



Photoinduced electron transfer oxidation of α -methylstyrene with molecular oxygen sensitized by dimethoxybenzenes: a non-singlet-oxygen mechanism

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Abstract— α -Methylstyrene (**1**) was photooxidized with oxygen in the presence of a series of alkylated dimethoxybenzenes as a sensitizer in acetonitrile, affording the cleaved ketone (**2**), epoxide (**3**) as well as a small amount of the ene product (**4**) in ca. 1:1:0.04 ratio. A non-singlet-oxygen mechanism is proposed, in which an excited sensitizer is quenched by oxygen to produce a sensitizer radical cation and a superoxide ion ($O_2^{\bullet-}$), the former of which oxidizes **1**, while $O_2^{\bullet-}$ reacts with the resulting $1^{\bullet+}$ to give the major oxidation products. © 2001 Elsevier Science Ltd. All rights reserved.

Photosensitized oxygenations of various olefins using molecular oxygen have been extensively studied from the environmental,¹ synthetic and mechanistic points of view.² Photoactivation of molecular oxygen using Rose Bengal (RB) and Methylene Blue (MB) has been much investigated and shown to give a singlet oxygen (1O_2) as an essential intermediate. The photoinduced singlet-oxygen formation is widely recognized in such dye-sensitized oxygenations, although some other mechanisms are known to operate in distinctive systems.³ For example, singlet oxygen is almost inert to such olefins that possess no (reactive) allylic proton: e.g. 1,1-diphenylethylene, tetraarylethylene and adamantylideneadamantane. However, electron-deficient sensitizers such as dicyanoanthracene (DCA) are known to activate the photooxidation pathways. Electron transfer from substrate to photoexcited DCA affords substrate radical cation and DCA radical anion, the latter of which oxidizes the ground state oxygen to give superoxide ion ($O_2^{\bullet-}$), while the former reacts with $O_2^{\bullet-}$ to give oxidation products.³

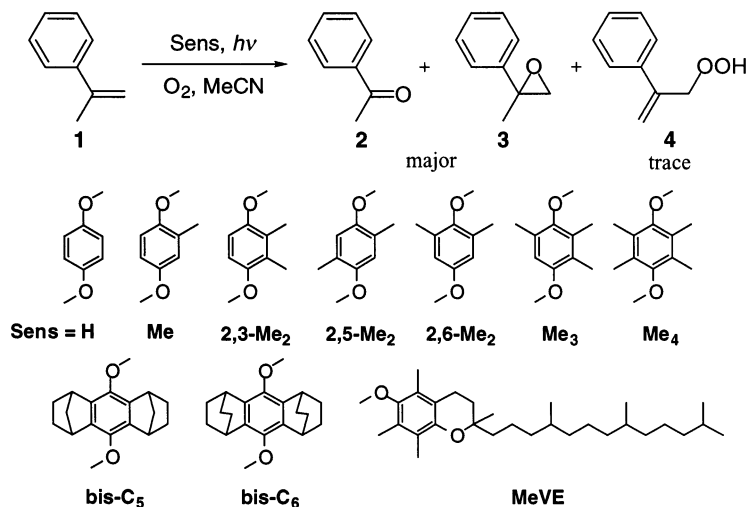
α -Methylstyrene is photooxidized in the presence of MB, but the reaction details (such as yield and conditions) are not clearly described in the literature.⁴ Although α -methylstyrene is almost inert to (chemically

and photochemically generated) singlet oxygen, this alkene is cleanly oxidized by molecular oxygen upon irradiation with dimethoxybenzene added as a sensitizer.⁵ However, in order to establish a practical efficient photooxygenation system, photodegradation of sensitizers is a serious problem that must be overcome. It is well known that dye-sensitizers such as RB and MB, or cyanosubstituted aromatic compounds, decompose upon irradiation in the presence of oxygen.⁶ In this study, we employed a variety of alkylated *p*-dimethoxybenzenes as electron-donating sensitizers for photooxidation of α -methylstyrene with molecular oxygen, and investigated the effects of alkylation on the chemical and quantum yields and the distribution of oxidation products as well as the durability of the sensitizer.

Irradiation of an oxygen-saturated acetonitrile solution of α -methylstyrene (**1**, 2 mM) containing *p*-dimethoxybenzene (Sens=**H**, 1 mM) as a sensitizer at 0°C with a high pressure mercury lamp (Pyrex filter, $\lambda > 280$ nm) gave acetophenone (**2**) and 2-methyl-2-phenyloxirane (**3**) in ca. 1:1 ratio, together with a small amount of the ene product (**4**), as shown in Scheme 1. In the absence of a sensitizer, the progress of the reaction was retarded and the relative importance of the ene product **4** was increased. Practically no reaction was observed under an argon atmosphere. No ground-state interaction between **1** and oxygen was observed, as the absorption spectra in oxygen- and argon-saturated solutions of **1** were identical under the conditions for photooxidation.

