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Dye-Sensitized Oxygenation and Dimerization of 4-Methoxystyrene through Electron Transfer

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Photoreactions of 4-methoxystyrene (**1**) sensitized with dyes such as Acriflavine, Rhodamine 6G, and Methylene Blue in methanol under oxygen afforded 4-methoxybenzaldehyde, its dimethyl acetal, and 2-methoxy-2-(4-methoxyphenyl)ethanol as oxidation products together with the corresponding dimers, *cis*- and *trans*-cyclobutanes in a ratio of cis/trans ca. 5/95. On the basis of quenching studies of fluorescence and T–T absorption of the dyes, the oxygenation and dimerization are proposed to proceed through an electron transfer from **1** to excited singlet dyes but not to involve generation of singlet oxygen.

Dye-sensitized oxygenation of olefins has been investigated and in most cases singlet oxygen has been proposed as an oxygenating intermediate;[1] however, some oxygenations have recently been proposed to take place through an electron transfer from olefins to excited dyes to give olefin radical cations followed by their reactions.[2,3] This paper now reports, based on quenching studies of fluorescence and T–T absorption of the sensitizers, that the dye-sensitized oxygenation of 4-methoxystyrene (**1**) in methanol proceeds in the singlet state through the cation radical of **1** to afford oxidation products together with dimerization products, and that singlet oxygen usually resulting from sensitization with dye triplets plays no role in this reaction.

Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Fluorescence spectra were obtained on a Hitachi F-4000 fluorescence spectrophotometer. Fluorescence lifetimes were measured using a single photon counting apparatus, Horiba NAES 1100.

Materials. Acriflavine, Methylene Blue (Nakalai Tesque), Eosin Y, Rose Bengal (Wako), and Rhodamine 6G (Tokyo Kasei) were used without further purification in dye-sensitized oxygenation and dimerization reactions of **1**. The dyes were purified by recrystallization from ethanol/benzene for measurements of fluorescence spectra and lifetimes, and for laser flash photolyses.

4-Methoxystyrene (**1**),[4] *cis*- (**2**),[5] and *trans*-1,2-bis(4-methoxyphenyl)cyclobutane (**3**)[5] were prepared as described previously.

4-Methoxybenzaldehyde dimethyl acetal (**5**)[6] was prepared from 4-methoxybenzaldehyde (**4**) by refluxing with methyl orthoformate in the presence of a catalytic amount of ammonium chloride in methanol; bp 102 °C/5 Torr (1 Torr=133.322 Pa); ^{13}C NMR ($CDCl_3$) δ=159.7 (s), 130.5 (s), 127.8 (d), 113.5 (d), 103.1 (d), 55.0 (q), 52.4 (q); ^{1}H NMR ($CDCl_3$) δ=7.40—6.81 (q, 4H, aromatic H), 5.33 (s, 1H, CH), 3.75 (s, 3H, OCH_3), 3.28 (s, 6H, OCH_3). Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74%. Found: C, 66.05; H, 7.56%.

(4-Methoxyphenyl)oxirane (**7**)[7,8] was prepared from 4-methoxybenzaldehyde with dimethyloxosulfonium methylide;[9] yield 18%, bp 80 °C/2 Torr (lit,[7] bp 76 °C/0.037 Torr).

2-Methoxy-2-(4-methoxyphenyl)ethanol (**6**)[10] was prepared by stirring the oxirane, **7**, in methanol with a few drops of conc. HCl for 17 h; yield 55%, bp 140 °C/3 Torr (lit,[10] bp 137—139 °C/5.5 Torr); ^{13}C NMR ($CDCl_3$) δ=159.5 (s), 130.5 (s), 128.1 (d), 114.0 (d), 84.3 (d), 67.2 (t), 56.5 (q), 55.2 (q); ^{1}H NMR ($CDCl_3$) δ=7.28—6.84 (q, 4H, aromatic H), 4.34—4.18 (m, 1H, CH), 3.78 (s, 3H, OCH_3), 3.78—3.59 (m, 2H, CH_2), 3.30 (s, 3H, OCH_3), 2.86 (broad, 1H, OH).

