{Bk_{TO}}{k_T + k_{TO}[O_2]} \qquad (7)$$

$$= \frac{AK_{SV}[O_2]}{1 + K_{SV}[O_2]} + \frac{(\phi_{ST} + K_{SV}[O_2])B}{1 + K_{SV}[O_2]}, \quad (k_T \ll k_{TO}[O_2]) \qquad (7')$$

where $k_F = k_{FO} + k_{isc}$. Typical results of oxygen concentration effect on Φ_{SO} are shown in Fig. 1. In the case of Py sensitizer, the maximum value of Φ_{SO} equals 1.05, which corresponds to $A+B$ value from Eq. 7 but in the cases of AN and DCA, Φ_{SO} value seems to be over unity. Combining the equations of $K_{SV} = k_{SO}/k_F$ and $\phi_{ST} = k_{isc}/k_F$ with Eq. 7, we can derive Eq. 8 under the extreme condition of $k_F \ll k_{TO}[O_2]$ in order to estimate A and B values, respectively.

$$\Phi_{SO}(1 + K_{SV}[O_2]) = \phi_{ST}B + (A + B)K_{SV}[O_2] \qquad (8)$$

Since the plots of Eq. 8 hold a good linear-relationship as shown in Fig. 2, we can obtain A and B values from the interception and the slope respectively, substituting ϕ_{ST} and K_{SV} values. Further, substituting A and B values into Eq. 7 and using the other rate parameters for

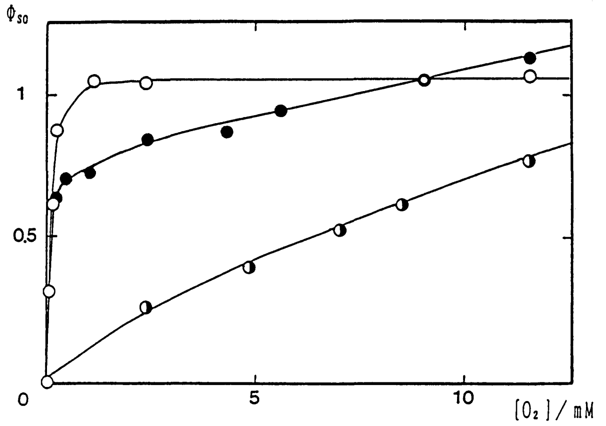


Fig. 1. Oxygen Concentration effect on the Φ_{SO} values in cyclohexane.
(○) Py(50 μM)/O_2/DPBE(5 μM)
(●) AN(200 μM)/O_2/DPBF(5 μM)
(◑) DCA(120 μM)/O_2/DPBF(5 μM)

Table 1. Rate Constants for the Relaxation and Oxygen Quenching of Excited Singlet and Triplet of Aromatic Hydrocarbons

Compounds	k_F/s^{-1}	k_{isc}/s^{-1}	ϕ_{ST}	K_{SV}/M^{-1}	$k_{SO}/M^{-1}s^{-1}$	k_T/s^{-1}	$k_{TO}/M^{-1}s^{-1}$
DCA	8.0×10^{7} a)	1.4×10^{6} §,e) 1.0×10^{7} §,c)	0.017 e) <0.13 c)	40 52 a)	4.7×10^{9}a	1.0×10^{4} f)	5.2×10^{8} g)
AN	2.0×10^{8} b)	1.3×10^{8} b′)	0.68 b)	125	2.5×10^{10} 2.4×10^{10} o) 3.1×10^{10} b′)	1.1×10^{2} d)	2.9×10^{9} b)
DMA	6.7×10^{7} b)	1.5×10^{6} i)	0.02 i) 0.03 b)	281 (435) j)	1.9×10^{10} 2.0×10^{10} b)	2.0×10^{2} l)	2.2×10^{9} g)
BA	2.0×10^{7} b′)	1.6×10^{7} §)	0.79 b)	1480	2.9×10^{10} 3.0×10^{10} b′) 2.8×10^{10} o)	1.5×10^{3} l)	1.9×10^{9} b′)
Py	3.3×10^{6} *)	1.1×10^{6} m)	0.50 n)	9800	3.0×10^{10} 3.4×10^{10} b′)	5.6×10^{3} n)	3.1×10^{9} n) 1.6×10^{9} b′)
Chr	2.2×10^{7} b′)	1.9×10^{7} §)	0.85 b)	1290	2.9×10^{10} 2.9×10^{10} b′) 3.0×10^{10} o)	1.4×10^{3} m)	1.0×10^{9} b′)
DBA	2.7×10^{7} b′)	2.6×10^{7} h)	0.90 b)	920	2.5×10^{10} 2.7×10^{10} o) 2.9×10^{10} b′)	3.0×10^{3} l)	1.3×10^{9} b′)

