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ONE-ELECTRON OXIDATION OF PHENANTHRENEQUINONE STUDIED BY PULSE RADIOLYSIS

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ABSTRACT The one-electron oxidation of phenanthrenequinone (PhQ) in aqueous solutions was investigated by pulse radiolysis using hydroxyl radical and sulphate radical as oxidants. Spectral and kinetic properties of the transients formed due to the reaction of PhQ with the oxidants were obtained. The reaction of hydroxyl radical with PhQ results in an initial species with an absorption spectrum centered at 370nm and a weak broad band in the long wavelength regions at neutral pH. The bimolecular rate constant for the formation of initial species was determined to be $(1.5\pm0.2)\times10^{10}dm^3\cdot mol^{-1}\cdot s^{-1}$. The absorption in the short wavelength region decays with a concomitant increase in the longer wavelength region resulting in a subsequent species with absorption maximum at 400nm and a broad band centered at 500nm. The absorption in visible region increases with increasing pH. Similar transient absorption was obtained at pH 9.9. At pH 4.0, the initial spectrum also shows absorption maximum at 370nm. However, the subsequent absorption spectrum shows a maximum at a shorter wavelength than those found at pHs 7.1 and 9.9. The absorption increase in visible region was not seen at low pH. The transient spectrum obtained at neutral pH by the reaction of sulphate radical with PhQ are similar to the subsequent spectra for the reaction of hydroxyl radical with PhQ showing two bands centered at 400 nm and 500 nm. The bimolecular rate constant was estimated at $(4.0\pm0.6)\times10^9dm^3\cdot mol^{-1}\cdot s^{-1}$. On the basis of spectral similarity and kinetic analysis, a possible mechanism for the oxidation of PhQ by both hydroxyl radical and sulphate radical is given.

KEYWORDS Pulse radiolysis, One-electron oxidation, 9,10-Phenanthrenquinone
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1 Introduction

For quinonoid compounds in general, contrary to the reduction studies, which have been well documented, little is known about one-electron oxidation of such molecules. This may be because quinones are strong electron acceptors rather than electron donors[1]. However, from a few studies on reactions of quinones with hydroxyl radicals[2-5], it was reported that hydroxyl radicals react with such molecules by adding to the aromatic ring to form •OH adducts. Such addition reactions have also been observed with 1,10-phenanthroline[6,7] and with some five or six-membered heterocyclic compounds which contain carbon-carbon double bonds and carbonyl groups such as oxazole and 4-methyloxazole[8], thymine and uracil[9].

In the previous work, it has been shown that the reaction of PhQ with e_{aq}^- and $CO_2^{\bullet-}$ and $(CH_3)_2\dot{C}COH$ produce semiquinone anions and semiquinone neutral radicals[10]. For some quinones such as naphthazarin, which contains phenolic hydroxyl groups, the semiquinone can also be formed by •OH reaction via an addition/elimination mechanism[5]. In order to investigate whether similar reactions are also possible with PhQ, the reactivity of this compound towards to hydroxyl radicals has been studied. Furthermore, as one of the model compounds for PQQ, knowledge of oxidation should also be important before investigation of the respective complexes could be initiated. Therefore, the one-electron oxidants: the sulphate radical ($SO_4^{\bullet-}$), the thallium ion (Tl^{2+}) and its monocomplex [$(TlOH)^+$] were employed to oxidize PhQ.

2 Materials and methods

2.1 Materials

9,10-phenanthrenequinone was purchased from Sigma Chem. Co. Thallous sulphate was purchased from

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B.D.H. Chem Ltd., England. All reagents used at least of analytical purity.

For studies of pulse radiolysis, water was triply distilled by double redistillation using a Bibby Aquatron W4D double distillation water still and then by carrying out a further redistillation from an alkaline permanganate solution. Buffers used were Na_2HPO_4- NaH_2PO_4 (pH 5.0—8.2), NaH_2PO_4-H_3PO_4 (pH 3—5) and NaOH-Na_2HPO_4 (pH 8.2—9.0). Perchloric acid and sodium hydroxide were used for extremely low and high pHs, respectively.

