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Reduction of 1,4-quinone and Ubiquinones by Hydrogen Atom Transfer under UVA Irradiation

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1,4-Benzoquinone, coenzyme Q_0 and Q_{10} were reacted with a series of hydrogen donors in the ESR cavity in the presence or absence of UVA irradiation. The signals of the radicals generated from the hydrogen donors or of those of the semiquinones were detected. The reaction mechanism was interpreted by a hydrogen atom transfer instead of the usual electron transfer mechanism on the basis of the redox potentials of the reactants and the Marcus theory. The hydrogen atom transfer is explained by the excited triplet state of quinones, which, on the basis of quantum mechanic calculations, may be reached even under visible light. In some cases, hydrogen atom transfer was also observed without irradiation, although to a lesser extent.

Keywords: Ubiquinones; Hydrogen abstraction; Redox potentials; Marcus theory

INTRODUCTION

The most extensively investigated redox reaction of quinones in biological systems is the reversible reduction of ubiquinone (coenzyme Q) in the mitochondrial respiratory chain that occurs through an electron and proton transfer process.[1] Besides the well-known role in the mitochondrial respiratory chain, ubiquinone is present in different cellular membranes[2] where it probably exerts antioxidant function. The interest in the biological function of quinones has also stimulated basic chemical research in several areas. One of the most studied reactions of quinones was their behaviour as oxidants and dehydrogenating agents.[3] In the early 1950s the dehydrogenating properties of quinones were explained by hypothesising the transfer of a hydride ion.[4–6] In that period, the use of quinones as oxidants which had been limited to hydro-aromatic compounds, was extended to various other areas of organic chemistry and the mechanisms of their action were investigated. The reactions carried out on quinones with high oxidation power generally occur through an electron transfer process; whereas the reaction of quinones with a lower oxidation power, i.e. more negative reduction potentials, was explained by the transfer of a hydrogen atom, in a similar way to what has been hypothesised for biological systems.[7] These two mechanisms have been matter of debate in the last few decades and controversy still exists.[8,9] Quinones are very sensitive to light and in many cases can react through their triplet state even in conditions of natural light, as will be commented on in the discussion.

The aim of the present paper is to demonstrate that the reduction of quinones and ubiquinones may occur by hydrogen abstraction depending on the hydrogen donor and on the reaction conditions. This study is based on the redox potentials of the reagents, on the theory of electron transfer processes[10] and on the reaction conditions, such as excited states of quinones which could favour hydrogen abstraction. The studied quinones were 1,4 benzoquinone (BQ) coenzymes Q_0 and Q_{10}.

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MATERIALS AND METHODS

EPR spectra were recorded at room temperature on a Varian E4 and a Bruker EMX spectrometers. As UVA irradiating source, a Philips Original Home Solarium (model HB 406/A; Philips, Groningen, The Netherlands) equipped with a 400 W ozone-free Philips HPA lamp, UV type 3, was used. The fluence rate of the light between 300 and 400 nm is 0.75 mW/cm^2. It was pre-run for 15 min to allow the output to stabilise.

1,4 benzoquinone (BQ), 2,3-dimethoxy-5-methyl-1,4-benzoquinone (Q_0), diethylhydroxylamine **1**, phenothiazine **3**, phenoxazine **4**, 2,6-dimethyl-3,5-dicarbethoxy-l,4-dihydropyridine **6**, 2,6-di-*tert*--butyl-4-methylphenol **8**, *N*-benzoyl-tyrosin-ethyl-ester **9**, α-tocopherol **10**, ascorbic acid **11**, and glutathione **12** were purchased from Aldrich. NADH **7** was purchased from Sigma. Coenzyme Q_{10} was a kind gift from Kaneka, Japan. All these products were used without further purification. 2-Phenyl-3-phenylaminoindole **5** was prepared according to the literature.[11] All other reagents and solvents were from Carlo Erba or Aldrich (RP-ACS grade) and were purified as described.[12] The buffer used was PBS 5 mM, 0.1 mM EDTA, pH 7.4.

