

Selective photooxidation of styrene in organic–water biphasic media

YanJun Ren, Yanke Che, Wanhong Ma, XinZhi Zhang, Tao Shen and Jincai Zhao*

Key Laboratory of Photochemistry, Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing, 100080 China. E-mail: jczhao@iccas.ac.cn; Fax: +86-10-82616495

Received (in Montpellier, France) 19th July 2004, Accepted 20th August 2004
First published as an Advance Article on the web 9th November 2004

The photooxidation of styrene by molecular oxygen was investigated in organic–water biphasic media at room temperature under UV light irradiation. The photoreaction gave a high selectivity (>90%) of the product, benzaldehyde, with a formative yield of 29%. This new method was also operative for the oxidation of several styrene derivatives, such as 3-methylstyrene, 4-methoxystyrene, β -methylstyrene, and 1,1-diphenylethylene, into the corresponding aldehydes or ketones. It was demonstrated that both molecular oxygen and water were essential to these reactions. The mechanistic study revealed that the primary reaction involved mainly electron transfer from the excited styrene to triplet ground state molecular oxygen, forming the superoxide radical anion and styrene radical cation, followed by cleavage of the C=C bond *via* an adduct intermediate in the presence of water.

1. Introduction

Selective oxidation of hydrocarbons is one of the most important reactions in organic synthesis.^{1–2} Stoichiometric oxidation processes, such as the epoxidation of alkenes by peracids, alkylperoxides and iodosobenzene,^{3–10} have been widely used. However, those processes are expensive and produce large amounts of toxic by-products. Therefore, the exploration of a new oxidation process that has a minimal environment impact and low cost is necessary and remains a great challenge.

A ‘green’ oxidation process, using hydrogen peroxide or, ideally, molecular oxygen as the oxidant and water as the solvent, is the most attractive oxidation technology for selective organic synthesis and the treatment of organic pollutants.^{11–21} The key issue in the use of molecular oxygen as an oxidant is product selectivity. Homogeneous catalytic oxidation by O₂ under thermal conditions in general exhibits very low selectivities due to side reactions that are hard to control.^{1–2} In this regard, photoassisted oxidation processes can hold special promise. For example, photoinduced reactions of O₂ in many cases give some products that cannot be obtained by dark reactions. More importantly, photochemical reactions can be conducted at ambient temperature, which may minimize the probability of secondary thermal reactions occurring and thus improve the product selectivity.

Recently, Frei *et al.* have reported the selective photooxidation of hydrocarbons by O₂ in the gas phase over alkali- and alkaline-earth-exchanged zeolites under visible light irradiation.^{22–26} The reactions involve photoexcitation of a hydrocarbon–O₂ charge-transfer state. Tung *et al.* investigated the microreactor-controlled product selectivity in O₂-mediated photooxidation of alkenes.^{27–31} Remarkable product selectivity has been achieved in such a microreactor-controlled photoreaction. Ramamurthy *et al.* studied singlet-oxygen-mediated photooxidation of olefins within dye-exchanged X and Y zeolites.^{32–33} By the utilization of zeolite supercages as ‘an active reaction cavity’, the active oxygen has been directed toward a particular face of the olefins and thus a high selectivity was obtained. Organic reactions in water, on the other hand, have attracted extensive attention in recent

years.^{34–35} Sheldon *et al.* reported catalytic oxidation of alcohol in an environmentally friendly aqueous medium.³⁶

In this work, we report a new approach for the selective photooxygenation of styrene and its derivatives by O₂ in organic–water media under ambient conditions (Scheme 1). The photoreaction gave a high selectivity of the product, benzaldehyde. The reaction mechanism was investigated by the aid of several characterization experiments including NMR and ESR. The mechanistic study demonstrated that the primary reaction involves mainly electron transfer from the excited styrene to triplet ground state molecular oxygen.

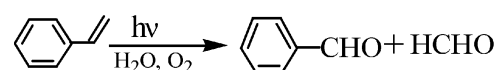
2. Experimental

2.1. Materials

Styrene, 4-methoxystyrene, 3-methylstyrene, 1,1-diphenylethylene, *cis*-stilbene, *trans*-stilbene, *trans*- β -methylstyrene, cyclohexene, 1-octene, benzaldehyde, styrene oxide, benzoic acid, 1-phenyl-1,2-ethanediol, *p*-anisaldehyde, 3-methylbenzaldehyde, benzophenone, cyclohexene oxide, 2-cyclohexen-1-one, and 2-cyclohexen-1-ol were purchased from Aldrich Co., Ltd., and were used without further purification. Acetonitrile, acetone, methanol, ethanol, chloroform and hydrogen peroxide were of analytical reagent grade. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO, Sigma) and 2,2,6,6-tetramethylpiperidine (TEMP, Acros) were used as the ESR spin-trapping reagents. Deionized and doubly distilled water was used throughout this study.