White spot nitrogen (>99.99%), nitrous oxide (atomic absorption grade, >99.9%) and oxygen (≥99.5%) were supplied by B.O.C. Ltd.

2.2 Methods

The pulse radiolysis experiments were carried out with an 8—14MeV Vickers electron linear accelerator as previously described[10, 11]. The path lengths of quartz cells used are 1.5 and 2.5cm. Radiation doses were established using air-saturated 1×10^{-2} mol•dm^{-3} aqueous of KSCN and taking $G[(SCN)_2^{\bullet-}]\varepsilon=2.23\times10^{-4}m^2\ J^{-1}\ cm^{-1}$[12].

The solutions for pulse radiolysis experiments were always freshly prepared and were purged for at least 30 minutes (for 100mL solutions) or 1h (for 250 and 500mL solutions) prior to pulsing, using nitrogen or nitrous oxide.

3 Results and discussion

3.1 Reaction with hydroxyl radicals

The reaction of PhQ with hydroxyl radicals at neutral and alkaline pHs was examined by pulsing nitrous oxide saturated aqueous solutions of PhQ. Under such conditions, all hydrated electrons are converted into •OH, thus doubling its yield (reaction 1). Since small amounts of $H^\bullet$ are also generated and the rate of the H atom reaction with PhQ is only half of that for the •OH reaction, the H atom reaction is unimportant at the same time scale of the •OH reaction and the spectra thus obtained are attributed largely to the reaction of •OH with PhQ

$$e_{aq}^- + N_2O \rightarrow \bullet OH + OH^- + N_2 \qquad (1)$$

Fig.1 shows changes in the uncorrected absorption spectrum with time at pH 7.1. The initial spectrum obtained was recorded 17μs after the pulse when the decay of •OH was complete. It shows an absorption band centered at 370nm and one weak broad band in the long wavelength regions. The absorption in the short wavelength region decays with a concomitant increase in the longer wavelength region resulting in a subsequent species with an absorption maximum at 400nm and a broad band centered at 500nm (spectrum at 83μs). Similar absorption spectra were obtained at pH 9.9 (Fig.2).

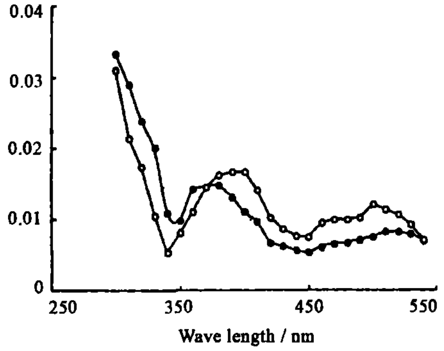


Fig.1 Uncorrected transient absorption spectra obtained 17 μ s. ● and 83 μ s, ○ after giving a 6.7Gy electron pulse to a N_2O-saturated aqueous solution of PhQ (1.4×10^{-5}mol•dm^{-3}) in the presence of phosphate buffer (1×10^{-2}mol•dm^{-3}), pH7.1, 2.5cm cell.

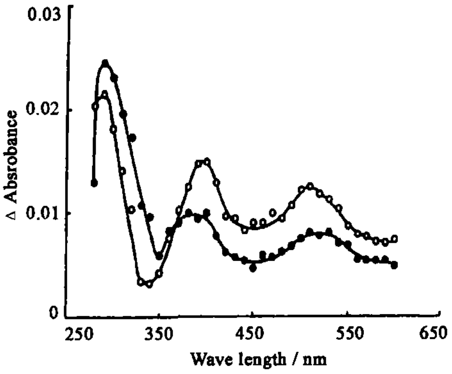


Fig.2 Uncorrected transient absorption spectra obtained 13 μ s. ● and 83 μ s, ○ after giving a 6.7Gy electron pulse to a N_2O-saturated aqueous solution of PhQ (1.3×10^{-5}mol•dm^{-3}) in the presence of phosphate buffer (1×10^{-2}mol•dm^{-3}), pH9.9, 2.5cm cell.