$k_F = 1/\tau_F = k_{FO} + k_{isc}$. $k_{isc} = \phi_{ST}k_F$. ϕ_{ST}: Probability of the intrinsic intersystem crossing. k_{SO} was estimated by the equation ($k_{SO} = K_{SV}k_F$), in which K_{SV} value was obtained from Stern–Volmer plot for oxygen quenching (see text).

§) From the calculation of $k_{isc} = \phi_{ST}k_F$. *) $k_F = 2.2\times10^{6} + 2.2\times10^{10}\times5\times10^{-5}$. After the correction for Pyrene concentration-quenching at [Py]=50 μM. a) Data from Ref. 20, in heptane. b) Data from Ref. 15, in ethanol or heptane. ϕ_{ST}(AN)=0.72 in toluene. b′) Data from Ref. 15, in cyclohexane. c) From the calculation of $\phi_{ST} = 1 - \phi_F$ and $\phi_F = 0.87$ in cyclohexane. cf., W. R. Ware and W. Rothman, *Chem. Phys. Lett.*, **39**, 449 (1976). d) M. Z. Hoffman and G. Porter, *Proc. R. Soc. London, Ser. A*, **268**, 46 (1962). e) ϕ_{ST}(DCA)=0.017 in acetonitrile. cf., L. E. Manring, C. Gu, and C. S. Foote, *J. Phys. Chem.*, **87**, 40 (1983). f) In heptane. c.f., I. V. Soboleva, N. A. Sadovskii, and M. G. Kuz'min, *Dokl. Akad. Nauk SSSR*, **238**, 400 (1978). g) Estimation as $k_{TO} = (1/9)k_{diff} = (1/9)k_{SO}$, and data from Ref. 8. h) Data from Ref. 35, in toluene. i) Data from Ref. 31, in benzene. j) Data from Ref. 24, in toluene. k) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press., New York (1971), p. 356. l) K. Kikuchi, "Triplet-Triplet Absorption Spectra," Bunshin, Tokyo (1989), pp. 87, 101, and 114. m) In hexane. W. Heinemann, and H. Labhart, *Chem. Phys. Lett.*, **4**, 20 (1969). n) In cyclohexane. Private comunication by Dr. K. Kikuchi. o) Data from Ref. 8.

Table 2. Efficiencies of Singlet Oxygen Formation (*A* and *B*) and Φ_{SO} Values in Aerated Cyclohexane ($[O_2]=2.3\times10^{-3}$ M)[*]

Compounds	Φ_{SO}[*]	ϕ_{ST}	$\phi_{ST}B$	$(A+B)K_{SV}$	A	B	$A+B$
Rub	0.95[a]	0.03	—	—	—	—	1.42[a,b] 1.9[c]
DCA	0.24	0.017	0.02	84	1.0	1.0	2.0
							1.6—2.0[d]
AN	0.82	0.68	0.67	162	0.3	1.0	1.3
					0.46[b]	1.0[b]	1.46[b]
DMA	0.46	0.02	0.02	330	0.20	1.0	1.2
							1.35[b] 2.0[g]
BA	1.0	0.79	0.80	1700	0.15	1.0	1.15
						1.0[#]	1.4[e]
Py	1.1	0.50	0.52	12000	0.15	1.05	1.2
						0.8[f]	1.54[h] 1.85[e]
Chr	1.1	0.85	0.88	1450	0.12	1.0	1.12
							1.2[e]
DBA	0.96	0.90	0.9	980	0.07	1.0	1.07
						1.0[#]	