Irradiation of 4-Methoxystyrene with Dye under Oxygen. 4-Methoxystyrene (**1**, 0.6 M, M=mol dm^{-3}) was irradiated in the presence of dyes (2—3×10^{-3} M) in methanol under oxygen in a uranium glass tube (⩾340 nm) with a 400-W high-pressure mercury lamp (Riko UVL-400HA) through a filter solution [K_2CrO_4 0.27 g and Na_2CO_3 1 g in 1 dm^3 of H_2O (optical path length, 1 cm)]. The yields of products were determined with a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector.

Quantum Yields. Quantum yields for the formation of *trans*-1,2-bis(4-methoxyphenyl)cyclobutane (**3**) and 4-methoxy benzaldehyde (**4**) were determined by using potassium tris(oxalato)ferrate(III) actinometry.[11] Irradiation was performed with 436-nm light from a 400-W high-pressure mercury lamp through a cut filter (Shibata Harzlas FS, ⩾400 nm) and a filter solution [$CuSO_4 \cdot 5H_2O$ in H_2O (4.4 g dm^{-3})+2.7 M NH_4OH]. The solutions were quantitatively analyzed on the gas chromatograph and a JASCO 800 series high-performance liquid chromatograph.

Laser Flash Photolyses. Laser flash photolyses were performed with 460-nm laser pulses (Coumarin 47, 10-ns fwhm) from a XeCl (308 nm) excimer laser(Lambda Physik EMG-101)-pumped dye laser (Lambda Physik FL-3002) and with a pulsed xenon arc (Wacom KXL-151, 150 W) as a monitoring light source. The monitoring light coming from a monochromator (JASCO CT-25C) was amplified by a photomultiplier (Hamamatsu Photonics R928) and stored in a storage scope (Iwatsu TS-8123), and the signals were transferred to a personal computer (NEC PC-9801VX21) and accumulated for 3—5 times to be averaged. The system was computer-controlled and the decay curves were analyzed by this computer system. Sample solutions containing Acriflavine (5.0×10^{-4} M) and **1** (0—4.8×10^{-2} M) were deaerated by bubbling with nitrogen for 30 min.

Redox Potentials. Redox potentials were measured by cyclic voltammetry with a potentiostat-galvanostat (Nikko Keisoku NPGS-501) and a function generator (Nikko Keisoku

NFG-3). The measurements were carried out in acetonitrile using a three-electrode cyclic voltammetric cell. A platinum disk and a platinum wire were used as the working and counter electrodes, respectively, and the reference electrode was a Ag/AgCl or an SCE. Tetraethylammonium perchlorate (0.1 M) was used as a supporting electrolyte.

Results and Discussion

Dye-Sensitized Oxygenation and Dimerization of 4-Methoxystyrene. Acriflavine (AF), Rhodamine 6G (R6G), Methylene Blue (MB), Eosin Y (EY), and Rose Bengal (RB) were used as sensitizer. Although these sensitizers exhibit fairly different absorption spectra in the visible region, they have an intense band with a molar extinction coefficient of $\approx 10^5$ at the absorption maximum (Table 1).

Irradiation of a methanol solution of **1** (0.6 M) in the presence of AF (2×10^{-3} M) under oxygen with visible light (>400 nm) gave *cis-* (**2**) and *trans*-1,2-bis(4-methoxyphenyl)cyclobutane (**3**), the corresponding cyclobutane dimers (yield 19% based on **1** consumed at 31% conversion, with an isomer ratio of **2**/**3**=3/97), 4-methoxybenzaldehyde (**4**, 23%), its dimethyl acetal (**5**, 15%), and 2-methoxy-2-(4-methoxyphenyl)ethanol (**6**, 8%), as shown in Scheme 1.