2.2. Photoreaction conditions

A 100 W medium pressure Hg lamp (Toshiba Lighting and Technology of Japan) was used as the UV light source. Unless otherwise noted, all the irradiation experiments were carried out in a Pyrex vessel ($\lambda = 330–400$ nm). In a typical reaction,



Scheme 1

the substrate (styrene: 100 μ l, 0.9 mmol) and the solvent (5 ml) were added to the vessel (20 ml) which was then sealed with a septum. The reaction mixture was stirred and irradiated by ultraviolet light under an oxygen atmosphere at ambient pressure and temperature for the desired time. After the reaction, the oxygenated products were extracted by diethyl ether and analyzed by GC and GC/MS using toluene as an internal standard.

2.3. Instrumentation and product analysis

Gas chromatographic analysis for the reaction kinetics was performed on a Hitachi G-3900 GC spectrometer using a hydrogen flame ionization detector, equipped with an integrator processor. Nitrogen was used as the carrier gas. The inner column (length 30 m; internal diameter 0.25 mm, film thickness 0.25 μ m) was packed with a SGE BP-5 5% phenyl-methyl siloxane film. The reaction products were identified by comparison of their retention times with the corresponding standard samples, using a Finnigan TRACE DSQ GC/MS spectrometer with electron ionization. For GC analysis of the styrene oxidation reaction, the following GC conditions were used: the oven temperature was set at 100 $^{\circ}$ C, injection temperature at 200 $^{\circ}$ C, and detection temperature at 250 $^{\circ}$ C. Formaldehyde was analyzed on an HP SP-502 GC spectrometer.

The reaction yields were calculated on the basis of all oxidation products. The selectivity was the fraction of benzaldehyde or the aldehydes among the oxidation products formed from the photooxidation of styrene or the styrene derivatives.

Electron paramagnetic resonance (EPR) experiments were conducted on a Bruker Model ESP 300E spectrometer at room temperature. The irradiation source was a Quanta-Ray Nd:YAG pulsed laser system (λ = 355 nm; 10 Hz). The reaction radicals were trapped by DMPO and TEMP. The ESR center field was set at 3486.70 G, sweep width at 100 G, microwave frequency at 9.82 GHz, modulation frequency at 100 KHz, and power at 5.05 mW. To minimize measurement errors, the same quartz capillary tube was used throughout the EPR measurements. In order to detect the active oxygen species effectively, a small amount of dimethyl sulfoxide (DMSO) was added to the styrene/H₂O system since styrene is insoluble in water.

Nuclear magnetic resonance (NMR) experiments were examined on a Bruker Avance DRX500 spectrometer using tetramethylsilane (TMS) as an internal standard. Similarly, a small amount of acetone was added to the mixture of styrene and water in the ¹H-NMR experiments so as to investigate the interaction between styrene and water. Since the water resonance obscures a large part of the spectrum, spin-spin relaxation methods were used to eliminate the water resonance.^{40,41} By making the spin-spin relaxation period long enough, the water resonance can be completely eliminated and sample resonances at the frequency of the water resonance can be observed.

3. Results and discussion

3.1. Effect of light, dioxygen and water on the oxygenation of styrene

The effects of light, molecular oxygen and water on the oxygenation of styrene were investigated under different reaction conditions. Fig. 1 shows the product yield of benzaldehyde, obtained after 11 h. In the dark (B), styrene was hardly oxygenated by dioxygen. Only a trace amount of benzaldehyde (less than 1% of the initial styrene) was found in the reaction mixture. Under ultraviolet light irradiation (A), selective oxygenation of styrene to benzaldehyde with a yield of 29% and a high selectivity of 91% was achieved in the aerated aqueous

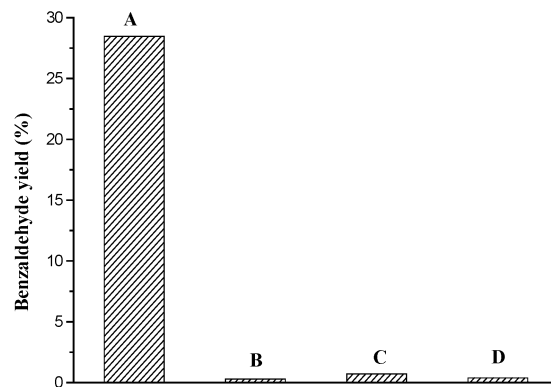


Fig. 1 The product yield of benzaldehyde obtained after 11 h of reaction under different conditions, bubbling with dioxygen during reaction: (A) in aqueous medium under UV irradiation; (B) in aqueous medium in the dark; (C) in ethanol under UV irradiation; (D) in O₂-free aqueous medium under UV irradiation.

