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Photoelectrochemistry using Quinone Radical Anions

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The photoelectrochemistry of quinone radical anions has been demonstrated qualitatively by the photoassisted reduction of methyl viologen with benzoquinone and of neutral red with chloranil. Data were then collected for the estimation of quenching rate constants using Marcus–Weller theory. Reduction potentials of seven quinones were obtained in four solvents (and two aqueous mixtures) by cyclic voltammetry. The solvent effects on these potentials were studied by fitting them to the Taft relationship. The effects of proton donors were also noted. Absorption spectra of the radical anions were measured and the solvent effects noted and commented upon. From the molar absorption coefficients of the radical anions, the mean lifetimes of the excited states were estimated. Fluorescence spectra were obtained for anthraquinone and naphthaquinone radical anions and excitation energies were calculated. These values were estimated for the other quinones. Values of redox potentials for the excited radical anions were thence obtained. The Gibbs energies of the electron transfers between the excited quinone radical anions and the various substrates were obtained and hence the Gibbs energies of activation were calculated using the Marcus equation. The quenching rate constants were calculated using the Rehm–Weller equation and plotted *vs.* ΔG giving a characteristic Marcus plot including some data in the inverted region. The significance of the inverted region is discussed.

An area of considerable interest has been the study of reactions involving single-electron transfers by homogeneous catalysis.[1] These are of course redox reactions and the catalysts are redox reagents, which may be inorganic metals or metal complexes, inorganic non-metallic reagents or organic reagents.[2–4] This area is of special interest to electrochemists as redox reagents may be generated at electrodes, detected at electrodes or the whole process may be studied by electrochemical techniques. In recent years Saveant *et al.*[5] have been pre-eminent in laying the foundations for such studies.

Another complementary technique for generating redox intermediates and for studying their reactions is photochemistry, especially fluorescence quenching techniques using the Stern–Volmer method.[6] A particularly powerful theoretical approach to single electron transfer reactions has been Marcus theory[7] and its Rehm–Weller application.[8] These methods have been applied by a number of workers to both electrochemical and photochemical situations.[2,9,10]

It is especially interesting to combine these two processes in photoelectrochemistry.[11] This may involve shining a light on an electrode surface, or photolysing an electrogenerated intermediate. The combination of photochemistry and electrochemistry can generate even more powerful redox reagents.[9]

If we consider the use of organic redox catalysts we are usually concerned with ions or, more often, radical ions.[12] These have been studied by a number of workers. Cations, radical cations, anions and radical anions have been used electrochemically, photochemically and photoelectrochemically.[9] Photoexcited cation radicals have been exploited by Moutet and co-workers[13] in synthetic work and in mechanistic studies by Eriksen *et al.*[9] Anions and anion radicals have been studied by more people.[9,10,14–16] Radical ions can be generated conveniently by electrolysis of the parent molecule in an aprotic solvent (or in an alkaline medium). Cyclic voltammetry is an ideal way of studying the redox behaviour of the parent molecules and measuring the standard redox potential of the radical ion. If solutions of radical ions generated in this way are then photolysed *in situ* their photoelectrochemical behaviour may be studied.

A general scheme showing donor (D) and acceptor (A) photo-electron transfers *via* radical ions is as follows:

$$D + e^- \rightarrow D^{\bullet -}$$

$$D^{\bullet -} + h\nu \rightarrow (D^{\bullet -}*)$$

$$(D^{\bullet -}*) + A \rightarrow D + A^{\bullet -}$$

or

$$A - e^- \rightarrow A^{\bullet +}$$

$$A^{\bullet +} + h\nu \rightarrow (A^{\bullet +}*)$$

$$(A^{\bullet +}*) + D \rightarrow A + D^{\bullet +}$$

Energy level diagrams and Jablonski diagrams are fairly well known for the photoexcitation of neutral molecules, but they are less so for anion radicals. Fig. 1 shows the various ground and excited states for radical anions. D_0 is the ground state, D_1, D_2 and D_3 are the three doublet states and Q_1 is the quartet state for the excited radical anions. This is considerably more complex than the singlet or triplet states found for neutral molecules. Fig. 2 shows the Jablonski diagram for the electron transfers between different energy levels. Of particular significance in this work is the $D_2 \rightarrow D_0$ fluorescence.

Very few studies have been made in this way using quinones. Eriksen, Lund and co-workers[9,17,18] have used electrochemically generated anthraquinone, anthracene and

