On the existence of quinone radical cations. A study in 1,1,1,3,3,3-hexafluoropropan-2-ol

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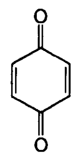
The strongly stabilizing influence of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) upon radical cations has been utilized to study the photolysis of a few quinones (Q), *viz.* benzoquinone, duroquinone, anthraquinone and tetrafluorobenzoquinone, in HFP containing 6% trifluoroacetic acid. The EPR spectra of the photolysed solutions are assigned to the radical cations of the corresponding hydroquinones ($QH_2^{\bullet+}$, the three first-mentioned quinones) or the protonated semiquinone ($QH^{\bullet}$, the tetrafluoro derivative), formed in a one-electron redox process involving excited Q as the reductant, in agreement with earlier studies in strongly acidic media.

1,4-Benzoquinone (BQ) is extremely resistant toward oxidation, as evidenced by the fact that it can be prepared in high yield by the anodic oxidation of benzene,[1] in itself a highly oxidation-resistant compound with $E^\circ(PhH^{\bullet+}/PhH)$ in acetonitrile ≈2.8 V *vs.* the saturated calomel electrode (SCE).[2] The same relationship is indicated by the gas phase ionization potentials of 1,4-benzoquinone and benzene, 9.67 and 9.24 eV, respectively.[3] It was therefore a matter of some surprise when it was claimed[4] that the EPR spectra obtained by irradiation of quinones (Q) in trifluoroacetic acid (TFA) containing trifluoroacetic anhydride (TFAnh) should be assigned to quinone radical cations ($Q^{\bullet+}$) or even protonated quinone radical cations ($QH^{\bullet 2+}$). Quinone radical cations would possess standard redox potentials $E^\circ(Q^{\bullet+}/Q)$ in excess of 3 V and thus be predicted to be extremely reactive species[5] and certainly not observable in fluid solution around ambient temperature. A large amount of early[6–11] and not so early work[12,13] indeed has shown that the EPR spectra observed from acidic solutions of many types of quinones or hydroquinones under thermal or photochemical conditions in all probability should be assigned to radical cations of hydroquinones, $QH_2^{\bullet+}$. Radical cations of phenols have been shown to be relatively stable in acidic media by electrochemical methods.[14] Hydroquinone radical cations should in fact be comparable to species like the radical cation of 1,4-dimethoxybenzene, possessing $E^\circ(ArH^{\bullet+}/ArH)$ around 1.5 V (ionization potential ≈8.0 eV).[3]

We repeated some of this work, using TFA or TFA–TFAnh as solvent, and could verify that weak EPR spectra of the reported appearance could be obtained from such solutions. However, rather high modulation amplitudes were needed to record the spectra, leading to less than optimal resolution. We recently found that 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) is a uniquely stabilizing solvent for radical cations,[15] with high resolving power for EPR spectroscopy, and decided to use this feature for a study of the quinone problem. We now report a brief study of a few quinone systems in this medium which fully confirms the view that the EPR spectra should be assigned to hydroquinone radical cations, $QH_2^{\bullet+}$.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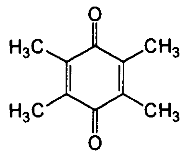
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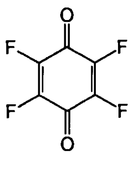
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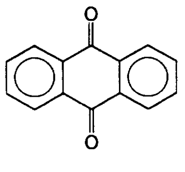
AQ

Results

Electrochemical oxidation of duroquinone (2,3,4,5-tetramethylbenzoquinone, DQ) and anthraquinone (AQ)

The expected very high E° of $Q^{\bullet+}/Q$ systems does not lend much promise to electrochemical studies, but an attempt was yet made with duroquinone, which should be a more easily oxidizable quinone in view of the four electron-donating methyl groups. HFP is an excellent solvent for anodic chemistry,[15b] and with tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) as the supporting electrolyte, an anodic peak at 2.46 V (*vs.* Ag/AgCl) could be recorded by cyclic voltammetry. No corresponding reduction peak was detected. The parent hydrocarbon, durene, showed reversible behaviour under these conditions at a sweep rate of $\geqslant 1$ V s^{-1}, $E^\circ(durene^{\bullet+}/durene)$ being 1.35 V (Ag/AgCl).

Similarly, anthraquinone exhibited an anodic peak potential of 2.25 V and anthracene a reversible couple ($\geqslant 0.2$ V s^{-1}) at 0.91 V.