Table 1. Absorption Spectrum Data for Dyes in Methanol

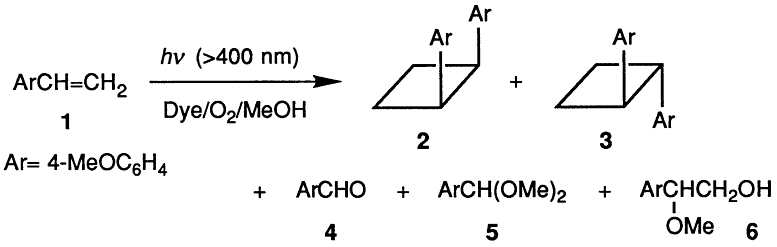
Dye	λ_{max}/nm	ε_{max}	ε_{436}
AF	461	67100	35600
R6G	527	108000	1960
MB	653	96200	730
EY	523	96300	1730
RB	557	110000	2000

The dimers, **2** and **3** (10% at 8% conversion), were also formed under nitrogen together with polymers on AF sensitization in methanol. In this case, however, AF was bleached completely during irradiation.

The photooxygenation and photodimerization of **1** proceeded similarly on sensitization with R6G, MB, RB, and EY to afford, with lower efficiencies, the same products as those from the AF sensitization (Table 2). The isomer ratio **2**/**3** (=3/97—7/93) under oxygen is independent of the dye employed except MB (12/88), and **3** was produced somewhat selectively compared to the reaction under nitrogen (**2**/**3**=23/77—11/89).

In control experiments, aldehyde **4** and (4-methoxyphenyl)oxirane (**7**) were methoxylated in methanol in the presence of a catalytic amount of benzoic or hydrochloric acid to give **5** and **6**,[10] respectively. These results indicate that **5** and **6** are the secondary products derived from the oxygenation products **4** and **7**, respectively, under the reaction conditions.[14]

Effects of Singlet Oxygen Quenchers and Solvents on Photooxidation of 4-Methoxystyrene. Oxygenation of olefins gives generally carbonyl compounds and epoxides in various pathways. 4-Methoxybenzaldehyde, **4**, might be afforded by a reaction of **1** with singlet oxygen possibly generated from dye sensitization.[12] Also, *N*-vinylcalbazole has been reported to dimerize in the



Scheme 1.

Table 2. Dye-Sensitized Oxygenation and Dimerization of **1** in Methanol

Dye	O_2/N_2[a]	Conv./%	Yield of products[b]/% (2+3)	4	5	6	Isomer ratio 2/3
AF	O	31	19	23	15	8	3/97
	N	8	10	—	—	—	23/77
R6G	O	10	14	34	—	1	7/93
	N	7	14	—	—	—	11/89
MB	O	4	22	28	—	—	12/88
	N	3	31	—	—	—	15/85
EY	O	17	6	35	2	4	7/93
	N	11	6	—	—	—	14/86
RB	O	18	5	10	—	8	7/93
	N	11	3	—	—	—	12/88

a) O: Under oxygen, N: under nitrogen. b) Yields of products based on **1** consumed.

Table 3. AF-Sensitized Oxygenation and Dimerization of **1** in Methanol in the Presence of TME and Dabco[a)]

Additive	Concn./M	Conv./%	Yield of products[b)]/%			
			(**2**+**3**)	**4**	**5**	**6**
TME	0	28	13	22	15	3
	0.2	26	14	12	20	4
	0.6	25	14	8	21	4
Dabco	0.01	11	10	3	Trace	Trace
	0.05	7	6	9	Trace	Trace
	0.1	5	5	9	Trace	Trace

a) [**1**]=0.6 M, [AF]=2×10^{-3} M. b) Yields based on **1** consumed.

Table 4. Quantum Yields for Formation of Dimer **3** (ϕ_3) and Aldehyde **4** (ϕ_4) on Dye-Sensitized Irradiation of **1**[a)]

Dye	ϕ_3	ϕ_4
AF	0.013 ± 0.002	0.58 ± 0.03
R6G	0.067 ± 0.003	0.28 ± 0.03
EY	$(2.1\pm0.2)\times10^{-4}$	0.067 ± 0.002
RB	$(3.4\pm1.0)\times10^{-4}$	0.025 ± 0.001

a) Irradiated with 436-nm light in oxygen-saturated methanol.

presence of singlet oxygen.[13)]

On AF-sensitized irradiation under oxygen the conversion of **1** was scarcely changed (within 3%) even in the presence of 2,3-dimethyl-2-butene (TME, 0.2 or 0.6 M in methanol) as an efficient singlet oxygen trap; the product distribution was similar to that in the absence of TME (Table 3). This observation indicates that singlet oxygen plays no role in the AF-sensitized oxygenation of **1**.

