High-performance Photooxidation of Phenol with Singlet Oxygen in an Ionic Liquid

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Photooxidation of phenol using singlet oxygen generated in ionic liquid was reported. Singlet oxygen is produced via photosensitized reaction of 5,10,15,20-tetrakis(4-sulfophenyl)porphine in ethylammonium nitrate. The production rate of singlet oxygen was 2.2 times faster than that in aqueous media containing the same. The resulting oxidized product from phenol was pure benzoquinone with no by-product like quinhydrone usually found in aqueous media. The advantage of this method is high yield of benzoquinone with no harmful agents like metal catalysis or oxidizer as well as easy product separation.

In recent decades, ionic liquids have attracted considerable attention as a medium for organic synthesis,[1] solvation of biomacromolecules,[2] and enzyme reactions[3] because solvation scheme is quite different in ionic liquids compared to nonionic solvent, promoting enhanced reactivity or producing other final products. In photochemistry, several studies utilizing ionic liquids have been reported. One study used various kinds of ionic liquids as a medium for photochemical reactions and found an enhancement of triplet excited states and elongation of lifetimes of radical ions.[4] Another report concentrated on the photoisomerization of *cis*- and *trans*-stilbene and found the mechanism involves the process of electron-transfer reactions from excited stilbene to cation, which is different from reactions in traditional solvents.[5]

Longer lifetime of the triplet excited state in ionic liquids means that there are increased chances of energy transfer with a reactant. Singlet oxygen can be produced in such a process because it is usually generated via energy transfer from an excited photosensitizer to oxygen in the ground state (Scheme 1). Singlet oxygen is a good oxidizer because its energy lies 94 kJ mol^{-1} above the ground state and it can oxidize a variety of species without any harmful agents. As for photochemical reactions in ionic liquids, highly efficient production of singlet oxygen is expected and it has a potential for industrial use as an attractive oxidizer.

In this report, phenol was selected as a reactant oxidized by singlet oxygen since phenols are known to resist from biodegradation and have attracted particular interest in wastewater treatment. Oxidized product 1,4-benzoquinone is a precursor of Vitamin E and has various industrial applications. If the oxidation reaction proceeds efficiently, this method can be an ideal clean method for oxidation. It is because ionic liquids have little or no vapor pressure, and oxygen as the source of singlet oxygen can be easily supplied from the atmosphere without any special treatment generating environmental pollution. However, none have tried to oxidize phenols by singlet oxygen produced in ionic liquids. In this report, singlet oxygen produced in ethylammonium nitrate (EAN) was used to oxidize phenols aiming to a high yield and as an approach to green chemistry.

$$^1\text{S(Sensitizer)} + h\nu \longrightarrow {}^1\text{S}^*$$
$$^1\text{S}^* \longrightarrow {}^3\text{S}^*$$
$$^3\text{S}^* + {}^3\text{O}_2 \longrightarrow {}^1\text{S} + {}^1\text{O}_2$$

Scheme 1. Singlet oxygen generation via photosensitized reaction.

EAN was synthesized by mixing equimolar amounts of $EtNH_2$ and HNO_3 in an ice bath. EAN was dried at 70 °C for 3 h on a rotary evaporator under reduced pressure before use. Singlet oxygen produced by photosensitized reaction was measured with UV–visible absorption spectroscopy using trapping agent 9,10-diphenylanthracene (DPA) without phenol in solution. DPA is known to react quantitatively with singlet oxygen producing 9,10-diphenylanthracene endoperoxide. The absorption maximum of DPA is around 355 nm while DPA-endoperoxide has no absorption band in the range 300–500 nm. Decrease in the absorbance value at 355 nm can be used to calculate the amount of DPA-endoperoxide formed, which is proportional to the amount of singlet oxygen produced.[6] The measurement was carried out after irradiation with a Xe lamp (StockerYale, 150W) to a sample solution (2.5 mL) under ambient atmosphere. Initial concentration of photosensitizer 5,10,15,20-tetrakis(4-sulfophenyl)porphine (TSPP) was 1.0×10^{-5} M and that of trapping agent DPA was 1.0×10^{-4} M, which is enough to trap all of the dissolved oxygen.

The rate of singlet oxygen production can be calculated by the initial slope of curves in Figure 1 that shows the decrease of the absorption at 355 nm with the period of light irradiation time. The rate is faster in EAN than in nonionic solvents, H_2O and CH_3CN. The factors of the rate acceleration/deceleration are (1) initial concentration of oxygen in solution, (2) efficiency of light absorption by the photosensitizer, (3) viscosity of the solvent, and (4) lifetime of transient species. Initial oxygen concentration can be estimated as the saturated solubility for each solvent. The data are available for H_2O and CH_3CN and the values are 2.69×10^{-4} and 1.99×10^{-3} M, respectively, but

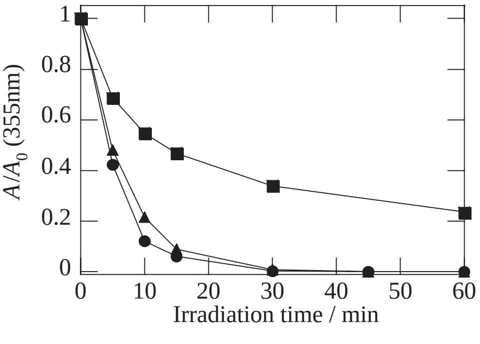

Figure 1. Temporal change in absorbance at 355 nm of DPA, for (●) TSPP in EAN, (▲) TSPP in CH_3CN, (■) TSPP in H_2O.