EPR spectroscopy from photolysis of a solution of duroquinone (DQ) in HFP containing 6% TFA

A solution of duroquinone in HFP with 6% trifluoroacetic acid present upon irradiation at 22 °C gave a medium strong, well-resolved spectrum with $a^H = 0.207$ (12 H) and $a^H = 0.265$ (2 H) mT [Fig. 1 (*a*)]. A simulated spectrum is shown in Fig. 1(*b*). The spectrum recorded in neat TFA was weaker, the hfs constants being 0.208 (12 H) and 2.60 (2 H) mT. In [^{2}H]TFA the hfs constants were $a^H = 2.07$ (12 H), $a^D = 0.40$ (2 D) mT.

EPR spectroscopy from photolysis of a solution of anthraquinone (AQ) in HFP containing 6% TFA

A solution of anthraquinone in HFP with 6% trifluoroacetic acid present upon irradiation at 22 °C gave a medium strong, well-resolved spectrum with $a^H = 0.162$ (4 H), $a^H = 0.106$ (4 H) and $a^H = 0.106$ (2 H) mT [Fig. 2(*a*)]. The simulated spectrum is shown in Fig. 2(*b*). In neat TFA, the spectrum was weaker, $a^H = 0.151$ (4 H), $a^H = 0.109$ (4 H) and $a^H = 0.053$ (2 H) mT,

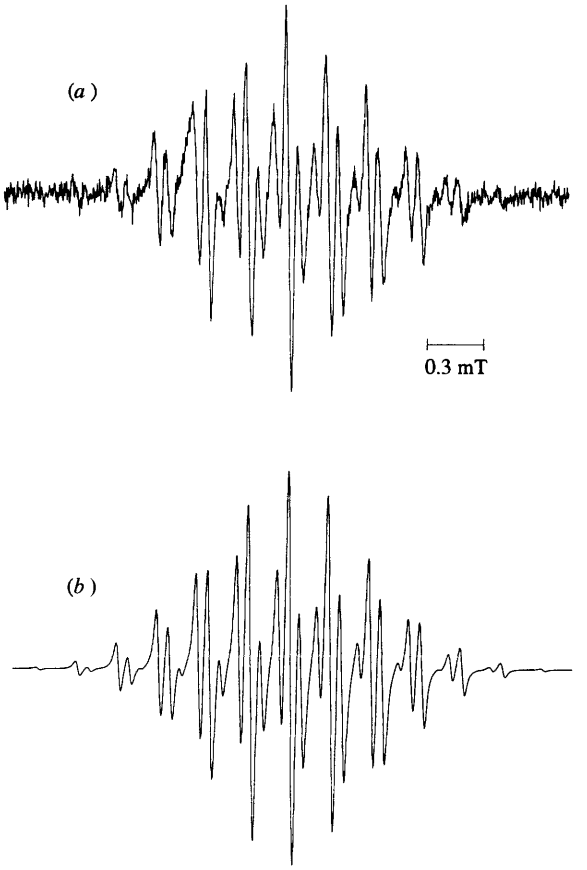

Fig. 1 (*a*) EPR spectrum of a UV irradiated solution of duroquinone in HFP–TFA (6%) at 22 °C. (*b*) Simulated spectrum, using a^H = 0.207 (12 H) and a^H = 0.265 (2 H) mT, line-width 0.040 mT

as also in [^{2}H]TFA, a^H = 0.156 (4 H), a^H = 0.106 (4 H) and a^D = 0.0082 (2 H) mT.

EPR spectroscopy from photolysis of a solution of 1,4-benzoquinone (BQ) in HFP containing 6% TFA

A solution of 1,4-benzoquinone in HFP with 6% trifluoroacetic acid present upon irradiation at 22 °C gave an EPR spectrum with a^H = 0.208 (4 H) and a^H = 0.333 (2 H) mT. In neat TFA the corresponding values were 0.216 (4 H) and 0.322 (2 H) mT.

EPR spectroscopy from photolysis of a solution of tetrafluoro-1,4-benzoquinone (TFQ) in HFP containing 6% TFA

A solution of tetrafluoro-1,4-benzoquinone in HFP with 6% trifluoroacetic acid present upon irradiation at 22 °C gave a medium strong, well-resolved spectrum with a^F = 1.17 (2 F), a^F = 0.246 (2 F) and a^H = 0.152 (1 H) mT. In TFA–TFAnh (10%) at −10 °C the parameters were a^F = 1.15 (2 F), a^F = 0.206 (2 F) and a^H = 0.206 (1 H) mT, whereas in acetonitrile with 1.5% TFA added at 22 °C they were a^F = 1.21 (2 F), a^F = 0.304 (2 F) and a^H = 0.126 (1 H) mT.