#) $B=1.0\pm0.05$ was suggested for AN, BA, and DBA. Data from Ref. 31. a) $A+B=1.42$(Rub) in cyclohexane. Data from Ref. 13. b) $A+B=1.46$(AN), 1.35(DMA), 1.4(Rub) in benzene. Data from Ref. 6. c) $A+B=1.9$(Rub) in benzene. Data from Ref. 36. d) Data from Ref. 23, in benzene and acetonitrile. e) Data from Ref. 22, in toluene. f) Data from Ref. 5, in hexane. g) Data from Ref. 24, in toluene. h) Data from Ref. 7, in benzene.

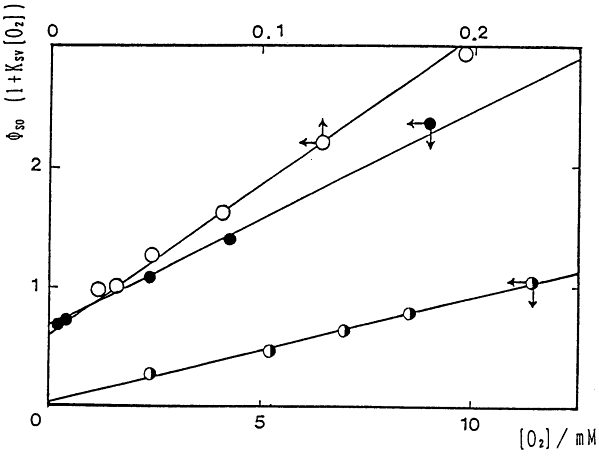


Fig. 2. Estimation of *A* and *B* values from Eq. 8.
(○) Py(50 μM)/O_2/DPBF(5 μM)
(●) AN(200 μM)/O_2/DFBF(5 μM)
(◑) DCA(120 μM)/O_2/DPBF(5 μM)

$^1M^*$ and ^3M listed in Table 1,[7,15–20] the computer simulation curves successfully coincide with the data of oxygen concentrations effect for the whole range of concentrations analyzed in Fig. 1.

The results obtained for *A* and *B* values are summarized in Table 2. $A+B$ values which have been reported in the literature, are also listed as reference. The present results for the respective values of *A* and *B* are considerably accurate and Φ_{SO} values in aerated solution ($[O_2]=2.3$ mM) are also the same as the ones reported.[4,6,8,21–26] In the case of DMA/O_2/DPBF, the concentration effect of DMA (43, 82, 166 μM) on ϕ_{SO} was checked since DMA was very reactive to $^1\Delta_g$ oxygen, i.e., DMA self-sensitized reaction. The effect was negligibly small, thus supporting the idea that the reaction of $^1\Delta_g$ oxygen with DPBF occurred predominantly. In regard to the analysis of the quenching of $^1\Delta_g$ oxygen by Py, no change in the Φ_{SO} values under [Py]=25, 50, 100, and 150 μM was observed.

Inhibition Effect on Φ_{SO} by $^1M^*$ and ^3M Quenchers. If the triplet state is selectively quenched in the present conditions, the *A* value can be obtained from the maximum value of Φ_{SO}, independently. Although a suitable amount of 1,3-pentadiene (Pi) i.e., an efficient triplet-quencher, was added to the air saturated solution in the Py/O_2/DPBF system, the inhibitiorn effect was hardly observed and the reaction (5) occured. $^3Py(T_1)$-quenching by 10 mM of Pi was not observed because the triplet level of Pi (20720 cm^{-1}) is higher than that of $^3Py(T_1$: 16800 $cm^{-1})$. Fluoresence intensity and triplet decay rate experiments confirmed that both excited states of $^1M^*$ and ^3M were quenched by the addtion of iodine (I_2) and NA.[27–30]

