EPR and Flash Photolysis Investigations of Some *p*-Quinone Radical Cations

Günter Grampp* and Kurt Neubauer
Institute of Physical and Theoretical Chemistry, University of Erlangen, Egerlandstrasse 3, D-910 58 Erlangen, Germany

EPR and flash photolysis investigations of some *p*-benzoquinone radical cations in a trifluoroacetic acid–trifluoroacetic anhydride solvent mixture (5:1 vol.) are reported. Coupling constants and *g*-values are estimated for the radical cations of *p*-benzoquinone, duroquinone, tetrachloro- and tetrafluoro-*p*-benzoquinone and anthraquinone. The electron transfer rate between *p*-benzoquinone radical cation and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine was measured by flash photolysis and found to be 4×10^9 dm^3 mol^{-1} s^{-1}. A protonation constant of 2.3×10^{-5} dm^3 mol^{-1} for *p*-benzoquinone in trifluoroacetic acid–trifluoroacetic anhydride was found from conductivity measurements. Quantum chemical MNDO, AM-1 and *ab initio* calculations lead to the conclusion that the SOMO of the *p*-benzoquinone radical cation is σ-type orbital.

There exist only a few papers in the literature[1-5] concerning the generation and chemical properties of radical cations $Q^{\bullet +}$ of quinones (Q), in contrast with the wealth of literature on the corresponding semiquinone radical anions $Q^{\bullet -}$.[6]

Normally quinones are considered as electron acceptors, but removal of an electron from a parent quinone in solution is also possible by photolysis.[1-5] An asymmetric σ-radical cation of *p*-benzoquinone has been reported under γ-irridation of *p*-benzoquinone in frozen $CFCl_3$ solution at 77 K.[7] Chemically induced electron polarization (CIDEP) measurements have also been reported on this cation.[1,2,3,4]

It is well established that organic cations are stabilized by interaction with trifluoroacetic acid (TFA) by solvation and by the acidity and low nucleophilicity of TFA.[8,9] In this paper we report on the photoinduced generation of various quinone radical cations and the determination of their EPR parameters. The decay kinetics of the *p*-benzoquinone cation $BQ^{\bullet +}$ has also been investigated by EPR spectroscopy using a rotating disc arrangement. The electron transfer kinetics between $BQ^{\bullet +}$ and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine were measured by kinetic flash photolysis.

Experimental

The radical cations of the quinones were generated by photolysis of the corresponding quinones in a mixture of trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAn) (5:1 volume mixture). The concentrations of the quinones were normally around 5×10^{-2} mol dm^{-3}. All solutions were deaerated by being bubbled with dry nitrogen for 15 min.

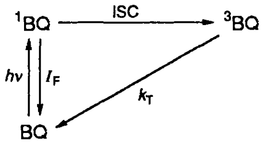
EPR spectra were recorded on a JEOL 3PX-spectrometer with 100 kHz field modulation using a cylindrical TE_{011}-cavity. The spectra were stored in a digital data processing system, described earlier.[10] Coupling constants were obtained by applying the autocorrelation method and from digital spectra simulations.[10]

A microwave preamplifier (Narda N6224 S-65) was installed before the microwave receiver diode to improve signal intensity.[11] Temperature variations were to within ± 1 °C with the JEOL temperature control unit VT-10. The samples contained in quartz tubes (OD = 5 mm, ID = 1.8 mm) were illuminated with unfiltered light from a mercury lamp. The photolysis unit consisted of a 500 W high-pressure mercury lamp (Osram HBO 500/2) and an IR water filter of 20 cm pathlength. Kinetic curves were obtained by irradiating the samples through a rotating sector disc at fixed magnetic field and averaging the EPR signal with a signal averager (Tracor TN-1710 with TN-1710/30/28/9 plug-in units) to improve the *S*/*N*-ratio. Concentrations were calibrated against Fremy's salt (ε = 1690 dm^3 mol^{-1} cm^{-1} at 248 nm).[12]

For *g*-values measurements the magnetic field strength was measured with an NMR-gaussmeter (Drusch RMN-2) and the microwave frequency was measured with GHz-frequency counter (hp 5245L). Flash-photolysis experiments were performed with conventional equipment consisting of two flash lamps mounted in a biellipsoidal cavity. Flash durations of 2 μs (fwhm) were obtained with an energy of 200 J (20 kV at 1 μF). The optical pathlength of the cell was 8 cm. Detection light came from a stabilized tungsten lamp (250 W, 24 V) and the absorption was monitored through a Bausch & Lomb monochromator with a Hamamatsu photomultiplier type R 928.

