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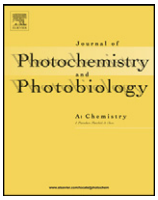

Hydrogen peroxide synthesis by direct photoreduction of 2-ethylanthraquinone in aerated solutions

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ABSTRACT

A new synthesis method of hydrogen peroxide was investigated by the photoreduction of 2-ethylanthraquinone (AQ) in water-insoluble organic solvents. Through optimizing the photoreduction condition including solvent, atmosphere and irradiated time, the photolysis system of 1,3,5-trimethylbenzene/trioctyl phosphate (3:1) solvent mixture under oxygen atmosphere was found to give a high yield of hydrogen peroxide. Furthermore, the formation mechanism of hydrogen peroxide was proposed, i.e. photoreduction and subsequent oxidation of AQ. The photoreduction of 2-ethylanthraquinone undergoes the hydrogen abstraction from solvent to form the anthrahydroquinone, which is subsequently oxidized by oxygen to give hydrogen peroxide.

1. Introduction

Hydrogen peroxide (H_2O_2) is widely used in almost all industrial areas, particularly in the chemical industry and environmental protection, and its demand is growing significantly in the chemical synthesis due to its “green” character. The only degradation product of its use is water, and thus it has played a large role in environmentally friendly methods in the chemical industry. Currently, H_2O_2 is produced on an industrial scale by the anthraquinone oxidation (AO) process. However, this process can hardly be considered as a green method. It is a multistep method that requires significant energy input and generates waste, which has a negative effect on its sustainability and production costs [1,2].

The AO process involves the sequential hydrogenation and oxidation of an alkylanthraquinone precursor dissolved in a mixture of organic solvents followed by liquid–liquid extraction to recover H_2O_2. The commercial production of H_2O_2 is mainly based on the four major steps: hydrogenation, oxidation, hydrogen peroxide extraction, and treatment of the working solution. The two main reactions are shown in Scheme 1. A 2-alkylanthraquinone (usually 2-ethylanthraquinone, AQ) in an appropriate solvent or mixture of solvents, which the anthraquinone/solvent mixture is commonly called working solution, is hydrogenated catalytically to the corresponding anthraquinol or anthrahydroquinone (AH_2Q). One main side reaction is that the unsubstituted aromatic ring of AH_2Q undergoes further hydrogenation to yield 5,6,7,8-tetrahydroanthrahydroquinone (THAHQ). The solution containing the AH_2Q and THAHQ is separated from the hydrogenation catalyst and then oxidized with air to the corresponding quinones, AQ and tetrahydroanthraquinone (THAQ), and simultaneously produce equimolecular amounts of hydrogen peroxide. The hydrogen peroxide is stripped from the organic working solution by demineralized water in a counter current column to produce a H_2O_2 solution, and the anthraquinone/solvent mixture is recycled. A series of side reactions can occur in this process, which leads to a net consumption of the anthraquinone.

The AO process can give a very high yield of hydrogen peroxide per cycle. However, its major disadvantages come from the side reactions, which require regeneration of the solution and the hydrogenation catalyst. Excessive hydrogenations and rapid deactivation of catalyst are two serious drawbacks of hydrogenation process. In view of this, more economical and environmentally cleaner routes have been explored for the production of H_2O_2 [1,2].

The photochemical reduction of AQ derivatives (AQs) is the simplest and most extensively studied reaction [3], and it involves the transfer of an electron or hydrogen atom from an appropriate donor to the oxygen atom of the carbonyl group of AQs in their excited states, and AQs are reduced to anthrahydroquinones [4]. The photochemical reduction of AQs may be intermolecular and intramolecular. Water and almost all organic compounds that can act as hydrogen donors may serve as reducing agents in intermolecular photochemical reduction [3–5]. Based on the photochemical property of AQs, it may become a synthesis method of hydrogen

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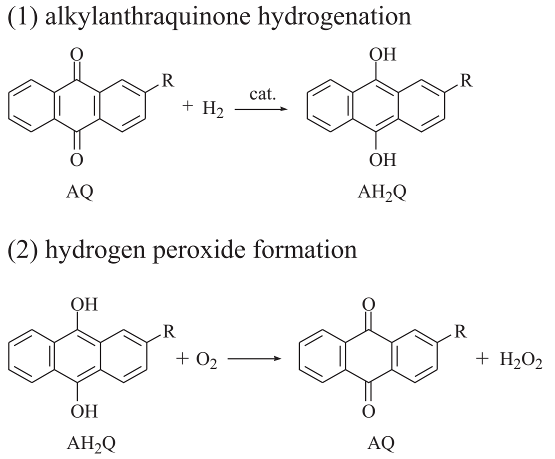

Scheme 1. Athraquinone autoxidation reactions.

peroxide that the photochemical reduction replaces the hydrogenation in the AO process.