media. In ethanol (*i.e.*, absence of water; C), no benzaldehyde was formed under the same conditions. In the absence of dioxygen (D), the photooxidation of styrene did not occur in either aqueous media or organic solvents such as chloroform, acetone, acetonitrile, methanol, and ethanol. Therefore, both water and dioxygen are essential to initiate the styrene photooxygenation. In addition, in aqueous media the yield of benzaldehyde reached 29% when dioxygen was continuously added during reaction, whereas the yield was 15% if dioxygen was added only before the UV irradiation. On the other hand, the solution pH values and ionic strength had little influence on the photooxygenation of styrene by O₂.

3.2. Photooxygenation of other olefins with dioxygen

The photooxygenation of other terminal and internal alkenes with dioxygen was also examined, for which 3-methylstyrene, 4-methoxystyrene, 1,1-diphenylethylene, *trans*-stilbene, *cis*-stilbene, *trans*- β -methylstyrene, cyclohexene and 1-octene were selected as model substrates (Table 1). The experimental results indicate that aromatic terminal alkenes such as 3-methylstyrene, 4-methoxystyrene, 1,1-diphenylethylene can be selectively oxidized to the corresponding carbonyl compounds with high selectivity. The oxygenated products are 3-methylbenzaldehyde, 4-methoxybenzaldehyde and benzophenone, respectively. Similar to styrene oxidation, the oxygenated product yields and selectivity in aqueous media are all much higher than those in organic solvents such as acetonitrile, chloroform and acetone, under the same conditions, while the photooxygenations did not occur in alcohol media. Interestingly, the aromatic internal olefin, *trans*- β -methylstyrene, can also be selectively oxygenated into benzaldehyde. The yield and selectivity of benzaldehyde in aqueous media was also higher than in organic solvents, such as acetonitrile. Almost 100% selectivity could be achieved in aqueous media. This suggests that the C=C double bond of the aromatic internal olefins can be oxidatively cleaved by O₂ in aqueous media under UV irradiation. However, oxidative cleavage of the C=C double bond of *trans*-stilbene and *cis*-stilbene could not be achieved in either aqueous media or organic solvents under identical conditions. Instead, *cis*-stilbene was photoisomerized to *trans*-stilbene, possibly due to the stability of the conjugated phenyl substituents in the stilbene molecule. The oxidative cleavage of the C=C double bond of cyclohexene by O₂ did not occur under UV irradiation in both aqueous and organic media. Only a small amount of the autooxidation products, 2-cyclohexen-1-one, 2-cyclohexen-1-ol and cyclohexene oxide, were found in the reaction mixture. 1-Octene could not be oxidized into carbonyl compound under identical conditions. This is

Table 1 Photooxygenation of other olefins with dioxygen^a

Substrate	Reaction media	Reaction time/h	Main product	% Yield	% Selectivity
PhCH=CH ₂	H ₂ O	7	PhCH=O	15	91
	CH ₃ CN	7	PhCH=O	3	83
(Ph) ₂ C=CH ₂	H ₂ O	6	(Ph) ₂ C=O ³⁷	8	80
	CH ₃ CN	6	(Ph) ₂ C=O	1	73
Ph-CH=CH ₂	H ₂ O	12	PhCH=O	18	98
	CH ₃ CN	12	PhCH=O	6	66
CH ₃ O-C ₆ H ₄ -CH=CH ₂ ^b	H ₂ O	12	CH ₃ O-C ₆ H ₄ -CHO ³⁸	10	88
	CH ₃ CN	12	CH ₃ O-C ₆ H ₄ -CHO	1	65
Ph-CH=CH-Ph	H ₂ O	12	No reaction	—	—
	CH ₃ CN	12	No reaction	—	—
Ph-CH=CH-Ph	H ₂ O	12	Isomerization	—	—
	CH ₃ CN	12	Isomerization	—	—
CH ₃ -C ₆ H ₄ -CH=CH ₂	H ₂ O	12	CH ₃ -C ₆ H ₄ -CHO ³⁹	5	92
	CH ₃ CN	12	CH ₃ -C ₆ H ₄ -CHO	2	83
Cyclohexene	H ₂ O	12	Traces of cyclohexanone, cyclohexanol, cyclohexene oxide	Traces	—
	CH ₃ CN	12	Traces of cyclohexanone, cyclohexanol, cyclohexene oxide	Traces	—
1-Octene	H ₂ O	12	No reaction	—	—
	CH ₃ CN	12	No reaction	—	—