For the compounds investigated the following abbreviations are used in this paper: *p*-benzoquinone (BQ), tetramethyl-*p*-benzoquinone (DQ, duroquinone), tetrachloro-*p*-benzoquinone (TClBQ, chloranil), tetrafluoro-*p*-benzoquinone (TFBQ, fluoranil), 9,10-anthraquinone (AQ) and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPPD). The substances were obtained from Merck (DQ, TC1BQ), Riedel de Haen (BQ), Fluka (AQ) and EGA (TFBQ, TMPPD). All substances were vacuum sublimed before use. Trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAn) were purchased from Merck and used as received. Conductivity measurements were performed with a conductimeter from WTW (*Wissenschaftlich Technische Werkstätte*) type LBR (*Leitfähigkeitsbrücke*).

Photolytical Generation of Quinone Radical Cations.—It is assumed[5] that the photolytical generation of the quinone radicals cations involves the formation of a triplet state ^3BQ [eqn. (1)]. In water a triplet decay rate of $k_T = 1.9 \times 10^6$ s^{-1} is reported.[14] The ^3BQ reacts with a protonated quinone BQH^+, according to eqns. (2) and (3):



(1)

$$BQ + CF_3COOH \xrightleftharpoons{K_A} BQH^+ + CF_3COO^- \quad (2)$$

Table 1 Measured coupling constants and g-values for some quinone radical cations in TFA–TFAn

Radical cation	a^H/mT	a^{OH}/mT	a^F/mT	g-value[a]	T/K
$BQ^{\bullet+}$	0.225 (4 H)	—	—	2.0035	303
	0.222 (4 H)[5]	—	—	2.0037	
	0.222 (4 H)[3]	—	—	2.0037	
$DQ^{\bullet+}$	0.219 (12 H)	—	—	2.0031	303
$TFBQH^{\bullet2+}$	—	0.179 (1 H)	0.228 (2 F) 0.152 (2 F)	2.0045	257
$TClBQH^{\bullet2+}$	—	0.164 (1 H)	0.082 (6 F)[b]	2.0036	311
$AQH^{\bullet2+}$	0.109 (4 H) 0.151 (4 H)	0.053 (1 H)	—	2.0020	308

[a] Uncorrected for second-order effects. [b] Couplings with two CF_3-moieties from the solvent TFA. Measured in 1 : 1 v/v TFA–CH_2Cl_2.

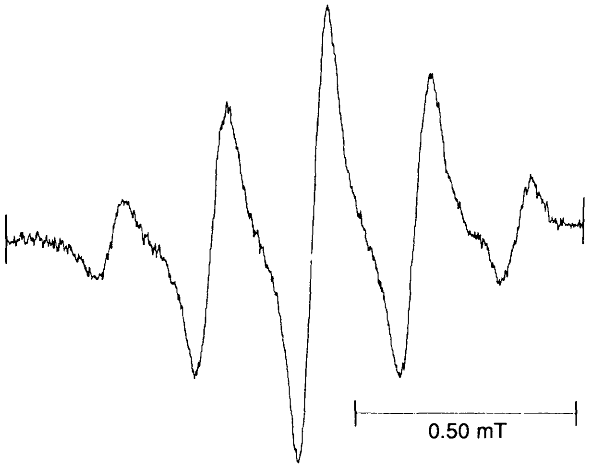


Fig. 1 EPR spectrum of the $BQ^{\bullet+}$ radical cation in TFA–TFAn (5 : 1) at 303 K during photolysis

$$^3BQ + BQH^+ \longrightarrow BQ^{\bullet+} + BQH^\bullet \quad (3)$$

$BQH^\bullet$ decays rapidly in acidic media as pointed out by Porter *et al.*[15] The photochemistry of BQ in water was investigated recently in great detail by Bolton *et al.*[16,17] and Ronford-Haret *et al.*[14] The conditions for observing radicals by EPR spectroscopy under steady-state photolysis have been described in detail recently.[18]

Results and Discussion

Conductivity Measurements on BQ in TFA–TFAn.—For the proposed mechanism of the generation of $BQ^{\bullet+}$ the existence of the protonated ground-state molecule BQH^+ is of central importance, see eqn. (3). To prove the proposed involvement of BQH^+ we made conductivity measurements on BQ in the TFA–TFAn system. According to Ostwald's dilution law one obtains the protonation constant K_A from the slope of a plot $(\Lambda_c)^{-1}$ *vs.* the concentration of BQ, provided that one knows the equivalent conductivity Λ_∞ of TFA. Λ_∞ is reported to be $26.2 \pm 4.1\ \Omega^{-1}\ cm^2\ mol^{-1}$.[19] A dissociation constant $K_A = 2.3 \times 10^{-5}\ dm^3\ mol^{-1}$ at $T = 298$ K is found for BQH^+, eqn. (2). This result is strong evidence for the proposed mechanism.