In this work, we investigated synthesis of hydrogen peroxide by direct photoinduced reduction of AQ. The concentrations of hydrogen peroxide under different photolysis conditions including solvent, concentration of AQ and irradiation time were measured, and the formation mechanism of the hydrogen peroxide was proposed.

2. Materials and methods

2-Ethylanthraquinone (AQ) and potassium permanganate were purified by recrystallization. Other materials obtained from commercial suppliers were used as received. Solvents of technical quality were distilled prior to use. UV–vis absorption spectra were recorded with a Shimadzu UV-2450 UV–Vis spectrophotometer. Fluorescence emission spectra were measured at room temperature on a Shimadzu RF-5301PC spectrofluorophotomer. ESR spectrum was recorded on JES-FA200 electron spin resonance spectroscopy.

Working solutions (30 mL) were prepared by dissolving AQ in different solvents in a 50 mL Pyrex pear-shaped flask, and irradiated with a 500 W Xe lamp (unfocused) for certain time. The flask was fixed in the same position to absorb similar photons for different samples. The irradiated solution of 20 mL was taken out, and extracted twice (2× 10 mL) with water. In order to inhibit the decomposition of hydrogen peroxide, the water containing 1% phosphorous acid was employed. The concentration of hydrogen peroxide in the aqueous extracts was then determined by titration with standard potassium permanganate solution. Meanwhile, as a comparison, the concentrations of H_2O_2 were also determined by iodimetry [6]. The measurement error is within 10%, from the unstable intensity of incident light, and decomposition of H_2O_2.

3. Results and discussion

To find an appropriate photoreduction condition, AQ solutions were irradiated with a Xe lamp under various conditions. Hydrogen peroxide in irradiation solution was extracted with the same volume of water, and then measured by titration with standard potassium permanganate solution.

3.1. Optimization of irradiation conditions

3.1.1. Selection of N_2/air/O_2 atmosphere

Table 1
The yields of hydrogen peroxide from photolysis under N_2/air/O_2 atmosphere[a].

Atmosphere	N_2	Air	O_2
H_2O_2 (mg L^{-1})	430	1020	1280

[a] 100 mM AQ, 1,4-dimethylbenzene/trioctyl phosphate (v/v, 3:1), bubbling the corresponding gas for 15 min, and irradiation for 1 h.

To decide what atmosphere achieves a high concentration of hydrogen peroxide, 100 mM AQ solutions of 1,4-dimethylbenzene/trioctyl phosphate (v/v, 3:1) solvent mixture were irradiated for 1 h under N_2, air or O_2 atmosphere, respectively. The concentrations of hydrogen peroxide were measured and listed in Table 1. As showed in Table 1, the yields of hydrogen peroxide show big differences for different atmospheres. Under oxygen atmosphere the concentration of H_2O_2 is the highest, 1280 mg L^{-1} among three atmospheres, near to three times than that under N_2 atmosphere. The reaction solution with bubbling air gave 1020 mg L^{-1} H_2O_2, similar to the bubbling O_2. AQ is excited to a singlet state ($^1AQ^*$), which undergoes a fast intersystem crossing process to a triplet excited state ($^3AQ^*$, Eq. (1)) [3]. Under N_2 atmosphere, AQ is photoreduced to AH_2Q (Eq. (2)). Besides a little of oxygen in the N_2-saturated solution of AQ, the formation of H_2O_2 may mainly derive from oxidation of AH_2Q by oxygen in the extraction process, which was exposed to air.

There are two possible reactions involving oxygen in the photolysis of AQ in solution: (1) oxidation of AH_2Q generating H_2O_2 (Scheme 1 (2)); (2) quenching of triplet AQ giving $^1O_2(\Delta_g)$ (Eq. (3)) [7]. Because the concentration of solvent as a hydrogen donor is very high, a hydrogen abstraction by triplet AQ should be predominant relative to its quenching by oxygen. Hence, the accelerating oxidation of AH_2Q in a high-concentration-oxygen solution should be responsible for a high yield of H_2O_2.