^a Reaction conditions: olefin 100 μ l, solvent 5 ml, bubbling with dioxygen before irradiation. ^b 4-Methoxystyrene 50 μ l.

possibly due to the fact that both cyclohexene and 1-octene do not absorb UV light ($\lambda = 330\text{--}400$ nm).

3.3. Effect of different solvents on the photooxygenation of styrene

We also investigated the photooxygenation of styrene in different solvents by O₂ (Fig. 2). The distribution of oxygenated products in the different media are illustrated in Table 2. The photooxygenation yield of styrene with dioxygen is the highest in aqueous media, but the lowest in methanol or ethanol media. This shows that the nature of the solvent has a dramatic effect on styrene photooxygenation. The yield of benzaldehyde obtained in the aqueous, acetonitrile, chloroform, acetone, methanol and ethanol media was 29%, 6%, 6%, 5%, 1% and 1%, respectively. In alcohol media, photooxygenation of styrene with dioxygen was scarcely observed. ESR experiments indicated that no active oxygen species were detected in alcohol reaction systems (see section 3.5 below), probably since alcohols quench the styrene radical cations or active oxygen species. The high yield (29%) and the high selectivity (91%) of benzaldehyde may be related to the fact that water noticeably accelerates the photooxygenation of styrene by O₂ with cleavage of the C=C bond, forming mainly benzaldehyde with only traces of other oxides. By contrast, in

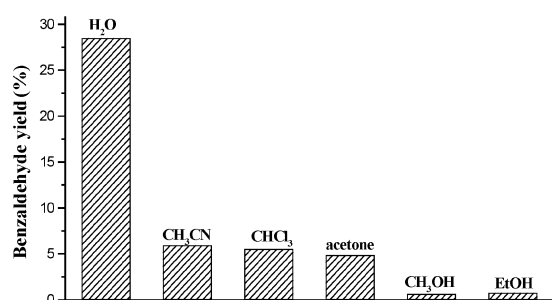


Fig. 2 The yield of benzaldehyde obtained from styrene photooxidation in different solvents under UV irradiation. Reaction conditions: styrene 0.9 mmol, solvent 5 ml, reaction time: 7 h, bubbling with dioxygen during reaction.

organic solvents, such as acetonitrile, chloroform and acetone, the selectivity towards styrene oxide is much higher than that in aqueous media (Table 2). In aqueous media, further photooxygenation of benzaldehyde with dioxygen did not occur so that only a small amount of benzoic acid (1%) was found in the reaction products. Formation of 1-phenyl-1,2-ethanediol is possibly due to the attack of water on the intermediate in the reaction process. On the other hand, photooligomerization of styrene was observed in aqueous media.


The influence of the mixed solvent chloroform–water on styrene photooxidation was also studied (Table 3). It was found that the photooxygenation of styrene was noticeably enhanced upon addition of H₂O into chloroform under UV irradiation. For example, the yield of benzaldehyde was increased by almost twofold (from 6 to 11%), when 10% H₂O (v/v) was added. Correspondingly, the selectivity of benzaldehyde also increased with increasing water content, from 78% (in 10% H₂O) to 85% (in 90% H₂O). Thus, both the yield and the selectivity of benzaldehyde are noticeably increased upon addition of H₂O into chloroform solutions.

In alcohol media, photooxygenation of styrene with dioxygen under UV irradiation seems to be prevented. Less than 1% benzaldehyde was observed, even after 11 h irradiation with ultraviolet light. Upon addition of water to methanol solutions (Fig. 3), the yield of benzaldehyde was noticeably increased. When 80% water was added into methanol, the yield of benzaldehyde increased to 8%. In aqueous media, the yield of benzaldehyde was 15% under otherwise identical conditions. These data suggest that addition of water can change the photooxygenation pathway of styrene in alcohol solutions, significantly promoting the photooxygenation of styrene with dioxygen.