EPR Investigations.—The measured EPR coupling constants and g-values of all investigated radical cations are listed in Table 1. Unlike quinone radical anions, the radical cations $Q^{\bullet+}$ are less persistent and their EPR signals decay immediately following interruption of the irradiation. To verify the appearance of radical cations, we used the electron transfer reaction with TMPPD given in eqn. (4) which gives rise solely to

$$Q^{\bullet+} + TMPPD \xrightarrow{k_{et}} Q + TMPPD^{\bullet+} \quad (4)$$

the well known EPR spectra of Wursters Blue cation ($TMPPD^{\bullet+}$). No EPR signal of $BQ^{\bullet-}$ or its protonated form $BQH^\bullet$ was detected, which would occur by a disproportionation reaction between BQ and TMPPD. Photolysis of TMPPD alone in TFA–TFAn mixture gave no EPR spectrum due to $TMPPD^{\bullet+}$. This test was performed for all investigated quinones, showing that the corresponding radical cations were generated in all cases.

The p-*Benzoquinone Radical Cation.*—The EPR spectrum of $BQ^{\bullet+}$ is shown in Fig. 1. The pattern indicates four equivalent protons, the intensity ratio being 1 : 4 : 6 : 4 : 1 with a coupling constant $a^H = 0.225$ mT. The g-value of 2.0035 and the coupling constant are in good agreement with literature data.[1–5] The $a^H(BQ^{\bullet+})$ value is smaller than the corresponding coupling of the semiquinone radical anion $a^H(BQ^{\bullet-}) = 0.235$ mT[20] and also smaller than the coupling of the diprotonated radical anion. The g-value is also smaller than its anionic counterpart, $g(BQ^{\bullet-}) = 2.0045718$. The peak-to-peak line widths ΔB_{pp} for all radical cations reported in this paper are larger than those of the corresponding radical anions. The rate constant for the decay of $BQ^{\bullet+}$ was measured as 388 s^{-1}, assuming pseudo-first-order kinetics.

Zhong-Li *et al.*[3] suggested a line-broadening effect caused by an electron self-exchange reaction, according to eqn. (5).

$$BQ^{\bullet+} + BQ \overset{k_{ex}}{\rightleftharpoons} BQ + BQ^{\bullet+} \quad (5)$$

Reaction (5) was investigated in more detail. Within the so-called slow-exchange region the line-broadening from an electron self-exchange reaction is given by eqn. (6),[21] where

$$(\Delta B_{pp} - \Delta B^{\circ}_{pp}) = \frac{k_{ex}(1 - p_i)}{2\pi\gamma_e(\sqrt{3}/2)}[BQ] \quad (6)$$

ΔB_{pp} is the peak-to-peak linewidth without electron exchange, γ_e is the gyromagnetic ratio and p_i is the population number of line i in the EPR spectrum.

According to eqn. (6) the peak-to-peak line width ΔB_{pp} must be a function of the neutral concentration [BQ]. We varied [BQ] keeping the illumination power constant and found no dependence of ΔB_{pp} on [BQ]. ΔB_{pp} remained constant. As a result it can be concluded that an electron self-exchange

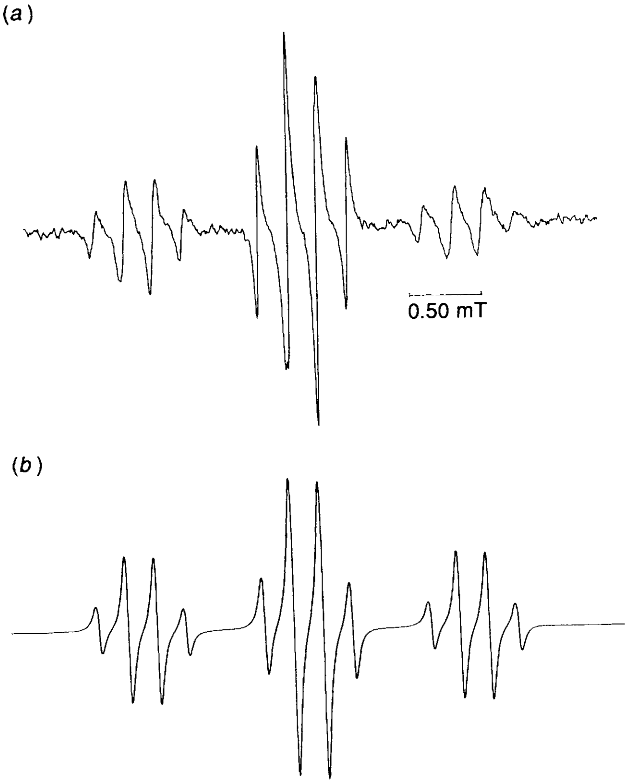


Fig. 2 EPR spectrum of the TFBQH$^{2\bullet+}$ radical cation obtained from TFBQ in TFA–TFAn (5:1) during photolysis at 257 K; (*b*) simulation of the spectrum in (*a*) with coupling constants listed in Table 1