As shown in Table 3, 1,4-diazabicyclo[2.2.2]octane (Dabco) quenched more efficiently the AF-sensitized oxygenation of **1** than the dimerization of **1**. Although Dabco is an effective singlet oxygen quencher, it also inhibits autoxidation[14)] and quenches radical cations of organic substrates as an electron donor;[15)] in fact, Dabco has a much lower oxidation potential (0.68 V vs. SCE) than **1** (1.31 V). These results together with the above observation that TME exerts no effects on the efficiency of reaction and the distribution of products suggest that Dabco quenches the reaction not only as a radical inhibitor but also an electron donor, but not as a singlet oxygen quencher; the oxygenation proceeds through electron transfer and autoxidation, but not through singlet oxygen oxidation.

In an acetonitrile–methanol (4:1 by volume) mixed solvent the conversion of **1** was analogous to that in methanol, but the yield of dimers was higher (33%) than in methanol. The use of Freon 113–methanol (4:1) decreased both of the conversion of **1** and the yield (8%) of dimers. These results show that the efficiency of dimerization of **1** is affected by the polarity of solvents but is not correlated with the reported lifetime of singlet oxygen.[16,17)]

Quantum Yields for Oxygenation and Dimerization. The quantum yields for formation of dimer **3** and aldehyde **4** were determined by irradiating methanol solutions of **1** (0.6 M) and dyes (ca. 5×10^{-3} M) at 436 nm under bubbling with oxygen, and are summarized in Table 4. At first glance the product distributions mentioned above seem to be inconsistent with these results; however, the discrepancy might be explained by photolability of **4** under oxygen. The high ϕ_4 values may be attributed to efficient formation of **4** through radical chain reactions as described below. It is noticeable that the AF- and R6G-sensitized reactions proceed with much higher efficiencies compared to those with EY and RB as sensitizer. According to Rehm–Weller's equation (Eq. 1),[18)] the changes of Gibbs' free energy (ΔG) associated with the electron transfer from ground-state **1** to excited singlet AF and R6G are estimated to be exothermic in acetonitrile (ΔG=-3.9 kcal mol^{-1} for AF and -2.4 kcal mol^{-1} for R6G), while those to excited singlet EY and RB are largely endothermic. The calculated ΔG values are listed in Table 5, where E_{ox}^{D} and E_{red}^{A} are the oxidation potential of a donor and the reduction potential of an acceptor, respectively, and E^* is the singlet or triplet excitation energy of the donor (or the acceptor). The efficiencies of the dye-sensitized reactions are consistent with the calculated ΔG values. AF is most effective among the sensitizers employed to give the dimers (**2** and **3**) and the oxidation products (**4**—**6**).

$$\Delta G = E_{ox}^{D} - E_{red}^{A} - E^{*} - 0.06\ \text{eV} \qquad (1)$$

Quenching of Dye Fluorescence by 4-Methoxystyrene and Oxygen. The fluorescence lifetime of AF (τ_f=5.34 ns in MeCN under argon) was quenched at nearly and completely diffusion-controlled rate constants by **1** and oxygen, respectively, as shown in Tables 5 and 6. However, the concentration of **1** (0.6 M) used in the present reaction was much higher than that of oxygen (8.1×10^{-3} M). Therefore, it is reasonable to consider that the excited singlet state of AF interacts with ground-state **1** to generate the cation radical of **1** and the anion radical of AF, but does not practically interact with oxygen. The estimation of the quenching rate, k_q[Q], shows that **1** quenches the excited singlet AF at the rate of 2.5×10^{9} s^{-1} (Table 6), which is larger by a factor of ca. 20 than that for oxygen ($k_q[O_2]=1.1\times10^{8}$ s^{-1}). This shows that 90% of the AF excited singlets interact with **1**, and under these conditions the quantum yield for AF triplet formation is estimated to be less than 0.06, even if oxygen quenching led to a complete formation of the AF triplets. Thus, singlet oxygen could not be efficiently generated in the present system.