Keywords: α -methylstyrene; dimethoxybenzenes; non-singlet-oxygen mechanism; electron transfer oxidation; molecular oxygen.

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Scheme 1.

Thus, the possible intervention of a charge–transfer complex is ruled out in the present system. It is noted that the progress of the reaction was extremely slow in a non-polar solvent.

Although a previous study⁵ claimed an exclusive formation of **2** and an 80% recovery of the sensitizer at 90% conversion in the photosensitized oxidation of **1** with *p*-dimethoxybenzene for 12 h, we could not reproduce the same results. Instead we obtained **2** in less than 50% yield with a poor recovery (10%) of the sensitizer and an 80% consumption of **1** after 6 h irradiation. Not only this particular photosensitizer but also others such as RB and MB, are frequently photodecomposed upon prolonged irradiations.⁶ For practical synthetic applications, it is desirable to develop efficient and durable photosensitizers. In an attempt to obtain more durable sensitizers against the photodegradation, we successively replaced the aromatic hydrogens of **1** by methyls or more bulky bridged methylenes. All alkylated methoxybenzenes employed in this study (Sens=**H**,

Me, **2,3-Me₂**, **2,5-Me₂**, **2,6-Me₂**, **Me₃**, **Me₄**, **bis-C₅**, **bis-C₆**, **MeVE**) have low lying singlet excited state energies which are accessible by Pyrex-filtered light.

Results of the photolyses are summarized in Table 1. Although all of the sensitizers employed gave the same oxidation products (**2–4**) in an almost similar ratio,⁷ the relative reactivity varied dramatically. Thus, the quantum yield of substrate consumption (Φ_{conv}) critically depends on the sensitizer employed, ranging from 0.04 to 0.22.⁸ This correlates well with the fluorescence quantum yield (Φ_{fl}) of each sensitizer in hexane, as shown in Fig. 1. On the contrary, no direct correlation was found between the oxidation potential (E°_{ox}) of the sensitizer and Φ_{conv} , with serious deviations particularly for sterically hindered sensitizers. These results are obviously incompatible with the singlet oxygen mechanism and clearly indicate that the reaction proceeds through the singlet manifold and the steric bulk or reduced oxidation potential of alkylated sensitizers are not directly related to the product quantum yield,

Table 1. Photoinduced electron transfer oxidation of α -methylstyrene (**1**) with oxygen in the presence of *p*-dimethoxybenzene derivatives as a sensitizer^a

Sens	Irrad. time (h)	Conv. (%)	Yield (%)			Φ_{conv}
			2	3	4	
None ^b	12	48	23	4	7	0.019
H	12	>99	46	43	2	0.15
Me	6	98	48	40	1	0.18
2,3-Me₂	6	>99	48	44	1	0.22
2,5-Me₂	6	99	51	38	3	0.19
2,6-Me₂	12	>99	49	28	1	0.073
Me₃	6	96	43	43	2	0.16
Me₄	12	83	34	25	3	0.044
bis-C₅	12	>99	41	44	1	0.11
bis-C₆	12	85	35	23	3	0.046
MeVE	12	>99	54	30	1	0.15

^a All irradiations were performed at 0°C in oxygen-saturated MeCN solutions containing sensitizer (1 mM) and **1** (2 mM) using a 300 W high-pressure mercury lamp fitted with a Pyrex filter ($\lambda > 280$ nm), unless otherwise indicated.

^b No sensitizer added.