$$AQ \xrightarrow{h\nu} {}^1AQ^* \xrightarrow{ISC} {}^3AQ^* \tag{1}$$

$$AQ^*\ ({}^1AQ^*, {}^3AQ^*) \xrightarrow{\text{solvent}} AH_2Q \tag{2}$$

$$^3AQ^* + O_2 \rightarrow AQ + {}^1O_2 \tag{3}$$

3.1.2. Selection of solvents

2-Ethylanthraquinone was dissolved in various solvents, and irradiated for 0.5 h accompanying with bubbling air. The concentrations of H_2O_2 generated were measured, listed in Table 2. Data showed that alkyl substituted benzene solutions gave high yields of H_2O_2, and alkyl substituted benzene/ester mixture such as butyl acetate and a phosphate gave higher yields of H_2O_2. In contrast, photolysis of AQ in three solvents with no good H-donating ability (tetrachlorocarbon, chloroform or benzene) gave very low yields of H_2O_2, and the formation of H_2O_2 may derive from self-photoreduction between AQ molecules, such as an intermolecular hydrogen abstraction. These results show that the yield of H_2O_2 relates to the hydrogen-donating ability of the solvent [3] and sol-

Table 2
The yields of hydrogen peroxide from photolysis in various solvents[a].

Solvents	H_2O_2 (mg L^{-1})
CCl_4	38
Chloroform	31
Benzene	41
Toluene	255
1,4-Dimethylbenzene	344
1,3,5-Trimethylbenzene	350
Diethyl ether	249
Butyl acetate	270
1,4-Dimethylbenzene/butyl acetate (3:1)	510
1,4-Dimethylbenzene/trioctyl phosphate (3:1)	509
1,3,5-Trimethylbenzene/trioctyl phosphate (3:1)	515

[a] 100 mM AQ solution, air-bubbling and irradiation for 0.5 h.

Table 3
The yields of H_2O_2 for various concentrations of AQ[a].

Conc. (mM)	5	10	50	75	100	125	150	200	250
H_2O_2 (mg L^{-1})	990	1080	1000	1220	1470	1070	1120	1110	1200

[a] 1,4-Dimethylbenzene/trioctyl phosphate (3:1), irradiation accompanying O_2 bubbling for 1 h.

Table 4
The yields of H_2O_2 in the AQ solution irradiated for different times[a].

t (min)	10	30	60	120	300	690
H_2O_2 (mg L^{-1})	250	750	1470	1960 (2970)[b]	4110 (6410)[b]	8370 (11,140)[b]

[a] 100 mM AQ, 1,4-dimethylbenzene/trioctyl phosphate (3:1),with O_2 bubbling.
[b] Values in brackets from extractions per irradiation for 30 min.

vent polarity. Namely, a high H-donating ability and a high-polarity solvent would favor to hydrogen abstraction of the excited AQ. In other measurements in this work, 1,4-dimethylbenzene/trioctyl phosphate (v/v, 3:1) solvent mixture was selected as the solvent of work solution.

3.1.3. Selection of concentration of AQ

In order to investigate a concentration effect on the yield of H_2O_2, various concentrations of AQ ranging from 5 to 250 mM, were employed to perform the photochemical synthesis, and the yield was measured after irradiation for 1 h accompanying with O_2 bubbling, as shown in Table 3. The results show that the yields of H_2O_2 generated increase initially with the concentration of AQ and reach to a maximum value, 1470 mg L^{-1}, and then decrease with increasing the concentration. The concentration giving the maximum yield of H_2O_2 is 100 mM, under our experimental condition. In the fact, the yield of H_2O_2 mainly depends on the intensity of incident light, which is completely absorbed for a high concentration of work solution. However, a small irradiation area for a very high-concentration solution would be unfavorable for the diffusion of photoproducts to the non-irradiation area. The photoproducts absorb competitively photons with the reactant AQ, and lead to a decrease in the yield of H_2O_2. This result also implies that photoreduction is not the reaction between two AQ molecules, but the reaction between AQ and a solvent molecule. Otherwise, the yield of H_2O_2 would increase with the concentration of AQ from beginning to end.

3.1.4. Irradiation time

100 mM AQ solution of 1,4-dimethylbenzene/trioctyl phosphate (3:1) mixture was irradiated for different times, and then H_2O_2 in these irradiated solutions were extracted and measured. The yield of H_2O_2 increased from 250 mg/L to 8370 mg/L, and its increase rate became to slow, with increasing irradiation time. There are two possible reasons for explaining this phenomenon: (1) the forming AH_2Q absorbs competitively photons with AQ; (2) H_2O_2 degrades under UV light. To avid the two factors leading to a decrease in the yield of H_2O_2, the extraction was performed per irradiation for 30 min, and all aqueous phases were combined, at last, the concentration of H_2O_2 was measured, and the total concentrations of H_2O_2 were listed in brackets of Table 4. As shown in Table 4, total concentrations of H_2O_2 by the extraction per 0.5 h are much higher than those by only once extraction after a continuous irradiation.