The pseudo-first-order rates of build-up of absorption at 370 nm and 340 nm yield a bimolecular rate constant of $(1.5\pm0.2)\times10^{10}$ dm^3•mol^{-1}•s^{-1} for the reaction of •OH with PhQ (Fig. 3). The intercept observed from the plot in Fig. 3 reflects partial decay of •OH by •OH recombination (reaction 2). The low concentration (due to the poor solubility of PhQ in aqueous solution) of PhQ could not scavenge all the •OH generated initially (about 85% of hydroxyl radicals react with PhQ at PhQ concentration of 1.4×10^{-5} mol •dm^{-3})

$$2\bullet OH \rightarrow H_2O_2 \qquad (2)$$

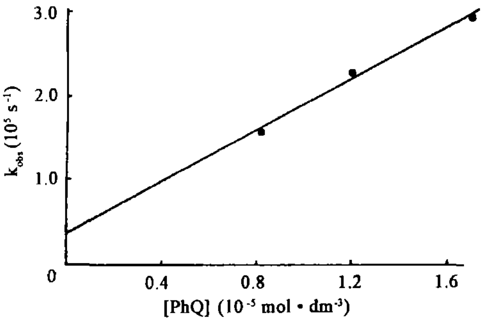


Fig.3 Dependence of the 1st-order formation rate contant,observed at 370nm, on concentration of PhQ in N_2O-saturated aqueous solutions of PhQ irradiated with a 6.0Gy electron pulse, pH 7.0.

On decreasing the pH to 4.0, the initial spectrum obtained at the end of the pulse also shows absorption maximum at 370 nm (Fig.4). However, the subsequent absorption spectrum at 99μs shows a λ_{max} at a shorter wavelength (—380 nm) than those found at pHs 7.1 and 9.9. The absorption increase in the visible region, observed at pHs 7.1 and 9.9 was not seen here. The subsequent absorption decays with the same rate over all the wavelengths indicating a singled species.

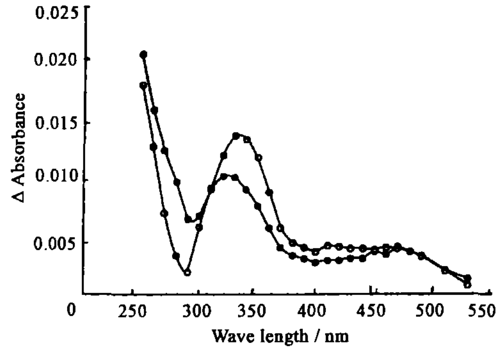


Fig.4 Uncorrected transient absorption spectra obtained 22 μ s. ● and 99 μ s, ○ after giving a 4.86Gy electron pulse a N_2O- saturated aqueous solution of PhQ (7.6×10^{-5}mol•dm^{-3}) in the presence of phosphate buffer (1×10^{-2}mol•dm^{-3}), pH4.0, 2.5cm cell.

Similar transient spectral changes were observed on further decreasing the pH. Fig.5 shows the uncorrected spectra obtained at different times on pulsing a nitrous oxide saturated solution of PhQ (1.5×10^{-5} mol •dm^{-3}) at pH 2. Under such conditions, 56% of hydrated electrons are converted into H atoms according to the reaction

$$e^-_{aq} + H_3O^+ \rightarrow H\bullet + H_2O \qquad (3)$$

Hence, about two-thirds of the primary radicals generated at the end of the pulse are •OH and one-third is $H^\bullet$. However, at least 83% of the H atoms thus produced (calculated according to Equation 4) would react with PhQ at 17μs when the initial spectrum was taken

$$k_1 t = -\ln\left(1 - \frac{\Delta[H\bullet]_t}{[H\bullet]_0}\right) \qquad (4)$$

Where, $k_1=k_2[PQ]_0$ (k_2 is the bimolecular rate constant for the reaction of H• with PhQ taken to be 7×10^9 dm^3 mol^{-1} s^{-1}); $[H\bullet]_0$ is the initial molar concentration of H atom; $\Delta[H\bullet]_t$ is the molar concentration of H atoms reduced at the time t.