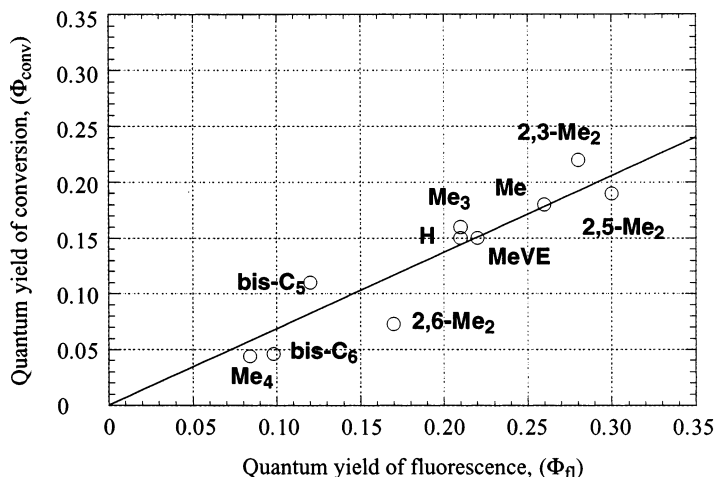


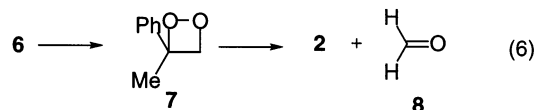
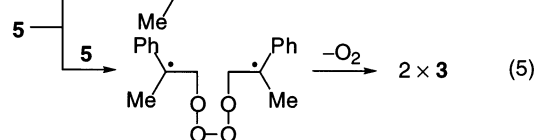
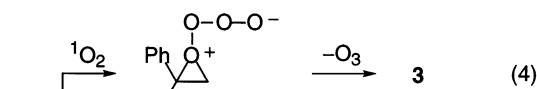
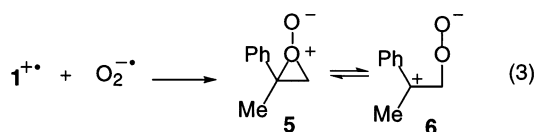
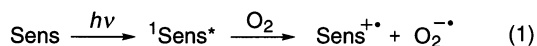
Figure 1. Correlation between fluorescence quantum yield of sensitizers (Φ_{fl}) and quantum yield of conversion (Φ_{conv}).

which is rather accounted for in terms of the abundance of the singlet species and the process derived therefrom. Concerning the photodurability of sensitizers, we obtained good to excellent sensitizer recoveries (>70% after 80% conversion) particularly for tetrasubstituted dimethoxybenzenes (Sens= Me_4 , bis-C_5 and bis-C_6), while less hindered ones (Sens= Me_3 or $2,6\text{-Me}_2$) gave only <50% recoveries after 6 h irradiation.

We propose an electron transfer oxidation mechanism illustrated in Scheme 2 for the present system, since the following observations clearly indicate the non-singlet-oxygen mechanism: (a) strong solvent dependence, which is not compatible with $^1\text{O}_2$ reaction; (b) good correlation between Φ_{fl} and Φ_{conv} , which is not expected for the singlet-oxygen mechanism; (c) highly favorable free energy change for electron transfer from excited sensitizer to ground-state oxygen. $\Delta G_{ET} < -40$ kcal/mol.⁹ As shown in Scheme 2, the singlet excited sensitizer reduces molecular oxygen to generate superoxide ($\text{O}_2^{\bullet-}$) (Eq. (1)), which in turn reacts with the substrate radical cation ($1^{\bullet+}$) to form the perepoxide intermediate **5** (Eq. (3)). $1^{\bullet+}$ is presumably derived from the (fast) hole transfer between the sensitizer radical cation and the substrate (Eq. (2)). The perepoxide affords the corresponding epoxide **3**, either through the reaction with singlet oxygen¹⁰ or through the recombination with another molecule of **5**¹¹ (Eqs. (4) or (5)). Dioxetane intermediates are often isolated in the photooxygenation of sterically hindered alkene substrates such as adamantylideneadamantane.¹² Hence, it is reasonable to assume that this type of dioxetane (**7**) may be formed but cannot survive under the reaction conditions employed,¹³ affording the acetophenone (**2**) and formaldehyde (**8**) (Eq. (6)). Barton-type oxidation,¹⁴ i.e. the addition of triplet (ground state) oxygen to the radical cation of the substrate, leading to the chain oxidation process, may not be operative as a major pathway because the quantum yields of the reaction are much lower than unity.

In summary, an efficient photosensitized oxidation of alkene with molecular oxygen was achieved using tetra-

substituted dimethoxybenzenes as a sensitizer. Mechanistically, this photooxidation proceeds through the initial quenching of an excited singlet sensitizer by molecular oxygen producing a sensitizer radical cation and a superoxide, followed by the electron transfer from the substrate alkene to the sensitizer radical cation and the subsequent recombination of the resulting substrate radical cation with the superoxide, producing the ketone and epoxide as the major oxidation products in excellent combined yields. Photodurability of dimethoxybenzene sensitizers is dramatically improved by the tetraalkylation of dimethoxybenzene. It has been demonstrated that the reactions of singlet oxygen with *trans*-4-propenylanisole¹⁵ and with benzyl ethyl sulfide¹⁶ can be completely changed by adding a catalytic amount of acid. Similar switching of photoreactivity by acid has also been recognized by us¹⁷ and by



Scheme 2.

others,¹⁸ recently. The effect of added acid, detailed reaction mechanism and further synthetic applications of this photosensitized oxidation are currently under investigation.

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