Theoretical calculations were performed using the semiempirical quantum-mechanical molecular orbital methods MNDO/d, AM1 and PM3. The Roothan and Pople–Nesbet equations were used to explore the lowest excited state S_1 and T_1. The molecular geometry was optimised to gradient 0.02.

Synthesis of Phenylhydroxylamine 2

Zinc powder (85 g) in small portions was added to a suspension of nitrobenzene (50 ml) in 1 l of water containing ammonium chloride (30 g) under mechanical stirring at 40°C. The addition was regulated in order to maintain the temperature below 75°C. After the addition (10 min) the reaction was kept at 75°C for a further 10 min under stirring. The mixture was filtered and the filtrate poured on crushed ice (1 kg). The phenylhydroxylamine was precipitated by scraping the solution on the sides of the beaker. The precipitate was filtered off, dried and crystallised from ligroin 60–80°C: obtained 20 g, m.p. 81–82°C.

EPR Measurements

The solvent used in the majority of experiments where the radical deriving from the hydrogen donor was stable enough to be detected and recorded was benzene. In all the other cases where this radical was unstable even in benzene the sought after radical was that of the semiquinone recorded in DMSO/buffer 1:4 v/v. The experiments with ascorbic acid were also carried out in DMSO/buffer and the detected signal was the one corresponding to the ascorbyl radical and the semiquinone, which were superimposed. The experiments performed are reported in Table I and the hyperfine coupling constants of the detected EPR signals are shown in Table II.

The appropriate quinone (1 ml of a 10 mM solution) and the hydrogen donor (1 ml of a 10 mM solution) were placed, respectively in each of the two legs of an inverted U cell as described by Russell *et al.*[13] and degassed with nitrogen. The solutions of the reactants were mixed and the aqueous cell was then transferred into the EPR cavity at room temperature.

For the experiments carried out in DMSO, the buffer solution was added to the leg containing the hydrogen donor. In the experiments with Q_{10} 0.5 ml of acetone were also added in order to increase its solubility.

Electrochemical Measurements. Oxidation Potentials of *N*-benzoyl-tyrosine Ethylester 9

A three-electrode multipolarograph AMEL 472 coupled with a digital x/y recorder AMEL 863 was used for the voltammetric measurements, carried out at a pulsed (polarographic measurement) or static (cyclic voltammetry) glassy-carbon electrode in anhydrous MeCN containing tetraethylammonium

TABLE I List of experiments carried out in the EPR cavity between the quinones BQ/Q_0/Q_{10} and hydrogen donors **1**–**12**

Hydrogen donor	Radical detected	Solvent
Diethylhydroxylamine (**1**)	$Et_2N–O^{\cdot}$	Benzene
Phenylhydroxylamine (**2**)	$Ph(H)N–O^{\cdot}$	Benzene
Phenothiazine (**3**)	Phenothiazinyl	Benzene
Phenoxazine (**4**)	Phenoxazinyl	Benzene
2-phenyl-3-phenylaminoindole (**5**)	$BQ^{-\cdot}/Q_0^{-\cdot}/Q_{10}^{-\cdot}$	DMSO/buffer, 4:1, (v/v)
2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine (**6**)	$BQ^{-\cdot}/Q_0^{-\cdot}/Q_{10}^{-\cdot}$	DMSO/buffer, 4:1, (v/v)
NADH (**7**)	$BQ^{-\cdot}/Q_0^{-\cdot}/Q_{10}^{-\cdot}$	DMSO/buffer, 4:1, (v/v)
2,6-di-*tert*-butyl-4-methylphenol (**8**)	BHT-phenoxyl	Benzene
N-benzoyl-tyrosin-ethyl-ester (**9**)	$BQ^{-\cdot}/Q_0^{-\cdot}/Q_{10}^{-\cdot}$	DMSO/buffer, 4:1, (v/v)
α-tocopherol (**10**)	α-tocopheryl	Benzene
Ascorbic acid (**11**)	$BQ^{-\cdot}/Q_0^{-\cdot}/Q_{10}^{-\cdot}$ ascorbyl	DMSO/buffer, 4:1, (v/v)
Glutathione (**12**)	$BQ^{-\cdot}/Q_0^{-\cdot}/Q_{10}^{-\cdot}$	DMSO/buffer, 4:1, (v/v)