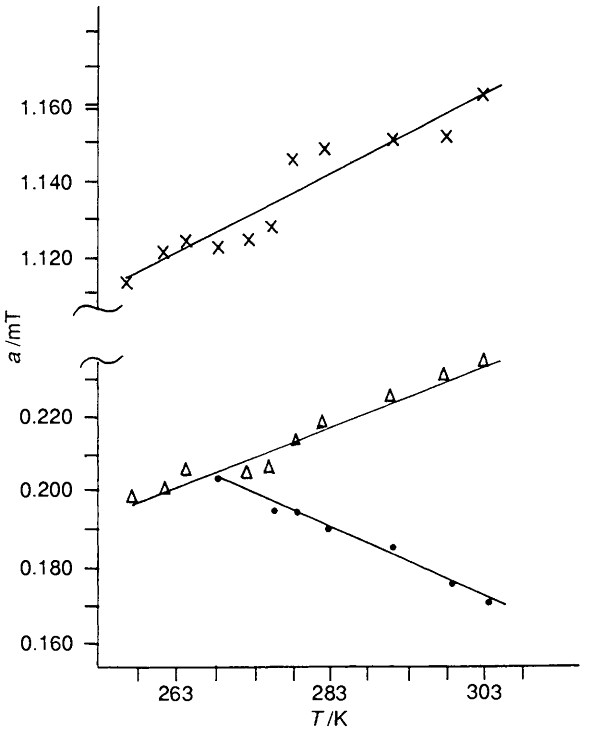


Fig. 3 Temperature dependence of the fluorine and proton coupling constants of the TFBQH$^{2\bullet+}$ radical cation: ●, a^{OH}; △, $a^F(2,6)$; ×, $a^F(3,5)$

reaction after eqn. (5) is too slow to be measured by EPR line broadening. The frequency of the electron self-exchange process must fall within the range 10^4–10^9 s^{-1} to be detectable by EPR spectroscopy.

In contrast, the rates of the corresponding reactions, eqn. (7), are well known in the literature.[22] As an activated reaction the activation energy ΔG^* of reaction (5) seems to be much higher

$$BQ^{\bullet-} + BQ \underset{}{\overset{k_{ex}}{\rightleftharpoons}} BQ + BQ^{\bullet-} \qquad (7)$$

than in the corresponding reaction (7) resulting in a much slower electron self-exchange rate. The broader linewidth may be attributed to a specific radical cation–solvent interaction probably caused by a strong interaction of BQ$^{\bullet+}$ with the trifluoromethyl moiety similar to that proposed by Dannenberg.[23] The radical cations are only stable in such a solvation complex with TFA. Another indication of the TFA-solvation stabilization is the fact that BQ$^{\bullet+}$ can also be generated in a mixture of CH_2Cl_2–TFA (1:1 by volume), but not in pure CH_2Cl_2.

Since the stabilization of the cation radicals by TFA depends on the distance between BQ$^{\bullet+}$ and TFA molecules, we investigated different tetrahalogeno-*p*-benzoquinones with the larger halogens (Br and I). However, no EPR signals were detected in both cases during photolysis, indicating that the stabilization effect depends strongly on the distance.

Another possibility for line-broadening may arise from fast proton exchange reactions between the oxygen atoms of BQ$^{\bullet+}$ and the solvent trifluoroacetic acid. Such proton-exchange reactions are well established in quinone chemistry and have been measured for different semiquinone radical anions by means of EPR line-broadening effects.[24] Proton exchange should lead to alternating line width effects with broadening of certain lines only.[24]

*The Tetramethyl-*p*-benzoquinone Radical Cation.*—The EPR spectrum of DQ$^{\bullet+}$ clearly shows the splitting of twelve equivalent protons with $a^H(DQ^{\bullet+}) = 0.219$ mT and a *g*-value of 2.0031. The corresponding values of $a^H(DQ^{\bullet-})$ are 0.196 mT and $g(DQ^{\bullet-}) = 2.0049$ measured in aqueous alkaline solution.[20]

*The Tetrafluoro-*p*-benzoquinone Radical Cation.*—The EPR spectrum of a photolysed solution of TFBQ in TFA–TFAn at 257 K is shown in Fig. 2(*a*). It can clearly be seen that the spectrum is not interpretable with an assumption of four equivalent fluorine atoms ($I_F = \frac{1}{2}$) as in the case of the semiquinone anion radical with $a^F(TFBQ^{\bullet-}) = 0.408$ mT and $g(TFBQ^{\bullet-}) = 2.004818$ in EtOH. The protonated semiquinone radical anion TFBQH$^\bullet$ is reported to have a^F (2,6) = 1.246 mT, a^F (3,5) = 0.324 mT and $a^{OH} = 0.108$ mT.[25]

The spectrum obtained indicates a protonated species TFBQH$^{\bullet2+}$, with two sets of equivalent fluorine atoms $a^F(3,5) = 1.114$ mT and a^F (2,6) = 0.197 mT together with an additional proton coupling of $a^H = 0.197$ mT. A spectrum simulation with these parameters is given in Fig. 2(*b*).