Discussion

The photoexcitation of a quinone Q initially leads to the lowest singlet excited state $^1Q^*$ which either can act as a one-electron donor to an available acceptor or undergo intersystem crossing to give the triplet state $^3Q^*$, also a potentially one-electron donating species although weaker than the singlet. The possible acceptors in the system are Q and/or its protonated form [eqn. (1)]. The value of K_1 was determined to be 2.3 × 10^{-5} dm^3 mol^{-1} in TFA–TFAnh (20%).[4d]

$$CF_3COOH + Q \underset{}{\overset{K_1}{\rightleftharpoons}} CF_3COO^- + QH^+ \qquad (1)$$

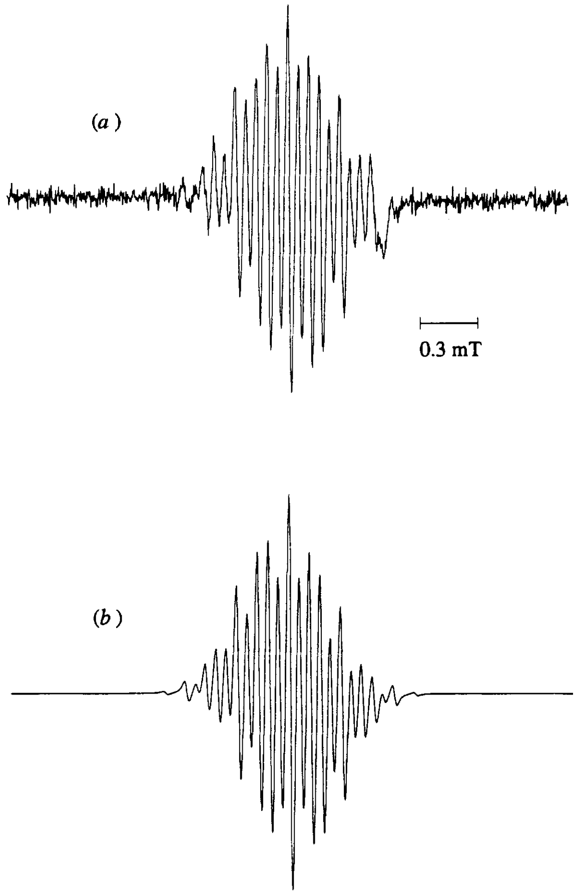

Fig. 2 (*a*) EPR spectrum of a UV irradiated solution of anthraquinone in HFP–TFA (6%) at 22 °C. (*b*) Simulated spectrum, using a^H = 0.162 (4 H) and a^H = 0.106 (6 H) mT, line-width 0.040 mT

The excited singlet state redox properties of quinones can be derived from the singlet excitation energy, $\Delta E_{0,0}$, and the ground state redox potentials $E°(Q^{\bullet+}/Q)$ and $E°(Q/Q^{\bullet-})$ through eqns. (2) and (3). In the present case, $E°(Q^{\bullet+}/Q^*)$ is of interest since it relates to the electron transfer process taking place after excitation of the quinone molecule, transfer of an electron from Q* to Q and/or QH$^+$, the strongest electron acceptors present in the solution [eqns. (4) and (5)]. The quinone radical cation is judged to be an extremely reactive species, more so than the radical cation of the parent ArH, and is expected to decay very rapidly by nucleophilic interaction with trifluoroacetic acid. The quinone radical anion (with a p*K* of about 3.7 in the 1,4-benzoquinone case)[9] formed through eqn. (4) will be protonated to give QH$^\bullet$, known to exist in equilibrium with $QH_2^{\bullet+}$, the hydroquinone radical cation [eqns. (6) and (7)]. QH$^\bullet$ can also be formed directly *via* eqn. (5).