3.4. Photooxygenation of styrene with hydrogen peroxide


In aqueous media, when hydrogen peroxide was employed as the oxidant for styrene photooxygenation under deaerated conditions, only small amounts of benzaldehyde were observed (less than 1% yield). However, in some organic solvents, such as chloroform, acetonitrile and acetone, the yield of benzaldehyde became somewhat higher (Fig. 4). These results suggest

Table 2 Product distribution from the oxygenation of styrene with dioxygen under UV irradiation^a

Reaction media	% Yield (all products)	% Selectivity			
		PhCH=O	Ph- 	PhCOOH	PhCH(OH)CH ₂ OH
H ₂ O	17	91	1	1	7
CH ₃ CN	3	83	13	3	1
CHCl ₃	9	76	22	1	1
Acetone	2	84	16	Trace	Trace
CH ₃ OH	1	—	Trace	Trace	Trace
Ethanol	1	—	Trace	Trace	Trace

^a Reaction conditions: styrene 0.9 mmol, solvent 5 ml, charging with dioxygen before irradiation, reaction time: 7 h.

Table 3 Effect of mixed CHCl₃–H₂O solvent on the photooxygenation of styrene under UV irradiation^a

Solvent (by volume)	% Yield PhCH=O	% Selectivity			
		PhCH=O	Ph- 	PhCOOH	PhCH(OH)CH ₂ OH
100% CHCl ₃	6	76	22	1	1
10% H ₂ O ^b	11	78	2	7	13
40% H ₂ O	10	82	4	8	6
50% H ₂ O	12	82	7	5	6
80% H ₂ O	14	85	3	4	8
90% H ₂ O	16	85	5	5	5
100% H ₂ O	29	91	1	1	7

^a Reaction conditions: styrene 0.9 mmol, solvent 5 ml, reaction time: 12 h, bubbling with dioxygen during reaction. ^b *i.e.*, the ratio H₂O : CHCl₃ = 1 : 9 (v/v).

that the pathway of styrene photooxygenation by H₂O₂ is different from that of O₂ oxidation in aqueous media. When both dioxygen and hydrogen peroxide were used simultaneously as the oxidant, the photooxygenation of styrene proceeded effectively in aqueous media, but the yield of benzaldehyde was lower than when using O₂ alone. This implies that the presence of dioxygen can promote the photooxygenation of styrene in aqueous media, while the presence of hydrogen peroxide may quench the photooxidation of styrene in aqueous media. Interestingly, in alcohol media, the photooxygenation of styrene with hydrogen peroxide resembles somewhat that using dioxygen as oxidant. In alcohol media, the photooxygenation of styrene by H₂O₂ could not proceed effectively, the same as when using O₂.

3.5. Photooxidation reaction mechanism

¹H-NMR techniques were used to investigate the interaction of styrene and water. Since the water resonance obscures a large part of the spectrum, spin-spin relaxation methods were used

to eliminate the water resonance.^{40,41} NMR experiments indicated that the presence of water had a great influence on the chemical shifts of styrene. The chemical shifts of the hydrogens of both the aromatic ring and the C=C double bond were shifted to lower field. For instance, the chemical shift of methylene (=CH₂) moved from 5.133, 5.657 ppm to 5.226, 5.792 ppm, the methenyl group (–CH=) signal shifted from 6.633 ppm to 6.745 ppm and the aromatic ring signal from 7.274 ppm to 7.431 ppm. The hydrogen bond and the polarization interaction between styrene and water molecules alter the electron density of the styrene to a lower value, thus its chemical shifts become bigger. The presence of water molecules activates the C=C double bond.

The formation of hydrogen peroxide was observed during styrene photooxygenation by O₂ in aqueous media under ultraviolet light irradiation, but its concentration was very low. In order to verify the reaction mechanism, we compared the oxidation reactions of styrene using Rose Bengal as a sensitizer to generate singlet oxygen and by the photo-Fenton

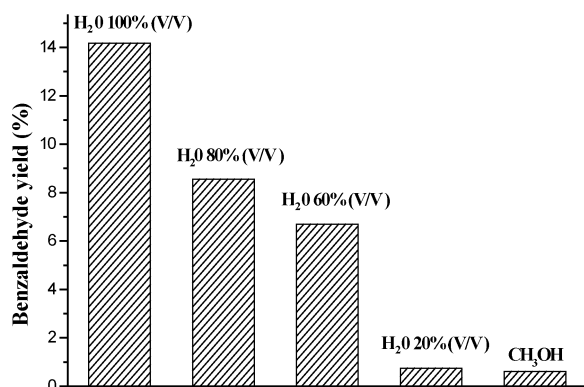


Fig. 3 Changes of benzaldehyde yield with water content in the photooxidation of styrene under UV irradiation in mixed alcohol–water solution. Reaction conditions: styrene 0.9 mmol, solvent 5 ml, purged with dioxygen before irradiation, reaction time: 8 h.