For the TFBQH$^{\bullet2+}$ radical cation we measured extensively the temperature dependence of all coupling constants in the range $257 \leqslant T/K \leqslant 304$. The temperature dependence of a^{OH}, $a^F(2,6)$ and $a^F(3,5)$ are shown in Fig. 3. The straight lines can be expressed by the following eqns. (8)–(10).

$$da^{OH}/dT = -8.36 \times 10^{-4}\,\text{mT K}^{-1} \qquad (8)$$

$$da^F(2,6)/dT = 9.30 \times 10^{-4}\,\text{mT K}^{-1} \qquad (9)$$

$$da^F(3,5)/dT = 10.13 \times 10^{-4}\,\text{mT K}^{-1} \qquad (10)$$

The temperature dependence of the hyperfine coupling constants may arise *via* a number of different mechanisms. Generally accepted mechanisms are the vibrations of the atoms out of the nodal plane of the ring system. In cases where there is near orbital degeneracy, the change in orbital contributions

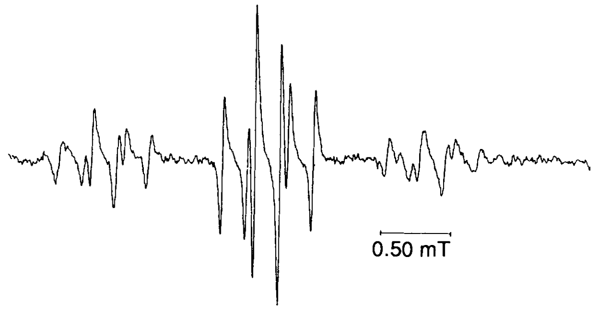


Fig. 4 EPR spectrum of TFBQH$^{\cdot 2+}$ at 304 K showing the additional splittings of a^{OH}

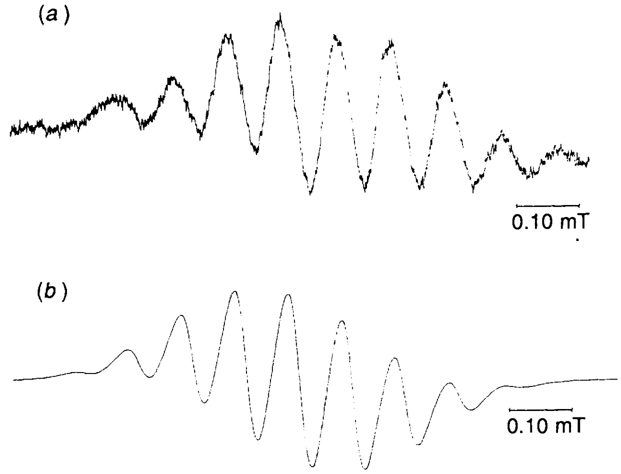


Fig. 5(*a*) EPR spectrum of TClBQH$^{\cdot 2+}$ showing an interaction between two CF_3 groups from the solvent and the protonated radical cation; (*b*) simulation of the spectrum in (*a*) with the coupling constants listed in Table 1

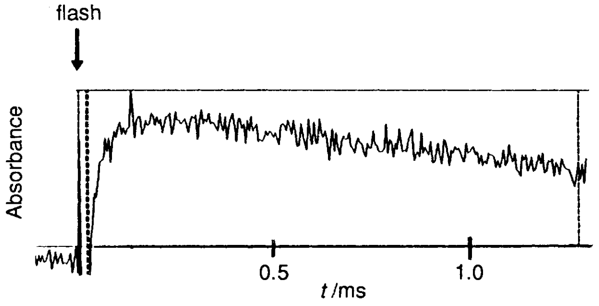


Fig. 6 Electron transfer reaction between BQ$^{\cdot +}$ and TMPPD. Absorbance at λ = 610 nm, showing the increase of TMPPD$^{\cdot +}$ and its slow decay by acid deamination.

with temperature can also lead to a temperature dependence. It is also shown that the temperature-dependent splittings in ion pairs may be caused by dynamic and static effects.[26] A positive temperature dependence of 11.5 mT K^{-1} is reported for fluorine splitting in the $\cdot CF_3$ radical.[27] The observed temperature dependences for a^{F} in TFBQH$^{\cdot 2+}$ are in the same order of magnitude.