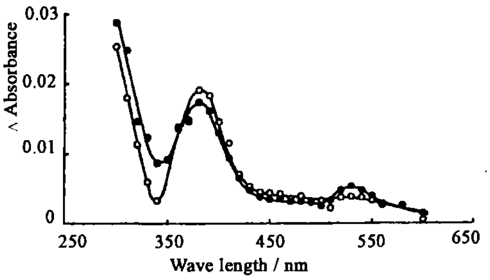


Fig.5 Uncorrected transient absorption spectra obtained 17 μ s. ● and 72 μ s, ○ after giving a 6.7Gy electron pulse to a N_2O-saturated aqueous solution of PhQ (1.5×10^{-5}mol•dm^{-3}) in the presence of $HClO_4$ (1×10^{-2}mol•dm^{-3}), pH2.0, 2.5cm cell.

The absorption due to the H atom reaction product was separated from that due to OH addition according to:

$$\Delta A(\bullet OH) = \Delta A_{obs} - \Delta A(H\bullet) \qquad (5)$$

Where ΔA(•OH) is the absorbance due to the adduct, ΔA_{obs} is the observed absorbance, and ΔA(H•) is the absorbance due to the H atom adduct given by the approximation.

$$\Delta A(H\bullet) = (\varepsilon_H - \varepsilon_g) \times l \times [H\bullet]_0 \frac{k_7[PhQ]}{k_7[PhQ] + k_8[H\bullet]_0} \qquad (6)$$

Where ε_H and ε_g are the molar extinction coefficients of the H adduct and parent PhQ, [PhQ] is the molar concentration of PhQ, $[H\bullet]_0$ is the molar concentration of H atoms generated initially which was calculated by taking the G value of H atoms to be 2.0, k_7 and k_8 are the bimolecular rate constants for the corresponding reactions.

$$H\bullet + PhQ \rightarrow PhQH^{\bullet} \quad (7)$$

$$2H\bullet \rightarrow H_2 \quad (8)$$

The extinction coefficients of the species formed initially at the end of the •OH reaction at the four pHs above were calculated. The molar concentration of •OH was given by

$$[\bullet OH] = [\bullet OH]_0 \times \frac{k_{10}[PhQ]}{k_{10}[PhQ] + k_2[\bullet OH]_0} \quad (9)$$

Where $[\bullet OH]_0$ is the •OH concentration generated initially (calculated taking total *G* value of •OH to be 5.6 at pHs 4.0, 7.1 and 9.9, and to be 4.1 at pH 2.0); k_2 and k_{10} are the bimolecular rate constants for the corresponding reactions. The concentration of •OH thus obtained represents the minimum concentration because $k_2[\bullet OH]_0$ will vary as the reaction proceeds. The initial absorption spectra thus obtained are shown in Fig.6. It is clear that the four spectra are identical and have a λ_{max} at 320 nm with a molar extinction coefficient of 6600±800 $dm^3 \bullet mol^{-1} \bullet cm^{-1}$.