Contrary to the cases of AF, R6G, and MB, fluorescence quenching by **1** was much less efficient for EY and RB; the rate constants (k_q) are 4.0×10^{8} and

Table 5. Kinetic Parameters for Fluorescence Quenching of Dyes by **1** and Calculation of Free-Energy Changes (ΔG) Associated with Electron Transfer from **1** to the Excited Singlet Dyes

Dye	ϕ_{isc}[a]	τ_f[b]	$k_q\tau_f$	k_q	E_{red}[c]	E_s[d]	ΔG[e]
		ns	$\mathrm{M^{-1}}$	$10^8\ \mathrm{M^{-1}\ s^{-1}}$	V	$\mathrm{kcal\ mol^{-1}}$	$\mathrm{kcal\ mol^{-1}}$
AF	0.53[f]	4.61	26.7	58	−1.06	59.2	−3.9
R6G	0.002[g]	4.16	7.6	18	−0.83	52.4	−2.4
MB	0.52[h]	0.75	13.9	185	−0.32	42.7	−4.4
EY	0.44[f]	4.44	1.8	4.0	−1.19	52.8	+5.5
RB	0.76[i]	2.68	1.0	3.7	−1.15	50.5	+6.9

a) Quantum yields for intersystem crossing of dyes. b) Fluorescence lifetimes of dyes in aerated MeCN. c) Reduction potentials of dyes vs. Ag/AgCl in MeCN. d) Singlet excitation energies of dyes estimated from the absorption and fluorescence spectra. e) Calculated using 1.40 V (vs. Ag/AgCl in MeCN) as the oxidation potential of **1**. f) K. Kikuchi, M. Ozaki, H. Kokubun, M. Kikuchi, and Y. Usui, *J. Photochem.*, **16**, 19 (1981). g) V. E. Korobov, V. V. Shubin, and A. K. Chibisov, *Chem. Phys. Lett.*, **45**, 498 (1977). h) M. Koizumi and Y. Usui, *Mol. Photochem.*, **4**, 57 (1972). i) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).

Table 6. Rate Constants for Quenching of Fluorescence Lifetime of AF by **1** and Oxygen[a]

Quencher	$k_q/10^9\ \mathrm{M^{-1}\ s^{-1}}$[b]	$k_q[\mathrm{Q}]/10^9\ \mathrm{s^{-1}}$[c]
1	4.1	2.5
$\mathrm{O_2}$	14	0.11

a) $[\mathrm{AF}]=5\times10^{-5}$ M. b) The lifetime of the excited singlet AF is 5.34 ns in MeCN under argon. c) [Q]= 0.6 M for **1** and 0.0081 M for oxygen.

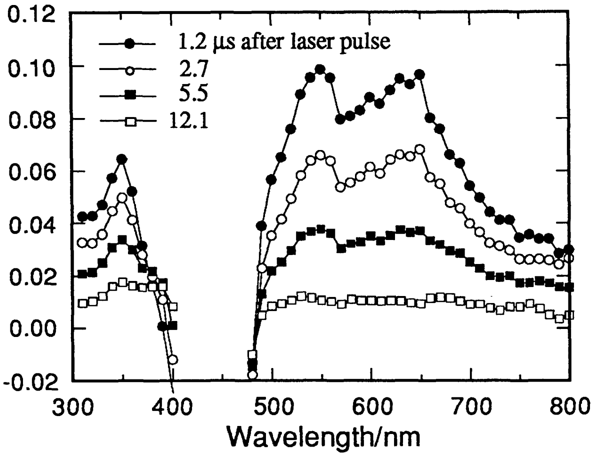


Fig. 1. T–T Absorption spectra of AF in acetonitrile.

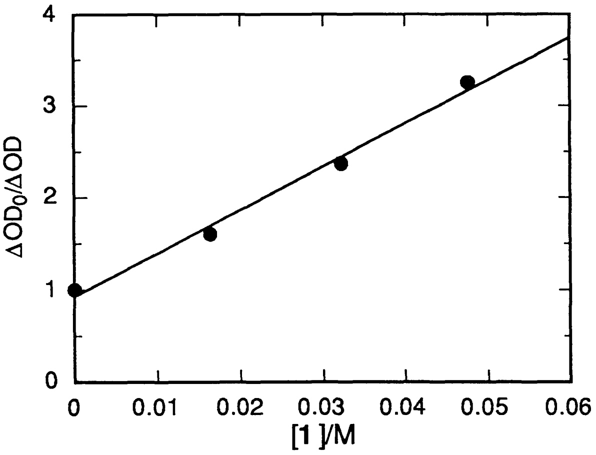


Fig. 2. Quenching of T–T absorption of AF by **1**.