The temperature dependences of hydroxy groups have been interpreted by Sullivan[28] with a potential barrier to rotation about the carbon–oxygen bond. Several diprotonated radical anions of quinones, dihydroxynaphthalenes and dihydroxyanthracenes were investigated. In each case the temperature coefficient $\mathrm{d}a^{\mathrm{OH}}/\mathrm{d}T$ was negative ranging from -0.83×10^{-4} mT K^{-1} to $-2.86 \cdot 10^{-4}$ mT K^{-1} for the different compounds.

Bullock and Howard[29] found 24 ± 2 kJ mol^{-1} for the twofold barrier to rotation of a hydroxy group in the 1,2,4,5-tetrahydroxybenzene radical cation. In nitromethane a temperature coefficient of -12.93×10^{-4} mT K^{-1} was observed. The value of $\mathrm{d}a^{\mathrm{OH}}/\mathrm{d}T = -8.36 \times 10^{-4}$ mT K^{-1} found for TFBQH$^{2\cdot +}$ is in good agreement with these literature data.

In accordance with the different signs in the temperature dependence of the fluorine and hydrogen coupling constants the difference in a^{OH} and $a^{\mathrm{F}}(2,6)$ can be observed in the EPR spectrum by a small additional splitting at higher temperatures. Fig. 4 shows the additional splittings appearing at 304 K.

*The Tetrachloro-*p*-benzoquinone Radical Cation.*—Tetrachloro-*p*-benzoquinone was photolysed in a mixture of TFA and dry CH_2Cl_2 (1:1 v/v) to improve the solubility of the quinone. A nine-line spectrum at $g = 2.0056$ was observed which can be simulated with two separate coupling constants caused by six equivalent nuclei together with an additional nucleus both with a spin number of $\frac{1}{2}$. The splitting indicates a coupling of six fluorine atoms with $a^{\mathrm{F}} = 0.082$ mT caused by an association complex formed between the tetrachloro-*p*-benzoquinone and two CF_3-moieties from two solvent molecules. An additional coupling of $a^{\mathrm{OH}} = 0.164$ mT arises from the protonated OH-group. The whole spectrum can be understood if a protonated radical cation forming an association complex with the solvent is assumed. A specific interaction must exist between the lone pairs of the chlorine atoms and the CF_3-moieties since no additional fluorine couplings are observed in the BQ$^{\cdot +}$ and DQ$^{\cdot +}$ cases. Figs. 5(*a*) and 5(*b*) show the experimental and the simulated EPR spectra, respectively. Similar EPR spectroscopic evidence for interactions between radical cations and fluorotrichloromethane has been reported by Symons *et al.*[30]

The 9,10-Anthraquinone Radical Cation.—The EPR spectrum also indicates a protonated form of the radical cation AQH$^{\cdot 2+}$. The line pattern can be simulated with two sets of four nearly equivalent protons with $a^{\mathrm{H}}(1,4,5,8) = 0.109$ mT and $a^{\mathrm{H}}(2,3,6,7) = 0.151$ mT. The assignment is made according to MNDO calculations. Also, an additional small coupling of $a^{\mathrm{OH}} = 0.053$ mT is attributed to the hydroxy proton. These splittings are quite different from the corresponding protonated semiquinone radical anion of anthraquinone (AQH$\cdot$) measured in dioxane which gave $a^{\mathrm{H}}(1,3,6,8) = 0.328$ mT, $a^{\mathrm{H}}(2,4,5,7) = 0.044$ mT and $a^{\mathrm{OH}} = 0.088$ mT.[31]

Kinetics of Electron Transfer between BQ$^{\cdot +}$ and TMPPD.—The rate constant of reaction (4) was investigated by flash photolysis. If a solution of BQ and TMPPD both 5×10^{-6} mol dm^{-3} in TFA–TFAn is flashed no radical cation of TMPPD$^{\cdot +}$ can be observed, which means that [TMPPD$^{\cdot +}$] is lower than 10^{-8} mol dm^{-3}, the lowest detectable concentration of our flash equipment. This implies, that the concentration of BQ$^{\cdot +}$ formed is also very low. The TMPPD$^{\cdot +}$ radical cation shows an intensive absorption at λ = 610 nm with an extinction coefficient of $\varepsilon(610)$ = 13000 dm^3 mol^{-1} cm^{-1}.[13] On the other hand, a more concentrated solution of 10^{-3} mol dm^{-3} BQ and 5×10^{-6} mol dm^{-3} TMPPD shows a rapid increase of TMPPD$^{\cdot +}$ at λ = 610 nm followed by a much slower decay after the flash. From the kinetic traces at λ = 610 nm a rate constant of 4×10^9 dm^3 mol^{-1} s^{-1} is found for reaction (4) at 295 K, which is in the normal region for organic electron transfer reactions.[32] After TMPPD$^{\cdot +}$ is formed it slowly decays in a first-order reaction with $k_{\mathrm{D}} = 3 \times 10^2$ s^{-1} by acid deamination.[33] Fig. (6) shows a typical kinetic trace at λ = 610 nm. The concentration of TMPPD$^{\cdot +}$ increases rapidly, followed by a much slower decay.