$$^1M^*+Q \rightarrow {}^1M+Q \qquad k_q^S \tag{9}$$

$$^3M\ +Q \rightarrow {}^1M+Q \qquad k_q^T \tag{10}$$

Using Py and AN as sensitizers and I_2 and NA as quenchers (Q), the values obtained from the analysis of Stern-Volmer constant for k_q^S are: 3.1×10^{10} for $^1Py^*+I_2$, 4.0×10^9 for $^1Py^*+NA$, 3.3×10^{10} for $^1AN^*+I_2$, 7.2×10^9 $mol^{-1}\,dm^3\,s^{-1}$ for $^1AN^*+NA$ reactions. k_q^T values of 1.3×10^{10} for $^3Py+I_2$ and 1.2×10^{10} for $^3AN+I_2$ and 4.5×10^9 $mol^{-1}\,dm^3\,s^{-1}$ for ^3Py+NA reactions were reported.[27] The contribution of the charge transfer complex between aromatic hydrocarbons and I_2 was negligible under the experimental conditions used because of the small formation constant value ($K=3$ M^{-1} for AN-I_2).[26] Thus, the concentration effect by the quencher on Φ_{SO} can be analyzed as the competition with the quenching and singlet oxygen formation proc-

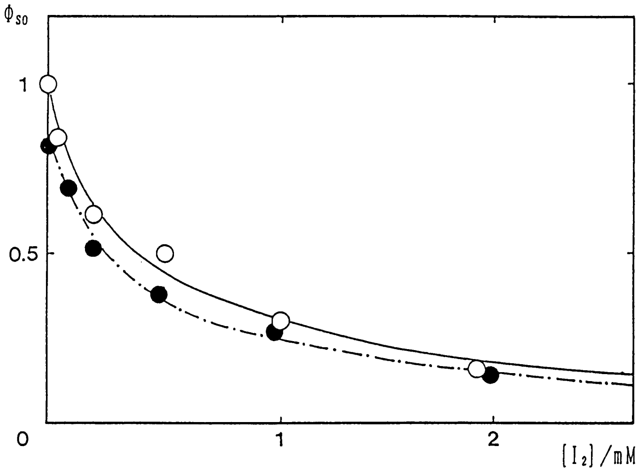


Fig. 3. Inhibition effect of iodine on the Φ_{SO} values in aerated cyclohexane solution.
(○) Py(50 μM)/O_2/DPBF(5 μM),
(●) AN(200 μM)/O_2/DPBF(5 μM)

esses in the $^1M^*$ and ^3M states for the cases of the Py/O_2/DPBF/I_2 and AN/O_2/DPBF/I_2 systems, i.e.,

$$\Phi_{SO}=\frac{Ak_{SO}[O_2]}{k_F+k_{SO}[O_2]+k_q^S[I_2]}+\frac{k_{isc}+k_{SO}[O_2]}{k_F+k_{SO}[O_2]+k_q^S[I_2]}\,\frac{Bk_{TO}}{k_T+k_{TO}[O_2]+k_q^T[I_2]} \quad (11)$$

The resulffs are plotted in Fig. 3. Using k_q^S, k_q^T, A, and B values for Eq. 11, the computer simulation curves given in Fig. 3 suggest that the estimated values of A and B are acceptable. NA was a good quencher for the type of energy transfer from $^1Py^*$ and ^3Py, but not for ^3An because the energy levels for ^3AN and ^3NA are almost the same.[30]

Contribution of T_2 State of Sensitizer in A Values. Energy diagrams of some sensitizers are shown in Fig. 4 and the values are summarized in Table 3 together with the A and B values. Data for Rub having large values of A and B are added as reference. From the analysis