$$E°(Q^{\bullet+}/Q^*) = E°(Q^{\bullet+}/Q) - \Delta E_{0,0} \qquad (2)$$

$$E°(Q^*/Q^{\bullet-}) = E°(Q/Q^{\bullet-}) + \Delta E_{0,0} \qquad (3)$$

$$Q^* + Q \longrightarrow Q^{\bullet+} + Q^{\bullet-} \qquad (4)$$

$$Q^* + QH^+ \longrightarrow Q^{\bullet+} + QH^\bullet \qquad (5)$$

$$Q^{\bullet-} + H^+ \rightleftharpoons QH^\bullet \qquad (6)$$

$$QH^\bullet + H^+ \rightleftharpoons QH_2^{\bullet+} \qquad (7)$$

Table 1 EPR parameters of hydroquinone radical cations, $QH_2^{\bullet +}$

Compound[a]	Conditions[b]	Hfs constants/mT	Ref.
DQH_2	Sulfuric acid at 50 °C	0.210 (12 H), 0.27 (2 H)	6
DQH_2	Ce^{IV} and FSO_3H in nitromethane at −(27–37) °C	0.258 (6 H), 0.151 (6 H) [average 0.205 (12 H)], 0.263 (2 H)	12
DQH_2	$AlCl_3$–nitromethane at 2 °C	0.205 (12 H), 0.262 (2 H)	7
DQ	TFA, *hν* at 30 °C	0.219 (12 H)	4(*d*)
DQ	HFP–TFA (6%), *hν* at 22 °C	0.207 (12 H), 0.265 (2 H)	This work
DQ	[^{2}H] TFA, *hν* at 22 °C	0.207 (12 H), 0.040 (2 D)	This work
AQH_2	Sulfuric acid at 20 °C	0.166 (4 H), 0.107 (4 H), 0.131 (2 H)	11
AQ	TFA, *hν* at 35 °C	0.151 (4 H), 0.109 (4 H), 0.053 (1 H)	4(*d*)
AQ	HFP–TFA (6%), *hν* at 22 °C	0.162 (4 H), 0.106 (4 H), 0.106 (2 H)	This work
AQ	TFA, *hν* at 22 °C	0.151 (4 H), 0.109 (4 H), 0.053 (2 H)	This work
AQ	[^{2}H] TFA, *hν* at 22 °C	0.151 (4 H), 0.109 (4 H), 0.0082 (2 D)	This work
BQH_2	Ce^{IV} and FSO_3H in nitromethane at −(27–37) °C	0.249 (2 H), 0.206 (2 H) [average 0.227 (4 H)] 0.337 (2 H)	12
BQH_2	Sulfuric acid at 20 °C	0.236 (4 H), 0.344 (2 H)	11
BQH_2	Sulfuric acid at 20 °C	0.240 (4 H), not given	9
BQ	TFA, *hν* at 30 °C	0.225 (4 H)	4(*d*)
BQ	HFP–TFA (6%), *hν* at 22 °C	0.208 (4 H), 0.333 (2 H)	This work
BQ	TFA, *hν* at 22 °C	0.216 (4 H), 0.322 (2 H)	This work
TFQ	DCM, *hν*, trace of H^+ at 20 °C	1.264 (2 F), 0.320 (2 F), 0.117 (1 H)	10
TFQ	TFA–TFAnh (20%), *hν* at −16 °C	1.114 (2 F), 0.197 (2 F), 0.197 (1 H)	4(*d*)
TFQ	HFP–TFA (6%), *hν* at 22 °C	1.167 (2 F), 0.246 (2 F), 0.152 (1 H)	This work
TFQ	TFA–TFAnh (20%), *hν* at −10 °C	1.15 (2 F), 0.206 (2 F), 0.206 (1 H)	This work
TFQ	AN–TFA (1.5%), *hν* at −10 °C	1.21 (2 F), 0.304 (2 F), 0.126 (1 H)	This work

[a] DQ = duroquinone, AQ = anthraquinone, BQ = 1,4-benzoquinone, TFQ = tetrafluoro-1,4-benzoquinone. [b] TFA = trifluoroacetic acid, TFAnh = trifluoroacetic anhydride, HFP = 1,1,1,3,3,3-hexafluoropropan-2-ol, DCM = dichloromethane, AN = acetonitrile.

The processes of eqns. (4) and (5) can in principle also take place with the triplet $^3Q^*$ as the electron donor.

Since it is not possible to determine potentials of reversible processes for one-electron oxidation of Q, the value of $E°(Q^{\bullet +}/Q^*)$ can only be approximately estimated. The relationship between the E_{pa} of duroquinone, measured above to be 2.46 V in HFP, and durene (1.35 V) indicates that DQ is about 1.1 V more difficult to oxidize than its parent hydrocarbon. For anthraquinone and anthracene the corresponding difference is ≈1.3 V. If such a difference holds generally, 1,4-benzoquinone should have $E°(BQ^{\bullet +}/BQ) \approx 3.9$ V from $E°(PhH^{\bullet +}/PhH) = 2.8$ V and the minimum difference above, 1.1 V. The value of $\Delta E_{0,0}$ for the lowest singlet state of quinones is ≈2.9 eV,[16] so that the value of $E°(BQ^{\bullet +}/BQ^*) = 3.9 - 2.9 = 1.0$ V. Thus the efficiency of the ET reaction of eqn. (3) should be very low, keeping in mind that $E°(BQ/BQ^{\bullet -})$ is about −0.5 V.[17] Successive protonation of $BQ^{\bullet -}$ [eqns. (6) and (7)] will take place but it is doubtful if this would allow for sufficient $BQH_2^{\bullet +}$ to accumulate during irradiation.