TABLE II Hyperfine coupling constants* in Gauss of the radicals detected

Radical	Nuclei (position) [Gauss]	Solvent
$Et_2N-O^{\cdot}$	1N[16.05]; 1H[10.75]	Benzene
$Ph(H)N-O^{\cdot}$	1N[9.31]; 1H,NH[12.36];2H(2,6)[2.87] 1H(4)[3.05];2H(3,5)[0.99]	Benzene
Phenothiazinyl	1N[7.42];2H,(1,9)[3.05];2H(2,8)[2.71]; 2H(3,7)[0.98];2H(4,6)[0.74]	Benzene
Phenoxazinyl	1N[8.06];2H(1,9)[4.13];2H(2,8)[3.11] 2H(3,7)[0.99]; 2H(4,6)[0.75]	Benzene
α-tocopheryl	$2H(4\text{-}CH_2)$[1.47];$3H(5\text{-}CH_3)$[5.98] $3H(7\text{-}CH_3)$[4.57];$3H(8\text{-}CH_3)$[0.94]	Benzene
BHT-phenoxyl	$3H(4\text{-}CH_3)$[11.25] 2H(3,5)[1.64]	Benzene
Ascorbyl	1H[1.86]; 1H[0.23]	DMSO†
$BQ^{-\cdot}$	4H[2,3,4,5)[2.24]	DMSO†
$Q_0^{-\cdot}$	$3H(5\text{-}CH_3)$[2.24] 1H(6)[2.27]	DMSO†
$Q_{10}^{-\cdot}$	$3H(5\text{-}CH_3)$[2.13]; $2H(6\text{-}CH_2)$[1.07]	DMSO†,‡

*All data are in agreement with those reported in: *Landolt-Börnstein*, *Magnetic Properties of Free Radicals*, Vols. 1, 9, 17, Eds. H. Fischer and K.-H.Hellwege, Springer-Verlag, Berlin.
†In the presence of phosphate buffer, pH 7.4 [DMSO/buffer, 4:1, (v/v)].
‡In the presence of actone [DMSO/buffer/acetone, 1:0.25:0.05, (v/v)].

perchlorate 0.1 mol/l as supporting electrolyte. $Ag/AgClO_4$ 0.1 mol/l-MeCN/sintered glass disk/TEAP 0.1 mol/l-MeCN/sintered glass disk was used as reference electrode[14] and a platinum wire as counter electrode. The measurements were carried out starting from 1×10^{-3} mol/l solutions.

RESULTS

All quinones (BQ, Q_0 and Q_{10}) were reacted in the appropriate solvent with the hydrogen donors (**1–12**). The experiments are listed in Table I and the hyperfine coupling constants of the detected radicals are reported in Table II. The redox potentials of all the compounds studied are shown in Table III.

Reactions of quinones (BQ, Q_0 and Q_{10}) with 1–4 and 8–10

In these cases, the reactions were performed in benzene and the spectrum of the radical deriving from the hydrogen donor was observed in every reaction without UVA irradiation, except with α-tocopherol. In each case, the intensity of the recorded spectrum increased when exposed to UVA irradiation and decreased back to the initial level after the lamp had been switched off. The EPR spectra of phenylnitroxide and phenoxazinyl radicals are reported in Fig. 1a and b, respectively.