3.2. Recycling number of work solution

To test the cycle number of work solution, three concentrations of work solutions (10 mM, 100 mM, and 300 mM) were preformed for ten times. The concentrations of H_2O_2 formed were listed in Table 5. For the work solution after 10 cycles, the concentration of hydrogen peroxide has no significant decrease. This implies that the non-photoreduction reaction such as a photodegradation is minor.

Comparing data in Table 5 with Table 4, total sum of H_2O_2 yields for 10 cycles (11,770 mg/L and 13,450 mg/L for 10 mM and 100 mM AQ solutions respectively) is higher than that (11,140 mg/L) from the extraction per 0.5 h during the irradiation for 690 min. Because the latter is multi-extraction (per 30 min), and one-time measurement, initial extracted aqueous solutions were placed for a long time, and decomposition of H_2O_2 may partly occur, leading to a decrease in the yield.

Furthermore, the quantum yield of H_2O_2 formed in the modified AO process was measured through preparing in 1,4-dimethyl benzene/trioctyl phosphate (3:1) solution (3 mL) of AQ in a quartz cuvette (10 × 10 mm), and irradiated with 350 nm monochromatic light from a fluorescence spectrometer for 1 h, bubbling with air for three times (5 min per one time) during the irradiation, then extracting with 10 mL water for three times. The obtained aqueous solution of H_2O_2 was titrated by iodimetry. The intensity of light beam was determined with ferrioxalate actinometry [8]. Based on these values, the formation quantum yield of H_2O_2 was calculated, $\Phi = 0.19$. This shows that the photochemical process for H_2O_2 formation is very efficient.

3.3. Mechanism of formation of hydrogen peroxide

The photochemical reduction of AQs may be intermolecular and intramolecular via electron transfer or direct hydrogen-abstraction. Almost all organic compounds that can act as hydrogen donors may serve as reducing agents in intermolecular photochemical reduction [3,4]. However, there is a large difference in the hydrogen-donating ability for different solvents [4c, 5c, 9]. Based on results from solvent effect and concentration effect, the intermolecular photoreduction should be a key step in the formation of hydrogen peroxide. Fig. 1a shows absorption spectra of the N_2-

Table 5
The yields of hydrogen peroxide *vs* the recycling number of work solution[a].

N	1	2	3	4	5	6	7	8	9	10
10 mM	1290	1240	1170	1190	1180	1180	1150	1120	1120	1130
100 mM	1330	1360	1180	1360	1450	1520	1330	1220	1360	1340
300 mM[b]	760	621	791	691	851	578	706	515	696	757

[a] 1,4-Dimethylbenzene/butyl acetate (3:1), O_2-bubbling and irradiation for 1 h.
[b] Irradiation for 0.5 h.

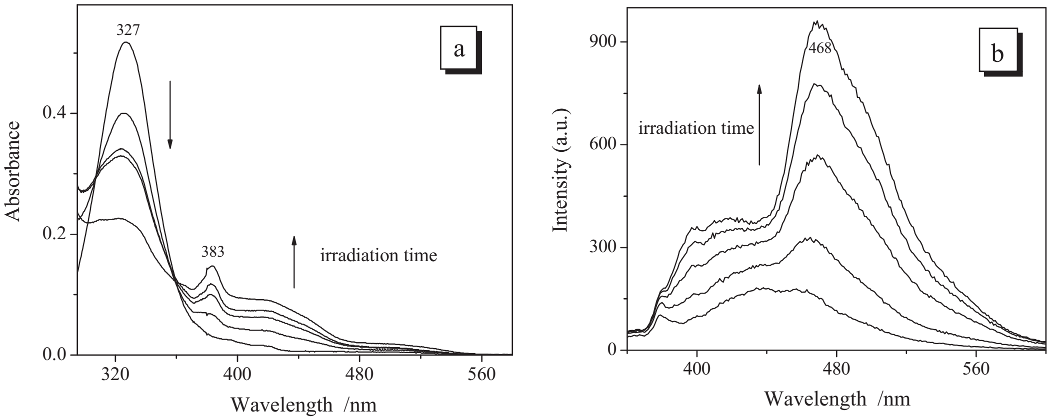

Fig. 1. Absorption (a) and fluorescence emission spectra (b) of AQ in deaerated 1,4-dimethylbenzene/trioctyl phosphate (3:1) solutions recorded at different irradiation times (0 → 12 min) under 350 nm light.