The process of eqn. (5) should be more favourable for the generation of $QH^{\bullet}$. Protonation of Q leads to a more easily reducible species, perhaps with $E°(QH^+/QH^{\bullet})$ around 0.5 V.[18] In this situation, eqn. (5) will be weakly endergonic and allow for fast electron transfer between Q^* and QH^+. It is also possible that the triplet state can participate in eqn. (5), but then it must be recalled that triplet states are less effective electron donors than singlets, for quinones by a term between 0.2 and 0.6 eV.[16]

Similar behaviour is expected for tetrafluoro-1,4-benzoquinone; the electron-withdrawing fluorine atoms will increase $E°(TFQ^{\bullet +}/TFQ)$ and thus it is likely that eqn. (5) will be endergonic and the concentration of any protonated form of $TFQ^{\bullet -}$ ($TFQH^{\bullet}$ see below) low.

For anthraquinone $E°(AQ^{\bullet +}/AQ)$ comes out at ≈2.25 V (measured in HFP) and thus $E°(AQ^{\bullet +}/AQ^*)$ is $2.25 - 2.9 = -0.65$ V for the singlet state; in this case eqn. (4) becomes weakly exergonic and the concentration of $AQH_2^{\bullet +}$ becomes much higher than in the BQ case. For duroquinone $E°(DQ^{\bullet +}/DQ)$ is ≈2.5 V and $E°(DQ^{\bullet +}/DQ^*)$ $2.5 - 2.9 = -0.4$ V, making eqn. (4) approximately thermoneutral and allowing for higher concentrations of $DQH_2^{\bullet +}$ to build up upon irradiation. For both the AQ and DQ cases, eqn. (5) will be even more favourable for production of $QH^{\bullet}$.

EPR data

Table 1 lists EPR data for $QH_2^{\bullet +}$, obtained under various conditions from both QH_2 and Q. Looking at data for the DQ system under conditions where all 12 methyl hydrogens are equivalent, it is evident that the same species is formed both when DQH_2 or DQ is used as starting material and that there is an additional coupling to two hydrogens, as shown by the spectrum of Fig. 1. This coupling pattern is in good agreement with the structure of $DQH_2^{\bullet +}$ but not with that of $DQ^{\bullet +}$ or a species formed by single protonation of the latter. This would require double protonation of a highly energetic species in trifluoroacetic acid, a very unlikely situation.

Similarly, EPR data for the AQ and BQ systems are in good agreement with the $QH_2^{\bullet +}$ structure, irrespective of the nature of the starting material. Fig. 2 clearly shows the coupling to two additional protons apart from those of the aromatic rings of AQ, thus excluding the earlier proposed $AQH^{\bullet 2+}$ structure.

The TFQ system deviates from the other systems, in that the additional coupling besides that to the fluorine atoms, is to one hydrogen only. This was earlier[10] interpreted in terms of the protonated radical anion structure, $TFQH^{\bullet}$, assumed to be the favoured species of the equilibrium of eqn. (3). This suggestion is reasonable in view of the expected much higher acidity of the fluorine-substituted system.

Experimental

Materials and methods

Tetramethyl-1,4-benzoquinone (DQ, Aldrich), anthraquinone (AQ, Baker), 1,4-benzoquinone (BQ, Kebo), hydroquinone (BQH_2, Kebo), tetrafluorobenzoquinone (TFQ, Aldrich) and tetrafluorohydroquinone ($TFQH_2$, Sigma) were used as received. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) and trifluoroacetic acid (TFA) were of Merck UVASOL quality.

EPR spectra were recorded by the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using unfiltered light from the 50 W high-pressure Hg lamp from Bruker (ER 202). The substrate (≈5 mg) was dissolved (complete dissolution was not always feasible with the hydroquinones) in 0.70 cm^3 of HFP with 6% TFA added and the solution bubbled with argon in the EPR sample tube. The tube was then sealed and the EPR spectrum recorded at room temperature (100 kHz modulation frequency, microwave effect 0.4–1.6 mW, modulation amplitude 0.01–0.04 mT).

Cyclic voltammetry was performed in HFP–Bu_4NPF_6 (0.15 mol dm^{-3}), using a BAS-100 instrument.

Acknowledgements

Financial support (to L. E.) from the Swedish Natural Science Research Council is gratefully acknowledged.

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Paper 5/05471K
Received 16*th August* 1995
Accepted 1*st September* 1995