Quantum-chemical Calculations.—Several quantum chemical calculations on various levels have been performed on the *p*-benzoquinone radical cations investigated.

HMO-calculations corrected for radical cations. Honeybourne[34] pointed out that Hückel calculations normally used in the McLachlan version[35] should be corrected if applied to radical cations. In addition to the McLachlan procedure the atom–bond polarizability must be included to obtain the correct π-spin densities for radical cations. The π-spin density of an atom i is then given by eqn. (11) where π_{ik} is the atom–atom polarizability, $\lambda = 1.1$ (McLachlan factor), $\pi_{i,il}$ is the atom–bond polarizability between atoms i and l and c_{Ji} is the LCAO-coefficient of the atom i in the molecular orbital J. Calculations of this type are only applicable to π-systems and gave good results for radical cations.[36]

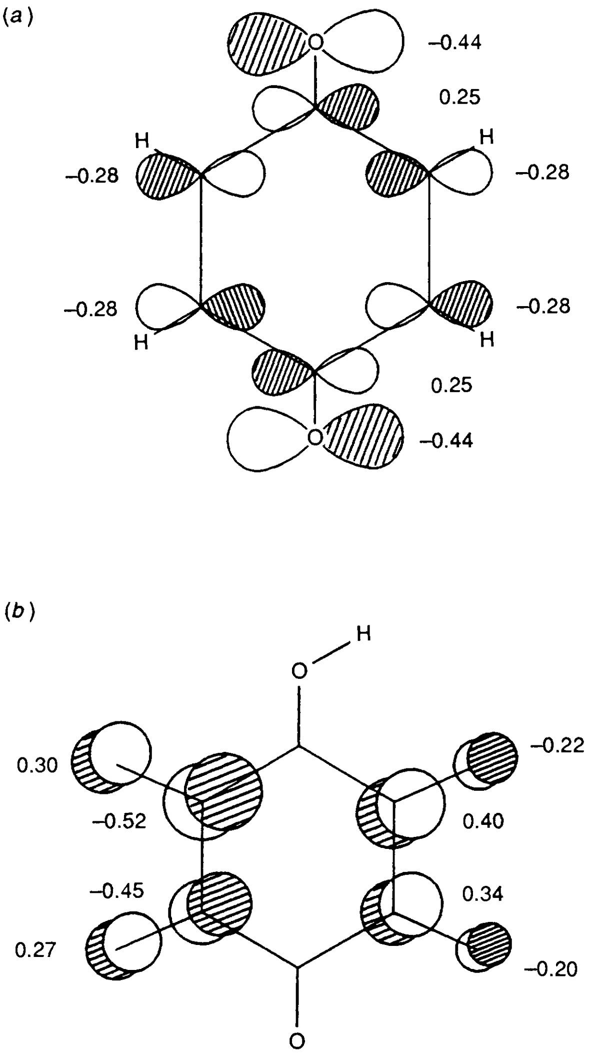


Fig. 7 SOMO representation derived from MNDO calculations for (*a*) $BQ^{\cdot+}$ ($\sigma_{b_{1g}}$-symmetry) and (*b*) $TFBQH^{\cdot 2+}$ (π_{a_2}-symmetry) together with the calculated AO coefficients

$$\rho_i = c_{Ji}^2 + \lambda \sum_{k=1}^{n} \pi_{ik}\, c_{Jk}^2 + \lambda \sum_{i,l} \pi_{i,il}\, c_{Ji}\, c_{Jl} \qquad (11)$$

Uncorrected McLachlan calculations are well established for neutral radicals and radical anions in the interpretation of the π-spin densities *via* the McConnell relation, eqn. (12).

$$a_i^{\mathrm{H}} = |Q_{\mathrm{CH}}|\rho_{\mathrm{C}i} \qquad (12)$$

A simple HMO calculation of $BQ^{\cdot-}$ with the perturbation parameters $a_{\mathrm{O}} = \alpha + 1.2\beta$ and $\beta_{\mathrm{CO}} = 1.56\beta$ gives π-spin densities $\rho_{\mathrm{C}}(\mathrm{HMO}) = 0.107$ and $\rho_{\mathrm{C}}(\mathrm{McL}) = 0.104$ in the McLachlan version for the carbon atoms in the 2,3,5,6-positions of the *p*-benzoquinone radical anion. This leads to the commonly accepted Q_{CH}-value of 0.22 ± 0.016 mT derived from a linear regression of a^{H} *vs.* $\rho_{\mathrm{C}i}$ including various *para*-quinone radical anions.[37]