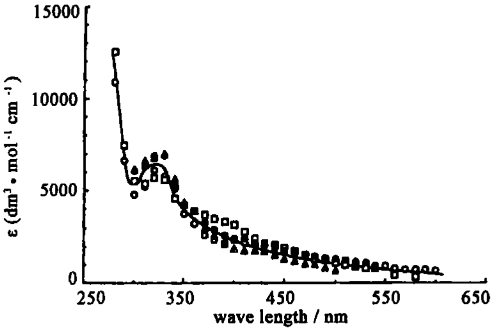


Fig.6 Corrected transient absorption spectra of OH-adduct formed on the pulse radiolysis of N_2O-saturated solutions of PhQ. ▲ pH2.0, 17μs, □ pH4.0, 22μs, ● pH7.1, 17μs, ○ pH9.9, 13μs. Conditions as those Figs. 4.1, 4.2, 4.4 and 4.5.

On the basis of general reactive properties of •OH towards quinones and other unsaturated compounds as mentioned in the Introduction, the first species observed can be considered to be an •OH adduct ($PhQOH^{\bullet}$, reaction 10)

$$\bullet OH + PhQ \rightarrow PhQOH^{\bullet} \quad (10)$$

It was further found that the growth of the absorption due to the second species mainly followed first-order kinetics. The first-order rate constant was independent of does between 3.9 and 9.6 Gy. This indicates the absence of a second-order process and implies that the •OH adduct does not decay by disproportionation or other second-order processes.

Assuming that all PhQ •OH adducts formed initially are converted to the second species, the subsequent spectra at different pHs (Figs 1, 2, 4 and 5) were normalized to same amount of hydroxyl radicals (assuming 100% conversion) and same path length, and are superimposed in Fig.7. It is seen from Fig.7 that the absorption in the visible region increases with increasing pH and the λ_{max} in the 350—400 nm region shifts to shorter wavelength as the pH is decreased. The insert shows the plot of absorbance at 500 nm vs pH.

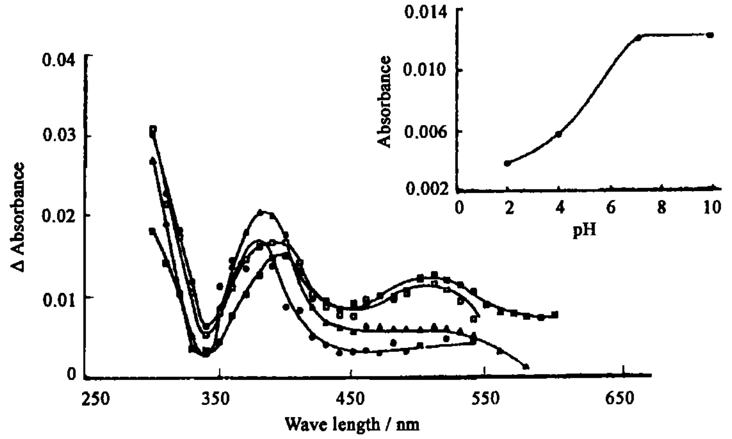


Fig.7 Uncorrected transient subsequent absorption spectra at different pHs. ● pH 2.0, ▲ pH 4.0, □ pH 7.1 ■ pH 9.9, normalized to G(•OH)=4.74 and dose=6.7Gy, 2.5cm cell. (see Figs 4.1, 4.2,4.4 and 4.5 for other corresponding conditions). Insert: dependence of absorbance at 500nm on pH.

In order to ascertain whether the second species formed in OH reactions is an one-electron oxidized form (i.e. cation radical) formed by elimination of water from the OH adduct, oxidation of PhQ using other oxidizing radicals such as azide radicals ($N_3^{\bullet}$) and sulphate radicals ($SO_4^{\bullet -}$) was attempted and the results are presented below.