Reactions of quinones (BQ, Q_0 and Q_{10}) with hydrogen donors 5–7, 9, 11 and 12

All these reactions were carried out in DMSO which was chosen either for solubilizing some of the product or for making the addition of the aqueous buffer solution possible. In these cases, the radicals deriving from the hydrogen donors are unstable no matter the solvent, with the exception of the ascorbyl radical. Under these reaction conditions, the protonated semiquinones are also unstable. Therefore, in order to observe the semiquinone radicals a small quantity of buffer (pH 7.4) was added to stabilise the

TABLE III Oxidation potentials of compounds **1–12** and reduction potentials of BQ, Q_0 and Q_{10}

Compounds	Oxidation potentials, V	Solvent	Reference
1	0.50 vs SCE	MeCN	[15]
2	0.13 vs SCE	$ETOH/H_2$	[16]
3	0.50 vs SCE	MeCN	[17]
4	0.63 vs Ag/Ag^+	MeCN	[18]
5	0.47 vs SCE	MeCN	[19]
6	0.81 vs SCE	MeCN	[20]
7	1.02 vs NHE	H_2O	[21,22]
8	1.21 vs SCE	MeCN	[23]
9	1.00 vs Ag/Ag^+	MeCN	This paper, see Materials and Methods
10	0.82 vs SCE	CH_2Cl_2/TFA*	[24]
11	0.30 vs SCE	MeCN	[25]
12	−0.48 vs SCE†	H_2O	[26]
Reduction potentials, V			
BQ	−0.46 vs SCE	DMF	[27]
Q_0	−0.62 vs SCE	DMF	[27]
Q_{10}	−0.68 vs SCE	DMF	[27]

*TFA, triflouoroacetic acid.
†The measurement is referred to an alkaline solution.

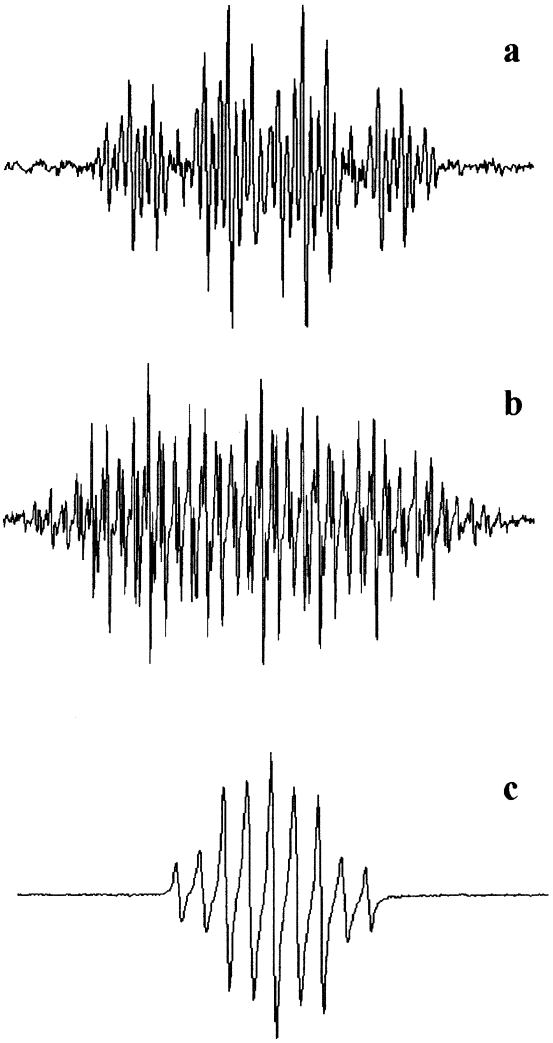

FIGURE 1 (a) EPR spectrum of phenylnitroxide recorded in benzene and obtained by mixing benzene solutions of Q_{10} and phenylhydroxylamine. (b) EPR spectrum of phenoxazinyl radical recorded in benzene and obtained by mixing benzene solutions of Q_{10} and phenoxazine. (c) EPR spectrum of Q_{10}-semiquinone radical recorded in DMSO/acetone/PBS buffer pH 7.4 and obtained by mixing solutions of Q_{10} and NADH. All spectra were recorded under UVA irradiation.

protonated semiquinones, which were the radical species detected and recorded in these cases. Fig. 1c shows the EPR spectrum of $Q_{10}^{-\cdot}$. When ascorbic acid was used both the signals of the semiquinone and of the ascorbyl radical were detected.