$3.7\times10^8\ \mathrm{M^{-1}\ s^{-1}}$ for EY and RB, respectively. This might be due to the positive ΔG values (Table 5).

Laser Flash Photolysis. On laser flash photolysis of AF (5×10^{-5} M) with 460-nm pulses in deaerated acetonitrile a transient absorption spectrum was obtained in the region of 300—800 nm ($\lambda_{\max}$ 550 and 650 nm), the lifetime being 4.6 μs as monitored at 550 nm (Fig. 1). This spectrum can be attributed to AF triplets.[19] The initial intensity (ΔOD) and lifetime of the absorption decreased with increasing concentration of **1** added (1.6—4.8×10^{-2} M). A Stern–Volmer plot of $\Delta\mathrm{OD_0}/\Delta\mathrm{OD}$ ($=\phi_{\mathrm{isc}}{}^0/\phi_{\mathrm{isc}}$) against [**1**] gives a good linear relationship (Eq. 2); the slope ($=k_q\tau_f$) is 47.2 $\mathrm{M^{-1}}$ (Fig. 2), where $\Delta\mathrm{OD_0}$ and ΔOD are the initial optical densities at 550 nm, and $\phi_{\mathrm{isc}}{}^0$ and ϕ_{isc} are the quantum yields for intersystem crossing, in the absence and presence of **1**, respectively. The reduced formation of AF triplet with **1** can be attributed to the quenching of the excited singlet AF by **1**. By using $\tau_f=5.34$ ns, k_q is estimated to be $8.8\times10^9\ \mathrm{M^{-1}\ s^{-1}}$, which is in agreement with the rate constants obtained from quenching of the fluorescence spectrum and lifetime of AF by **1**, 5.8×10^9 and $4.1\times10^9\ \mathrm{M^{-1}\ s^{-1}}$, respectively.

$$\Delta\mathrm{OD_0}/\Delta\mathrm{OD}=\phi_{\mathrm{isc}}{}^0/\phi_{\mathrm{isc}}=1+k_q\tau_f[\mathbf{1}] \qquad (2)$$

The decay rate of T–T absorption of AF was accelerated on addition of **1**; however, the quenching rate constant was as small as ca. $10^6\ \mathrm{M^{-1}\ s^{-1}}$. The ΔG value for electron transfer from the ground-state **1** to the excited triplet AF is largely endothermic. Therefore, it is reasonably concluded that olefin **1** interacts efficiently with the excited singlet state of AF, but much less efficiently with its excited triplet state.

Mechanism. We reported previously that the photodimerization of **1** to give **2** and **3** with a ratio of **2**/**3**=3/97 under oxygen in acetonitrile proceeds through the cation radical of **1** generated on excitation of the contact charge transfer paor (UV absorption: 320—370 nm) between **1** and molecular oxygen.[5] Moreover, Yamamoto et al. have also reported that the photodimerization of **1** in the presence of 1,4-dicyanobenzene proceeds through the same intermediate.[20] A similar dominant formation of **3** over **2** in the present dye-sensitized cases indicates the intermediacy of $\mathbf{1}^{+\cdot}$ as the key intermediate.

The fluorescence quenching and laser flash photolyses together with the energetic considerations show that the excited singlet state of the dyes undergoes electron transfer with **1**. Also, the aforementioned AF-sensitized reactions of **1** in the presence of TME or Dabco rule out the possibilities of dimerization of **1** catalyzed by singlet oxygen and of electron transfer from **1** to singlet oxygen to generate superoxide anion, though *N*-vinylcalbazole has been reported to dimerize in the presence of singlet oxygen.[12]