The situation completely changes with regard to the corresponding radical cations. The singly occupied molecular orbital (SOMO) of $BQ^{\cdot+}$ would be the orbital with b_{3g}-symmetry ($J = 4$), instead of $J = 5$ (b_{2g}-symmetry) as in the corresponding radical anion. The HMO-spin densities would now be $\rho_{\mathrm{C}}(\mathrm{HMO}) = 0.25$. The semiempirical ASMO-CI calculations give the same spin densities as pointed out by Harada.[38] These π-spin densities lead to an unacceptably low value of Q_{CH} of 0.9 mT for $BQ^{\cdot+}$.

More sophisticated MNDO calculations[39] indicate that the SOMO of the $BQ^{\cdot+}$ radical cation is a σ-type orbital with $\sigma_{b_{1g}}$-symmetry. Fig. 7(*a*) gives an orbital representation of this SOMO. The calculated carbon spin densities are $\rho_{\mathrm{C}} = 0.078$ leading to a Q_{CH} value of 0.287 mT, a value in the accepted range for this polarization parameter.

Further MNDO calculations indicate that substituted *p*-benzoquinone radical cations are π-type radicals, for example see the SOMO of $TFBQH^{2\cdot+}$, shown in Fig. 7(*b*). Fig. 8 shows an energy-level diagram of the singly occupied (SOMO) and

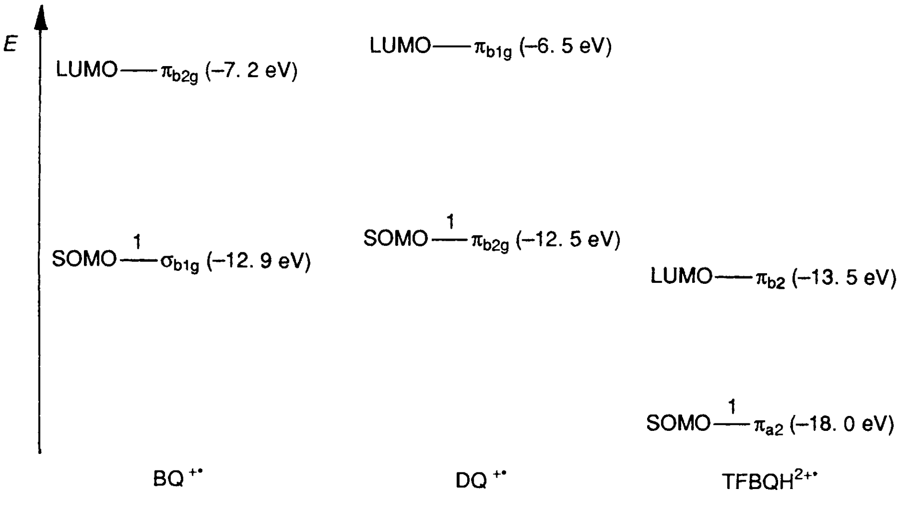


Fig. 8 LUMO and SOMO energies derived from MNDO calculations for $BQ^{\cdot+}$, $DQ^{\cdot+}$ and $TFBQH^{2\cdot+}$, showing a σ–π level crossover

the lowest occupied molecular orbitals (LUMO) in $BQ^{\bullet +}$, $DQ^{\bullet +}$ and $TFBQH^{\bullet 2+}$ summarizing the σ–π-orbital crossover scheme. A contrasting energy-level crossover of π–σ type is reported for fluorinated pyridine radical anions in an adamantane matrix.[40]

Ab-initio calculations of $BQ^{\bullet +}$ also indicates that this radical is σ-type radical.[41]

Conclusions

The EPR-coupling constants and *g*-values of several *p*-benzoquinone radical cations reported differ from the corresponding values of the radical anions. MNDO calculations show that the SOMO of $BQ^{\bullet +}$ is a σ-type orbital in contrast with substituted *p*-benzoquinone radical cations. The radical cations of tetrafluoro-*p*-benzoquinone and anthraquinone are protonated under the investigated conditions. The electron transfer rate of $BQ^{\bullet +}$ to TMPPD is found to be 4×10^9 dm^3 mol^{-1} s^{-1} and clearly confirms the existence of $BQ^{\bullet +}$. No electron self-exchange reaction takes place within the $BQ^{\bullet +}$/BQ-couple in the solvent mixture used.

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