DISCUSSION

As mentioned in the introduction, quinones and ubiquinones are commonly believed to react through an electron transfer process. Several years ago we[28] found that 1,4-benzoquinone was reduced by 3-phenylaminoindole **5** at room temperature in aprotic solvent and the reaction was interpreted by an electron transfer process. This mechanism should now be excluded on the basis of the redox potentials of the reagents (see Table III). In fact, according to the Marcus theory,[29] electron transfers generally occur when the difference between the oxidation potential of the donor and the reduction potential of the acceptor is lower than 0.4 V. In the above mentioned study[28] this difference was 0.93 V. Assuming that ΔS for an electron transfer is negligible we should have an endothermicity higher than 20 kcal/mole and thus a very high activation energy. On the basis of the redox potentials of the reagents (Table III), with the exception of the reaction between phenylhydroxylamine **2** and BQ that may be on the borderline for an electron transfer process, this mechanism should be forbidden for all the other cases. Therefore, the reduction of quinones must be explained by hydrogen abstraction that may only be justified by an excited triplet state of quinones.[30] Our hypothesis concerning with the hydrogen atom transfer is also supported by the fact that compounds such as diethylhydroxylamine **1**, phenoxazine **4** and BHT **8** have a very low bond dissociation energy (BDE) [75.9, 77.2, 81.1 kcal/mol for **1**,[31] **4**,[17] and **8**,[32] respectively].

On the other hand, it has already been observed that the first triplet state T_1 is the one primarily responsible for hydrogen abstraction.[33–35] It has been demonstrated that the direct transition from S_0 (ground state) to T_1 (triplet state) has a low efficiency but the triplet state may be reached by a $S_0 \rightarrow S_1$ transition followed by an intersystem crossing $S_1 \rightarrow T_1$. Quantum mechanic calculations performed on BQ by using AM1 Hamiltonian[36] showed that $S_0 \rightarrow S_1$ transition requires 71.6 kcal/mol corresponding to an excitation wavelength of $\lambda = 399$ nm; whereas the triplet state T_1 which is only 35.0 kcal/mol over S_0, could be reached by a wavelength of $\lambda = 817$ nm. Similar results were obtained with MNDO/d[37] and PM3.[38,39] These data show that all the wavelengths which produce excited states fall in the visible region and this is in perfect agreement with the findings that all quinones react with the best hydrogen donors (see above) under simple exposure to visible light since the triplet state T_1 is easily reached. Having observed that the reactivity of BQ, Q_0 and Q_{10} with BHT **8** as well as with other hydrogen donors, follows the sequence $BQ \gg Q_0 \geq Q_{10}$, it may be indirectly admitted that the triplet state (T_1) could be more easily reached for quinones with less negative reduction potentials (see Table III).

In every reaction there is hydrogen atom transfer leading to a pair of neutral radicals; the one deriving from the hydrogen donor, detected in most cases, and the protonated semiquinone, which was never detected, the reason being that it disproportionates with a very high rate constant as recently reported.[40] This is the reason why the reactions were carried out in benzene when the radical

deriving from the hydrogen donor was stable, whereas the reactions in which the semiquinone was the only detectable radical species were performed in DMSO/buffer (pH 7.4).

It is well known that $Q_{10}H^{\cdot}$ regenerates tocopherol from the tocopheryl radical by hydrogen abstraction;[41] this is in agreement with our results.

$$\alpha - \text{Tocopherol} + Q_{10} \rightleftarrows \alpha - \text{Tocopheryl}^{\cdot} + Q_{10}H^{\cdot} \quad (1)$$

In fact, the reaction (1) shifts to the right under irradiation; but when the light is switched off the EPR signal disappears in a few seconds as the initial conditions are restored in the dark.

The reduction of quinones by NADH and NADH-analogues was interpreted[42] by transfer of a hydride ion to the quinone; the results here described do not agree with such a mechanism, but they match better with hydrogen atom transfer as described in the reaction of NADH analogues with nitroxides.[43] Ubiquinones can be reduced by hydrogen atom transfer simply under irradiation by a wide range of UV/visible light. This could be of particular interest in view of the fact that ubiquinones are now widely used in several cosmetic cream formulations.

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