3.2 Reaction with sulphate radicals

On delivery of a pulse to a nitrous oxide saturated solution of PhQ in the presence of $NaN_3^{\bullet}$, the $N_3^{\bullet}$ generated according to the reaction 1 and 11 would be expected to oxidize PhQ. However, no absorption changes were observed. Furthermore the decay of $N_3^{\bullet}$ radicals in the presence and absence of PhQ was found to be same. It was therefore concluded that $N_3^{\bullet}$ does not react with PhQ.

$$\bullet OH + N_3^- \rightarrow N_3^{\bullet} + OH^- \qquad (11)$$

However, absorption changes were observed using $SO_4^{\bullet -}$ as an oxidant. On pulsing a nitrogen saturated aqueous solution containing PhQ (2.5×10^{-5} mol •dm^{-3}), potassium persulphate ($K_2S_2O_8$, 5×10^{-2} mol •dm^{-3}) and t-butanol (1 mol •dm^{-3}) at neutral pH, absorption changes in the visible region were observed. Under such conditions, $SO_4^{\bullet -}$, a stronger oxidant than $N_3^{\bullet}$ (one-electron reduction potentials for the couples $SO_4^{\bullet -}/SO_4^{2-}$ and $N_3^{\bullet}/N_3^-$ are 2.5-3.1 V and 1.3 V vs NHE, respectively[13]), was generated according to the reaction 12 which would thus be expected to oxidize PhQ to form the cation radical of PhQ, $PhQ^{\bullet +}$, (reaction 13).

$$e_{aq}^- (H\bullet) + S_2O_8^{2-} \rightarrow + SO_4^{\bullet -} + SO_4^{2-} (HSO_4^-) \qquad (12)$$

$$SO_4^{\bullet -} + PhQ \rightarrow PhQ^{\bullet +} + SO_4^{2-} \qquad (13)$$

Spectra thus obtained at different times are shown in Fig.8 and are similar to the subsequent spectra in Fig.1 and 2, showing two bands centered at 400 and 500nm. It is reasonable to expect $SO_4^{\bullet -}$ to react with PhQ to form the cation radical ($PhQ^{\bullet +}$) which may be also formed by the decay of the •OH-adduct. However, the molar extinction coefficients at 400 and 500 nm ($\varepsilon^{400}=3600\pm500$ and $\varepsilon^{500}=2400\pm400$dm^3 •mol^{-1} •cm^{-1}) obtained from $SO_4^{\bullet -}$ reaction were found to be higher than those ($\varepsilon^{400}=3100\pm500$ and $\varepsilon^{500}=1800\pm300$dm^3 •mol^{-1} •cm^{-1}) calculated from the subsequent absorption in •OH reaction by assuming 100% of conversion of the PhQ-•OH adduct to the subsequent species. This may indicate that the conversion from the PhQ-•OH adduct to the cation radical is not one hundred percent.

Estimation for the bimolecular rate constant for the reaction of with PhQ was found to be $(4\pm0.6)\times10^9$dm^3 mol^{-1} s^{-1} by monitoring the decay of $SO_4^{\bullet -}$ radical at 450 nm in the absence and presence of PhQ.

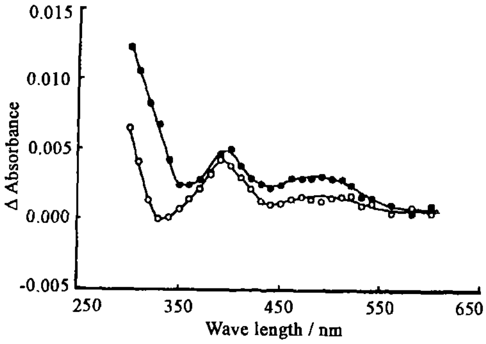
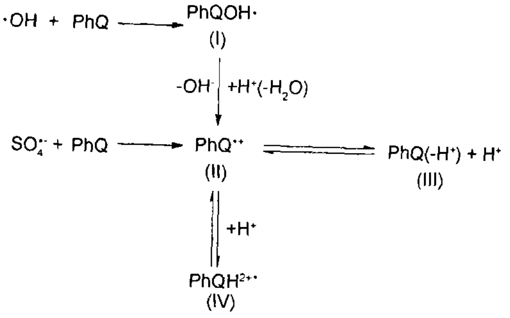


Fig.8 Uncorrected transient absorption spectra obtained 11 μs. ● and 201 μs, ○ after given a 11.2Gy electron pulse to a N_2-saturated aqueous solution containing PhQ (2.5×10^{-5}mol•dm^{-3}), potassium persulphate (5×10^{-5}mol•dm^{-3}) and t-butanol (1×10^{-5} mol•dm^{-3}), pH 6.4, 2.5cm cell.