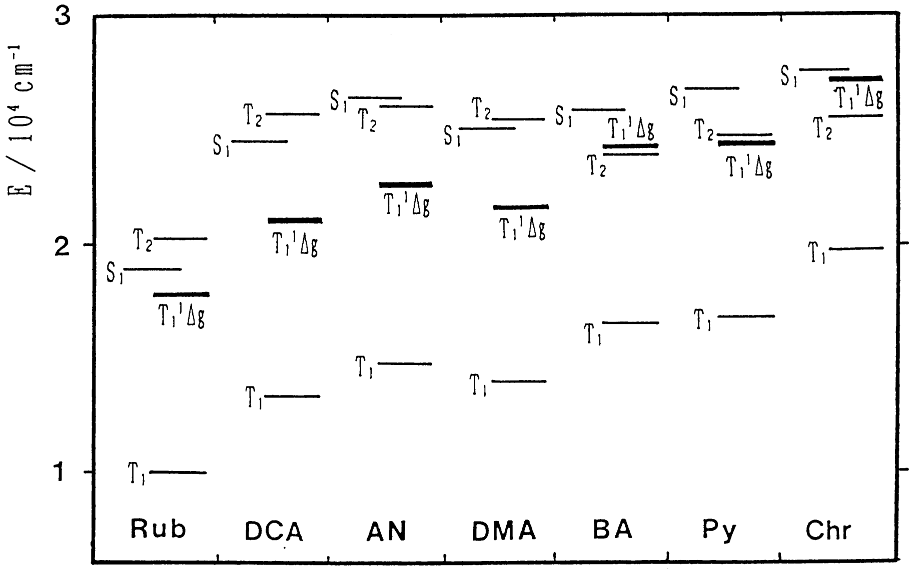


Fig. 4. The energy diagram of S_1, T_1, T_2, and $T_1{}^1\Delta_g$ levels for various sensitizers.

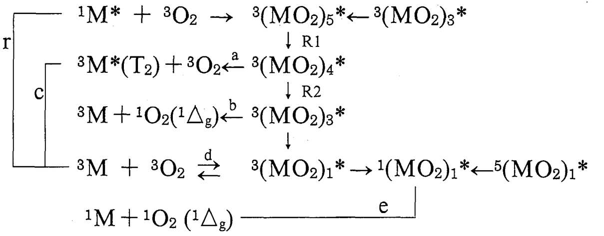
Table 3. Energy Values (cm^{-1}) for Excited Singlet, S_1($^1M^*$), Triplet T_1(^3M), Excited Triplet, T_2, Exciplex, ($T_1{}^1\Delta_g$) States, and Obtained A and B Values

Compounds	$E(S_1)$	$E(T_1)$[a]	$E(T_2)$	$E(T_1{}^1\Delta_g)$	$\Delta E(S_1-T_1)$	A	B
Rub	18900	10000	20100[b]	17880	8900	0.9[c]	1.0[c]
DCA	24600	13300[d]	25700[d]	21180	11300	1.0	1.0
AN	26500	14900	26100[e]	22580	11600	0.3	1.0
DMA	25100	14000[d]	25700[d]	21800	11100	0.2	1.0
BA	26000	16500	24000[f]	24380	9500	0.15	1.0
Py	26900	16800	24900[f]	24680	10100	0.15	1.0
Chr	27700	19800	25700[f]	27680	7900	0.12	1.0
DBA	25500	18300	—	26180	7200	0.07	1.0

a) Data for $E(T_1)$ values are listed from the Ref. 11 (p. 70), Ref. 34, and Ref: S. L. Murov, "Handbook of Photochemistry," M. Dekker, (1974), pp. 3—35. b) Data from Ref. 32. c) In benzene, data from Ref. 36. d) Private information by Dr. K. Kikuchi. e) R. E. Kellog, *J. Chem. Phys.*, **44**, 441 (1966). S. Kobayashi, K. Kikuchi, and H. Kokubun, *Chem. Phys.*, **27**, 399 (1978). f) Estimation from the data in Ref. 33.

with Eq. 8, the formation efficiency of $^1\Delta_g$ oxygen from ^3M (B value) was unity for all the sensitizers investigated, but the formation efficiency of $^1\Delta_g$ oxygen from $^1M^*$ (A value) varied according to the sensitizers. In the Φ_{SO} estimation, the contribution by excimer formation was neglected and the small effect of the concentration quenching on $^1M^*$ by M was corrected.