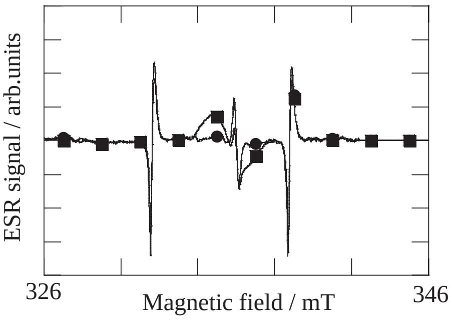

Figure 2. ESR spectrum of EAN solution including Mn marker (●) before irradiation and (■) under irradiation.

not for EAN. When DPA is 5.0×10^{-4} M, the absorption maximum of DPA is not disappeared completely. From the oxygen consumption behavior in EAN, the value can be roughly estimated around 5×10^{-4} M. Initial concentration of oxygen is not the origin of the rate acceleration in EAN. The light absorption efficiency can be estimated from absorption spectrum of photosensitizer in each solvent. The light absorption efficiency is in the order $CH_3CN > H_2O >$ EAN, and there is a discrepancy with the results of singlet oxygen production. The viscosity of the solvent is in the order of EAN $> H_2O > CH_3CN$ and molecular diffusion in the solutions containing singlet oxygen formation are assumed in the reversed order. The reaction rate controlled by diffusion should be faster in CH_3CN than in EAN. This conflicts with the experimental data. From above discussions, longer lifetime of the transient species can only explain the faster production of singlet oxygen in EAN. To prove the longer lifetime of transient species, electron spin resonance spectroscopy in the presence of sensitizer under irradiation was measured and the results are shown in Figure 2. In EAN a broad signal appeared between two strong marker signals (MnO). The broad signal was observed only in EAN, not observed in H_2O and CH_3CN. These results suggest that the broad ESR signal likely to originate from triplet TSPP. In ionic liquid, lifetime of triplet sensitizer was observed to have longer lifetime. However, the prolonged lifetime of triplet sensitizer is at most twice than in other solvent.[7] So it is considered that the transient species is exciplex consist of triplet TSPP derivative. The transient species is not assigned clearly but exciplex seems to be the most likely candidate because the broad signal is not observed in O_2-saturated EAN solution containing no sensitizer under irradiation.

Phenol was photooxidized for 5 h under the same irradiation conditions. Initial concentration of phenol and photosensitizer TSPP were 0.1 and 10×10^{-5} M, respectively. After irradiation the products were extracted repeatedly with hexane and the extracted part was characterized with NMR spectroscopy. The quantity of each product was analyzed with HPLC and a UV–vis detector. Results are listed in Table 1. Benzoquinone was obtained with no impurity in EAN, while quinhydrone was obtained as a by-product in H_2O and no benzoquinone was detected in CH_3CN. In EAN, ESR spectrum in the presence of phenol was similar to that observed without phenol and its intensity gradually decreased with time. This shows that transient species were continuously produced during the reaction and that it was consumed by photooxidation.

Table 1. BQ yield of EAN, H_2O, and CH_3CN solvent

Solvent	Yield of BQ[a]/%	By-product
EAN	10.0	—
H_2O	8.9	Quinhydrone
CH_3CN	—	—

[a] Yield of BQ was determined by HPLC system (Irradiation time: 5 h, PhOH: 0.1 M).

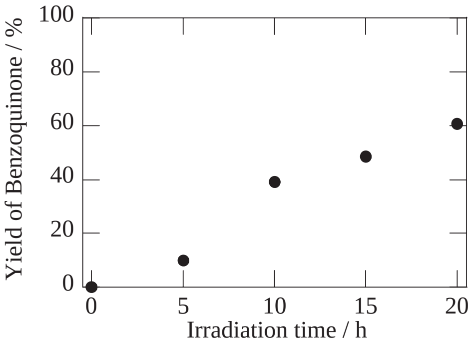

Figure 3. Irradiation time dependence of BQ yield in EAN.

The aerobic oxidation of phenol in the presence of heavy metal compounds as catalysis has some drawbacks. The yield of benzoquinone is much lower by conventional methods. For high yield and selective oxidation, almost or even more than a stoichiometric amount of catalyst is required.[8] Figure 3 shows the benzoquinone yield using singlet oxygen in EAN as a function of the irradiation time. The yield of benzoquinone increased linearly with the irradiation time. This suggests that photooxidation of phenol is possible until the phenol is completely consumed. Furthermore, it is possible to increase the yield by using a high power light source.

In conclusion, singlet oxygen generation and photooxidation of phenol were carried out in an ionic liquid, ethylammonium nitrate. Generation of singlet oxygen and its transient reactant was confirmed during the photooxidation reaction. Photooxidation of phenol by singlet oxygen in ionic liquids can be an efficient method because of the characteristics of high yield and high selectivity. A simple extraction treatment was used in this letter for separating the product, however, there is a possibility of autoseparation becoming unnecessary because the solubility in ionic liquids can be easily controlled by changing the component of either ion.

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