saturated AQ solution recorded at different irradiation times. The peak at 327 nm, which is assigned to absorption of AQ, is decreasing, and the absorption band from 360 nm to 550 nm is arising, with increasing irradiation time. The changes in the absorption spectra would derive from the photoreduction of AQ into anthrahydroquinone AH_2Q, which has a new absorbing region from 360 nm to 550 nm. Similarly, fluorescence spectra recorded after irradiation for different times show an increase in intensity of fluorescence emission with irradiation time, and because AQ is nonfluorescent, the fluorescence spectra should be assigned to the dihydroxyanthracene, AH_2Q (Fig. 1b). When the irradiated solution was exposed to air, the absorption spectrum became back the spectrum of the solution of AQ before irradiation (not shown), that is, the reduction product AH_2Q was oxidized into AQ by O_2.

The mechanism of photoreduction by solvents can be proposed. AQ is excited to the excited singlet state ($^1AQ^*$), and undergoes a fast intersystem crossing (ISC) to the excited triplet state ($^3AQ^*$). Because the concentration of H-donating solvent is very high (>10 M), hydrogen abstraction from the solvent via a singlet excited state cannot be ruled out. Hence, the excited anthraquinone (AQ^*) abstracts a hydrogen atom from solvent RH to form the semianthraquinone radical ($AHQ^\bullet$) and the solvent radical ($R^\bullet$) (Eq. (4)). The semianthraquinone radical can further abstract hydrogen from the solvent RH to produce AH_2Q and another solvent radical ($R^\bullet$), shown in Eq. (5). In the presence of oxygen, the AH_2Q is oxidized back to the original anthraquinone (AQ), meanwhile giving hydrogen peroxide (Scheme 1, (2)). Alternatively, two semianthraquinone radicals may undergo a disproportionation reaction to AH_2Q and AQ (Eq. (6)).

$$AQ^* + RH \rightarrow AHQ^\bullet + R^\bullet \qquad (4)$$

$$AHQ^\bullet + RH \rightarrow AH_2Q + R^\bullet \qquad (5)$$

$$2AHQ^\bullet \rightarrow AH_2Q + AQ \qquad (6)$$

The photolysis system under O_2 atmosphere gave the highest yield of H_2O_2 among photolysis systems under three atmosphere. In the formation process of H_2O_2, the reactions involving oxygen have: (1) oxidation of AH_2Q into AQ and H_2O_2; (2) quenching triplet AQ to give singlet oxygen $^1O_2$, which was conformed by EPR spectroscopy for photolysis of AQ solution containing 2,2,6,6-tetramethyl-4-piperidinol, but this process is minor comparing to hydrogen abstraction of the AQ triplet state from solvent due to its very high concentration. In the case of the former, AH_2Q is oxidized into AQ to prevent AH_2Q absorbing photons competitively, and achieve to a high yield of H_2O_2. This is why the O_2-saturated system gave the highest yield of H_2O_2 among three atmospheres.

Görner [5] has studied the photolysis of 9,10-anthraquinone, 2-methyl- and 2,3-dimethyl-9,10-anthraquinone in air-saturated acetonitrile/water solvent mixture with very poor H-donating ability in the presence of various donors: formate, ascorbic acid, alcohols, and amines. On the basis of steady-state and laser flash photolysis studies, the H_2O_2 generated mechanism was proposed. The photoreaction is initiated by H-atom or electron transfer from the donor to the AQ triplet state. The conversion of oxygen into hydrogen peroxide occurs *via* the superoxide radical and its conjugate acid [5]. In our photolysis system, hydrogen abstraction via the AQ triplet state may be a main process, but a singlet pathway cannot be excluded from the photo-induced hydrogen abstraction because the hydrogen donor is solvent, with a very high concentration.

4. Conclusion

In summary, a new synthesis method of hydrogen peroxide was investigated through using direct photoinduced reduction of AQ, and AQ solution of 1,3,5-trimethylbenzene/trioctyl phosphate (3:1) solvent mixture as a work solution gave the highest yield of H_2O_2 among water-insoluble solvents investigated under air atmosphere. The formation mechanism of hydrogen peroxide was proposed, i.e. hydrogen peroxide is produced from photoreduction of AQ undergoing hydrogen abstraction from solvent, and subsequent oxidation by oxygen. The modified AO process that direct photoreduction of 2-ethylanthraquinone replaces the hydrogenation would be more “green” than the normal AO process with expensive hydrogenation catalyst and accompanying with the side reactions. Furthermore, if the light source is sun light instead of Xe lamp light, the modified process will be a more “green” synthesis method of hydrogen peroxide. Of course, the concentration of hydrogen peroxide per cycle need to be improved by further modifying the process.

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