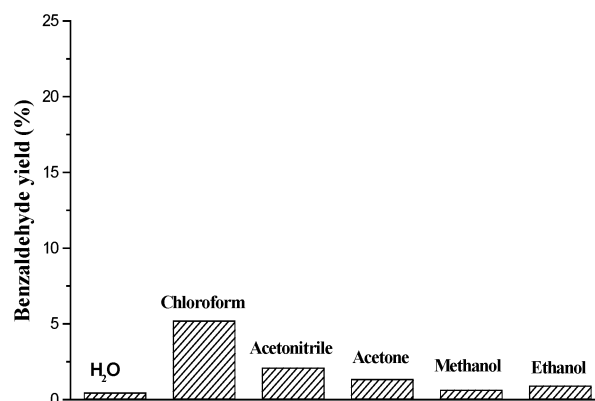


Fig. 4 Benzaldehyde yield using H₂O₂ as the oxidant for styrene oxidation under UV irradiation in different solvents. Reaction conditions: styrene 0.9 mmol, solvent 5 ml, H₂O₂ 1 mmol, deaerated before irradiation, reaction time: 8 h.

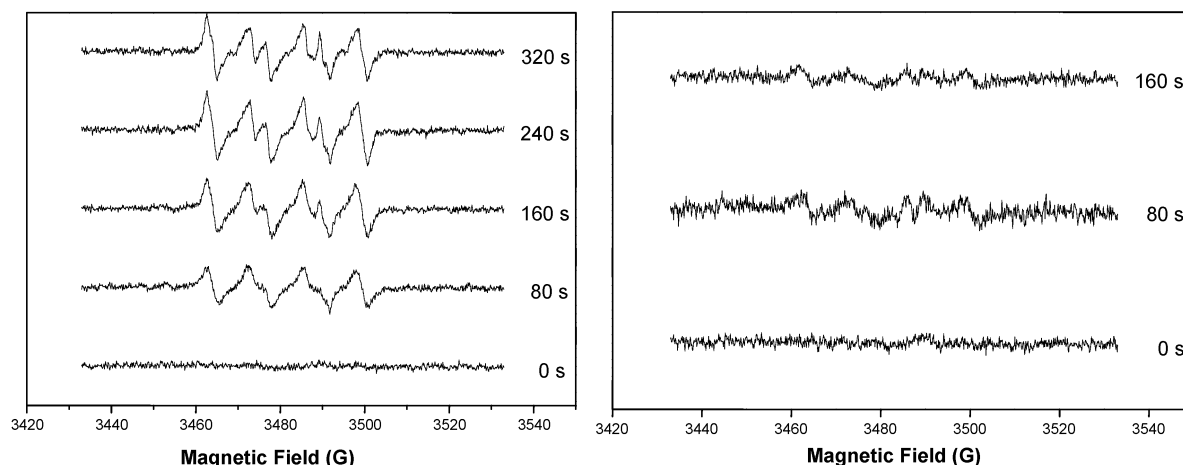


Fig. 5 EPR signals of the DMPO- \cdot OOH adducts as a function of irradiation time (left: styrene-H₂O-DMSO system; right: styrene-CH₃OH system) in the dark and under UV irradiation. Styrene: 0.2 M, DMPO: 0.04 M.

reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) to produce hydroxyl radicals. The sensitized photooxygenation of styrene was carried out in an oxygen-saturated aqueous media of Rose Bengal under visible light irradiation ($\lambda > 420$ nm). The photo-Fenton oxidation of styrene was conducted under UV irradiation ($\lambda = 330\text{--}400$ nm) in deaerated aqueous media. However, the yields of benzaldehyde from both the photosensitized oxidation and the photo-Fenton reaction, 1% and 2%, respectively, after 12 h of reaction, were much lower than the 29% obtained from styrene photooxygenation under UV irradiation in oxygen-saturated aqueous media. This demonstrates that the reactive intermediates for the styrene photooxygenation are neither singlet oxygen, generated by photosensitization of Rose Bengal, nor hydroxyl radical, generated by the photo-Fenton reaction.