3.3 Discussion of the mechanism

In conclusion, because of the poor solubility of PhQ in both systems (•OH and $SO_4^{\bullet -}$ oxidation studies), the concentrations of PhQ used were too low to be scavenged by all •OH and $SO_4^{\bullet -}$ radicals. Hence, it is not easy to study the oxidation of PhQ in aqueous solutions quantitatively. Nevertheless, the absorption spectra at the end of •OH reaction at various pHs have been obtained (Figs. 1, 2, 4 and 5), and it was found that the initial absorption spectrum is pH independent over the pH range 2.0 to 9.9. This initial absorption was assigned due to a PhQ-•OH adduct as in the case for benzoquinone[2] and substituted anthraquinones[3, 4]. It was also observed that the •OH adducts decayed mainly via first-order process to produce a species whose absorption was pH dependent. This subsequent absorption spectrum at neutral pH was similar to that formed by the reaction of $SO_4^{\bullet -}$ at neutral pH.

On the basis of spectral similarity and kinetic analysis, a possible mechanism for the oxidation of PhQ by both •OH and $SO_4^{\bullet -}$ is given below:



Possible mechanism for the oxidationof PhQ.

The adduct (I) formed by the reaction of hydroxyl radicals with PhQ decays by a proton catalyzed- elimination of water to form a cation radical (II) which is in an equilibrium either with its deprotonated form (III) or with its protonated form (IV). The cation radical can also be formed by direct oxidation of $SO_4^{\bullet -}$.

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用脉冲辐解技术研究菲醌的单电子氧化

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摘要 采用脉冲辐解技术，以羟基自由基和硫酸根自由基作为氧化剂，研究了 9，10-菲醌（PhQ）在水溶液中的单电子氧化行为，获取了瞬态产物的吸收光谱和有关动力学数据。在中性 pH 条件下，PhQ 与羟基自由基以 $(1.5\pm0.2)\times10^{10}$ $dm^3\cdot mol^{-1}\cdot s^{-1}$ 的速率反应，生成一个初级瞬态产物。该瞬态产物的吸收光谱呈现出位于 370nm 的吸收峰和在较长波长下的一个宽吸收带。进一步实验观察到，随着短波长区初级吸收的衰减，可见光区的吸收同步增加，在 400nm 处形成最大吸收峰，并产生以 500nm 为中心的宽吸收带，表明次级瞬态产物的形成。PH9.9 条件下得到的结果与中性 pH 的一致。降低 pH 至 2—4，尽管初始瞬态吸收谱也呈现出位于 370nm 的最大吸收峰，但伴随着初始吸收的衰减，没有观察到可见区域吸收的增加。在中性 pH 条件下，硫酸根自由基与 PhQ 反应的速率常数测定为 $(4.0\pm0.6)\times10^{9}dm^3\cdot mol^{-1}\cdot s^{-1}$，生成的瞬态吸收谱与羟基自由基反应得到的次级吸收谱一致，呈现以 400nm 和 500nm 为中心的两个吸收带。基于光谱的相似性和动力学分析，以及羟基自由基和硫酸根自由基的特性，本工作推断反应机理如下：PhQ 羟基自由基反应首先生成 OH 加成产物，OH 加成产物脱水生成阳离子自由基；阳离子自由基亦可通过硫酸根自由基的氧化直接产生。

关键词 脉冲辐解，单电子氧化，9，10-菲醌

中图分类号 0644