According to the scheme with the exciplexes between $^1M^*$ and O_2 presented by Birks and Stevens, the essential processes on exciplex relaxation, with the exception of a charge-transfer complex ($M^+\ O_2^-$), can be shown as follows:8,10,15)



In the diagram above, the reaction rate of $^1M^*$ with $^3O_2$ is fast and the radiationless processes will start from an exciplex, $^3(MO_2)_5{}^*$. It is suggested that $^3(MO_2)_5{}^*$ has a shallow basin in its Morse-type potential and it degradates to lower states, i.e., $^3(MO_2)_4{}^*$, $^3(MO_2)_3{}^*$, etc., with a high probability. The relaxation rate in exciplexes has been explained by the Robinson–Frosch theory. It is also known that the oxygen quenching of the excited sensitizers, $^1M^*$ leads to ^3M formation in a fluid media quantitatively, as shown in process (3).31) The spin states of the exciplexes generated from ^3M and $^3O_2$ are $^1(MO_2)_1{}^*$, $^3(MO_2)_1{}^*$, and $^5(MO_2)_1{}^*$ as shown in process (d), and only $^1(MO_2)_1{}^*$ state among them can dissociate to give a singlet oxygen as a spin-allowed process (e). The result of $B=1$ can be explained by the assumption that $^5(MO_2)_1{}^*$ is dissociative and the equilibrium between the three exciplexes tends to $^1(MO_2)_1{}^*$.8)

As for the A value, taking the dissociation of exciplex $^3(MO_2)_4{}^*$ to the second excited state, $T_2(^3M^*)$ and $^3O_2$, and comparing the energy difference between the dissociative exciplexes $^3(MO_2)_4{}^*$ and $^3(MO_2)_3{}^*$, the sensitized reactions are classified into three cases. The energy value, E of exciplexes can be equal to a sum of energy of the dissociated species approximately,i.e., $E(^3(MO_2)_4{}^*) = E(^3M^*\ ^3O_2)$, $E(^3(MO_2)_3{}^*) = E(^3M\ ^1\Delta_g)$. Case(1): The energy level of $^3(MO_2)_4{}^*$ is close to or slightly lower than that of $^3(MO_2)_3{}^*$ such as Py, BA, and Chr in Fig. 4, where the dissociation process (a) and the following internal conversion (c) are assumed to occur efficiently via the potential energy crossing of $^3(MO_2)_4{}^*$ and $^3(MO_2)_3{}^*$. In this case, $^1\Delta_g$ oxygen formation via process (b) will be small. ($A \approx 0.1$ and $B=1$) Case (2): The energy level of $^3(MO_2)_4{}^*$ is separated to and higher than that of $^3(MO_2)_3{}^*$ such as AN and DNA in Fig. 4, where the dissociation process (a) and the process (R2) are assumed to occur competetively. An appreciable probability of $^1\Delta_g$ oxygen formation via processes (R2) and (b) would be observed. ($A \approx 0.3$ and $B=1$) Case (3): The energy level of $^3(MO_2)_4{}^*$ is higher than that of $^3(MO_2)_5{}^*$ or $^1M^*$ such as DCA and Rub in Fig. 4, where the relaxation process from $^3(MO_2)_5{}^*$ to $^3(MO_2)_3{}^*$ directly, and the process (b) occur efficiently. The probability of $^1\Delta_g$ oxygen formation, A, will be unity if the dissociation of $^3(MO_2)_3{}^*$ to ^3M and $^1O_2(^1\Delta_g)$ is predominant.

Therefore, the maximum value of Φ_{SO} tends to 2 ($A=1$ and $B=1$) i.e., 200% efficiency, because of the following processes in the scheme:

$$^3(MO_2)_4{}^* \rightarrow {}^3(MO_2)_3{}^* \rightarrow {}^3M + {}^1O_2$$

$$^3M + {}^3O_2 \rightarrow {}^1M + {}^1O_2$$

According to the energy levels shown in Fig. 4, in the case of DBA, the energy balance to form $^1\Delta_g$ oxygen in the process (2), i.e. $E(^3(MO_2)_3{}^*) > E(^3(MO_2)_5{}^*)$, is not satisfied because the S_1—T_1 energy gap; ΔE_{ST}(DBA) is smaller than 7880 cm^{-1}. Thus, the values of $A=0$ and $B=1$ are suggested.

The present investigation deals only with the aromatic compounds whose energy values of T_1 and T_n states, as well as accurate photophysical rate parameters have been reported. Further studies are still required in order to achieve the mechanistic classification for the wide variety of known sensitizers.

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