The photooxygenation of styrene in water under UV irradiation may involve an electron transfer mechanism. In agreement with this idea, the reactive intermediates, $\text{O}_2^{\cdot-}$ and then \cdot OOH, were detected experimentally by EPR techniques (Fig. 5). No EPR signals were observed when the reaction was performed in the dark in aerated aqueous media. Under UV irradiation, the characteristic sextet peaks of DMPO- \cdot OOH/ $\text{O}_2^{\cdot-}$ appeared gradually in the aerated aqueous media, and their intensity increased with irradiation time. No EPR signals of DMPO- \cdot OOH/ $\text{O}_2^{\cdot-}$ adducts were observed in aerated methanol media when the reaction was performed either in the dark or under UV irradiation. Furthermore, upon addition of SOD, an efficient quencher of $\text{O}_2^{\cdot-}$, the photooxygenation reaction of styrene was observed to be prevented. On the other hand, with the addition of NaN_3 , an $^1\text{O}_2$ quencher, the photooxygenation reactions of styrene decreased only slightly. It is well-known that 1,1-diphenylethylene cannot react with singlet oxygen,⁴² but it could be easily be oxidized into benzophenone with high selectivity under the present conditions (Table 1). Based on the above results, we propose that the reactive intermediate involved in the styrene photooxidation process is mainly the superoxide radical anion. A possible photoreaction mechanism is proposed in Scheme 2. Upon irradiation with UV light, the excited styrene molecule transfers its electron to triplet ground state dioxygen, or an electron

transfer occurs in the charge-transfer complex⁴³ of styrene and dioxygen, generating the superoxide radical anion and styrene radical cation. Due to the polarization interaction between styrene and a water molecule, the electron density of styrene is altered so that the intermediate adducts are cleaved into benzaldehyde and formaldehyde in the presence of water. The formation of formaldehyde was confirmed by GC analysis during the photooxygenation of styrene with dioxygen in aqueous media. However, the amount of formaldehyde detected in the reaction mixture was relatively low due to easy photo-oligomerization of formaldehyde. In comparison runs, the active oxygen species ($\text{O}_2^{\cdot-}$, OH^{\cdot} , or $^1\text{O}_2$) were not detected in the photoreaction performed in alcoholic solution (Fig. 5). Probably the alcohol molecules quench the styrene radical cation or the active oxygen species, leading to the lower yield of the photooxygenation product of styrene with dioxygen.

4. Conclusions

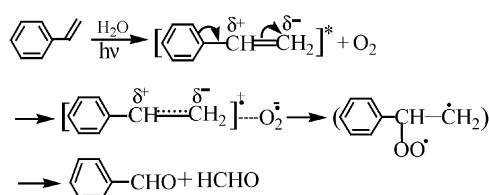
A new method for benzaldehyde synthesis *via* the photooxidation of styrene in organic-water biphasic media using molecular oxygen as the oxidant under ambient conditions was reported. The study shows that both dioxygen and water are essential to achieve the photooxygenation of styrene into benzaldehyde with high yield and selectivity. The primary step of this reaction involves mainly electron transfer from the excited styrene to molecular oxygen, which gives the superoxide radical anion and styrene radical cation as intermediates; successive reactions involve cleavage of the C=C bond in the adduct intermediate in the presence of water. By this method, several other aromatic terminal alkenes and internal alkenes can be also photooxygenated to the corresponding carbonyl compounds.

Acknowledgements

For this work, the generous financial support by the Ministry of Science and Technology of China (No. 2003CB415006), by the National Science Foundation of China (No. 50221001, No. 20133010, No. 20277038, and No. 20371048) and by the Chinese Academy of Sciences is gratefully acknowledged.

References

- 1 B. C. Gates, *Catalytic Chemistry*, Wiley, New York, 1992.
- 2 G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, Wiley, New York, 2nd edn., 1992.