As shown in Scheme 2, an electron transfer from the ground-state **1** to the excited singlet dye generates the radical ion pair of $\mathbf{1}^{+\cdot}$ and $\mathrm{Dye}^{-\cdot}$ The monomer cation radical ($\mathbf{1}^{+\cdot}$) reacts with another neutral **1** to afford the dimer cation radical of **1** (**8**), which finally collapses to the trans cyclobutane dimer **3** with high selectivity, or reacts with methanol to give a neutral radical (**9**), initiating autoxidation of **1** to afford the aldehyde, **4**, and the oxirane, **7**, through chain processes similar to those reported already.[14,21] The cation radical $\mathbf{1}^{+\cdot}$ would react with oxygen species ($O_2^{-\cdot}$ or O_2) or methanol to generate radical intermediates (**10** and **11**[22]), which also would be able to initiate autoxidation of **1**. The back electron transfer process from $\mathrm{Dye}^{-\cdot}$ to $\mathbf{1}^{+\cdot}$ to produce the excited triplet of **1** ($^3\mathbf{1}^*$, $E_T \approx 60$ kcal mol^{-1})[23] is safely ruled out, based on the consideration of the free energy change in the process [$\Delta G = E(\mathrm{Dye}/\mathrm{Dye}^{-\cdot}) - E(\mathbf{1}^{+\cdot}/\mathbf{1}) \approx -57$ kcal mol^{-1} (for AF)].

The free-energy change [$\Delta G = E(\mathrm{Dye}/\mathrm{Dye}^{-\cdot}) - E(O_2/O_2^{-\cdot})$] for the secondary electron-transfer process from the anion radical of dyes to molecular oxygen would be an important factor for reproducing neutral dyes [Process (4) in Scheme 2].[24] It has been reported that the electron transfer from the anion radical of MB ($\mathrm{MB}^{-\cdot}$) to O_2 is endothermic;[3] actually, in the present reaction MB was rapidly bleached under oxygen compared to AF.

Another factor affecting the reaction efficiency seems to be the singlet lifetime of the dye employed, but the quantum yield of intersystem crossing (ϕ_{isc} in Table 5) is not such a factor; actually, AF, the most effective sensitizer, has the longest fluorescence lifetime, but its ϕ_{isc} is much larger than ϕ_{isc} of R6G.

Conclusion

By use of high concentrations of the olefin, the dye singlets are almost quenched by the olefin under oxygen atmosphere. Under these conditions the yield of the dye triplets are nearly negligible, and therefore singlet oxygen plays no role in oxidation of the olefin. The oxygenation of the olefin proceeds in methanol mainly through electron-transfer induced autoxidation to give the carbonyl and oxirane compounds (and/or their methanol adduct) together with the dimerization products.

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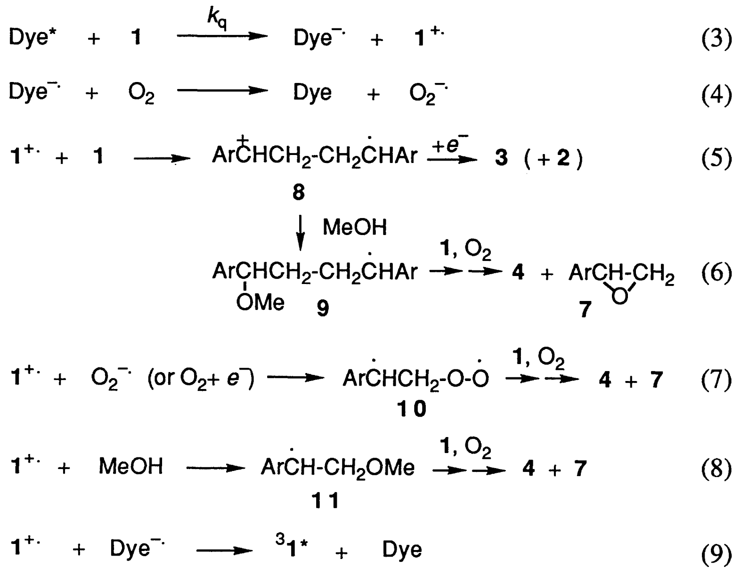

Scheme 2.

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23) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), p. 20.

24) The reduction potential of oxygen was −0.85 V vs. Ag/AgCl in acetonitrile.