Scheme 2

- 3 D. Swern, in *Organic Peroxides*, ed. D. Swern, Wiley, New York, 1972, vol. **II**, ch. V.
- 4 R. Hiatt, in *Oxidation*, eds. R. L. Augustine and D. J. Trecker, Marcel Dekker, New York, 1971, vol. **II**, ch. III, 113–140.
- 5 L. C. Yuan and T. C. Bruice, *J. Am. Chem. Soc.*, 1986, **108**, 1643–1650.
- 6 A. Murphy, G. Dubios and T. D. P. Stack, *J. Am. Chem. Soc.*, 2003, **125**, 5250–5251.
- 7 W. Nam, S. E. Park, I. K. Lim, M. H. Lim, J. K. Hong and J. H. Kim, *J. Am. Chem. Soc.*, 2003, **125**, 14674–14675.
- 8 M. Palucki, G. J. McCormick and E. N. Jacobsen, *Tetrahedron Lett.*, 1995, **36**, 5457.
- 9 S. Banfi, F. Montanari, S. Quici, S. V. Barkanova, O. L. Kaliya, V. N. Kopranenkov and E. A. Lukyanets, *Tetrahedron Lett.*, 1995, **36**, 2317.
- 10 W. Adam, C. M. Knoblauch, C. R. S. Moller and M. Herderich, *J. Am. Chem. Soc.*, 2000, **122**, 9685–9691.
- 11 W. Ma, J. Li, X. Tao, J. He, Y. Xu, J. C. Yu and J. Zhao, *Angew. Chem., Int. Ed.*, 2003, **42**, 1029–1032.
- 12 J. Li, W. Ma, Y. Huang, M. Cheng, J. Zhao and J. C. Yu, *Chem. Commun.*, 2003, 2214–2215.
- 13 C. L. Hill, *Nature (London)*, 1999, **401**, 436.
- 14 R. Neumann and M. Dahan, *Nature (London)*, 1997, **388**, 353.
- 15 C. Bolm, G. Schlingloff and K. Weickhardt, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1848–1849.
- 16 G. J. Brink, T. I. W. C. E. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636.
- 17 R. Neumann and M. J. Dahan, *J. Am. Chem. Soc.*, 1998, **120**, 11969.
- 18 T. Iwahama, G. Hattai, S. Sakaguchi and Y. Ishii, *Chem. Commun.*, 2000, 163.
- 19 Y. Ishii, S. Sakaguchi and T. Iwahama, *Adv. Synth. Catal.*, 2001, **343**, 393–427.
- 20 T. Matsushita, D. T. Sawyer and A. Soykowiak, *J. Mol. Catal.*, 1999, **137**, 127.
- 21 S. I. Murahashi, *Angew. Chem., Int. Ed. Engl.*, 1995, **3-4**, 2443.
- 22 F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1993, **115**, 7501–7502.
- 23 F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1994, **116**, 1812–1820.
- 24 H. Sun, F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1994, **116**, 7951–7952.
- 25 F. Blatter, F. Moreau and H. Frei, *J. Phys. Chem.*, 1994, **98**, 13403–13407.
- 26 H. Frei, F. Blatter and H. Sun, *CHEMTECH*, 1996, 24–30.
- 27 C. Tung, L. Wu, L. Zhang and B. Chen, *Acc. Chem. Res.*, 2003, **36**, 39–47.
- 28 C. Tung, H. Wang and Y. Ying, *J. Am. Chem. Soc.*, 1998, **120**, 5179–5186.
- 29 C. Tung, L. Wu, Z. Yuan and N. Su, *J. Am. Chem. Soc.*, 1998, **120**, 11594–11602.
- 30 C. Tung and J. Guan, *J. Am. Chem. Soc.*, 1998, **120**, 11874–11879.
- 31 H. Li, L. Wu and C. Tung, *J. Am. Chem. Soc.*, 2000, **122**, 2446–2451.
- 32 X. Li and V. Ramamurthy, *J. Am. Chem. Soc.*, 1996, **118**, 10666–10667.
- 33 J. Shailajia, J. Sivaguru, J. Rebecca and V. Ramamurthy, *Tetrahedron*, 2000, **56**, 6927–6943.
- 34 U. M. Lindstrom, *Chem. Rev.*, 2002, **102**, 2751–2772.
- 35 C. Li, *Acc. Chem. Res.*, 2002, **35**, 533–538.
- 36 G.-J. Ten Brink, I. W. C. E. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636–1639.
- 37 MS data (*m/z*): 51 (17%), 77 (83%), 105 (100%), 152 (6%), 182 (61%).
- 38 MS data (*m/z*): 51 (5%), 77 (32%), 107 (10%), 92 (7%), 135 (100%).
- 39 MS data (*m/z*): 39 (6%), 51 (6%), 63 (8%), 65 (17%), 91 (66%), 119 (100%).
- 40 (a) D. L. Rabenstein and S. Fan, *Anal. Chem.*, 1986, **58**, 3178–3184; (b) D. L. Rabenstein, S. Fan and T. T. Nakashima, *J. Magn. Reson.*, 1985, **64**, 541–546.
- 41 (a) R. Bryant and T. M. Eads, *J. Magn. Reson.*, 1985, **64**, 312–315; (b) T. M. Eads, S. D. Kennedy and R. G. Brayant, *Anal. Chem.*, 1986, **58**, 1752–1756.
- 42 J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 6083–6088.
- 43 S. Hashimoto and H. Akimoto, *J. Phys. Chem.*, 1989, **93**, 571–577.