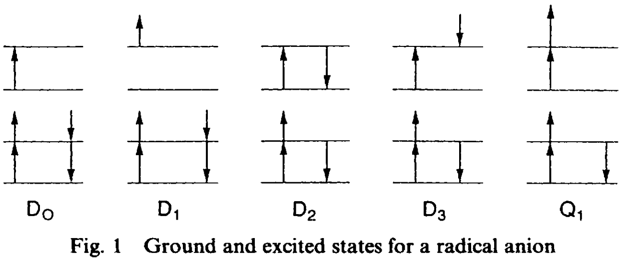


Fig. 1 Ground and excited states for a radical anion

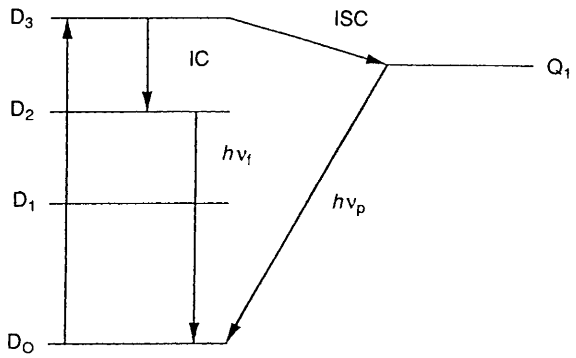


Fig. 2 Jablonski diagram for a radical anion

dicyanoanthracene radical anions, as well as thianthrene radical cations with fluorescence quenching with a range of up to twelve different quenching substrates. Eriksen[9,17] attempted to fit his quenching rate constants, and energetic data to a Marcus/Rehm–Weller curve. His curve had a similar shape, but it was shifted by 84–125 kJmol^{-1}. He suggested that the solvent reorganisation energy due to electron removal from, or addition to, involved molecules may make a much larger contribution to $\Delta G_0^{\ddagger}$ (the intrinsic Gibbs energy of activation when $\Delta G = 0$ [9,14]) than expected. Thus the value of $\Delta G_0^{\ddagger}$ may be up to 42 kJ mol^{-1} rather than the accepted[8] value of 10 kJ mol^{-1}.

Demonstration of the single-electron nature of reductions of this type was shown by the reduction of 1,2-dibromobenzene with photoexcited anthraquinone radical anions to give one-electron coupled products[18] but no benzyne derived products, as obtained with two-electron reductions.[19]

Quinones easily form radical anions and dianions which are stable in oxygen-free aprotic solvents and protic solvents at high pH. A wide range of quinones is known whose electrochemistry has been well studied.[20] Less well known is the behaviour of photoexcited quinone radical anions which should be powerful single-electron-transfer reducing agents. We have referred to the work of Eriksen *et al.*[9] using anthraquinone. Cauquis and co-workers[21] have also examined a few particularly stable quinone radical anions by cyclic voltammetry, coulometry and absorption spectroscopy. Willson[22] has studied a wide range of quinones by pulse radiolysis of their aqueous solutions.

In the first part of our study[23] cyclic voltammograms of quinones were recorded in the presence of various substrates: carbonyl compounds, halobenzenes, methyl viologen and neutral red. When the electrode was illuminated with visible light ($\lambda > 410$ nm) catalytic waves were observed. From these waves electron-transfer rate constants were obtained.

The third part of our study will describe the organic chemistry of these reactions, including the identification of products, yields and mechanisms.[24]

The present paper concerns: (1) The qualitative demonstration of the single-electron transfer effect with redox indicators. (2) The collection and presentation of voltammetric and spectroscopic data. (3) The application of selected data, using Marcus–Weller theory,[7,8] to the calculation of excitation energies, Gibbs energy changes and quenching rate constants for the electron transfer between six different quinones and a range of quenching substrates and (4) presentation of these data in the form of a Marcus–Weller plot.

In order to test the effectiveness of the quinones we submitted them to cyclic voltammetry, mainly to determine (or confirm) their electrode potentials for use in calculating the excitation energy ($E_{0,0}$, see eqn. 3, later). At the same time we noted the effect of solvents and proton donors. We then made a similar study of the absorption spectra of both the parent quinones and the radical anions.

We measured the fluorescence spectra of quinone radical anions. With the instrument available to us only anthraquinone and naphthaquinone showed overt fluorescence. An alternative approach was used for other quinones to estimate the fluorescence crossover wavelength.

Experimental

Materials

Anthraquinone (BDH) was recrystallised from acetonitrile, mp 289.4 °C; naphthaquinone (BDH) was recrystallised from ethanol, mp 120.2 °C. 2,6-Di-*tert*-butylbenzoquinone (Aldrich) was used as supplied; tetramethylbenzoquinone (duroquinone) (Aldrich) was recrystallised from ethanol, mp 112.5 °C; benzoquinone (Aldrich) was recrystallised from water and then twice from ethanol, mp 112.3 °C; tetrachlorobenzoquinone (chloranil) (BDH) was recrystallised twice from acetone, mp 287.5 °C; tetrafluorobenzoquinone (fluoranil) (BDH) was recrystallised from acetone, mp 187.8 °C.

Methyl viologen dichloride (Aldrich) was used as supplied. Ethyl viologen dibromide was prepared by quaternisation of 4,4′-bipyridyl with ethyl bromide by refluxing them together in DMF for 180 min. The resulting precipitate was filtered and recrystallised once from acetonitrile and twice from ethanol, yielding yellow crystals, which turned blue on addition of triethanolamine. Both viologens were converted to the ditetrafluoroborate form by the addition of a saturated solution of sodium tetrafluoroborate (BDH) to a solution of the viologen. In this form they were readily soluble in the aprotic solvents used.[26] Neutral red (BDH) was used as received.

Acetonitrile (AN) (BDH Spectrosol) was dried over molecular sieve (BDH Linde 4A) and then fractionally distilled over P_2O_5. Dimethylformamide (DMF) and dimethylacetamide (DMA) (Aldrich Spectrosol) were both dried over anhydrous copper sulfate and then distilled at reduced pressure (12 mmHg). Methanol (BDH HPLC grade) was dried over molecular sieve (BDH Linde 4A) and then fractionally distilled three times.

Tetramethylammonium perchlorate (TEAP) (Fluka) was recrystallised from water, mp 348 °C; tetramethylammonium tetrafluoroborate (TMABF) was prepared from tetrafluoroboric acid (Fluka 50%) and tetramethylammonium hydroxide (BDH 25%). The product was recrystallised from water, mp 130 °C. Tetrabutylammonium tetrafluoroborate (TBABF) was similarly prepared from tetrafluorboric acid and tetrabutylammonium hydroxide solution (BDH). The product was recrystallised from water and twice from 2 : 1 *n*-pentane–ethyl acetate, mp 170 °C. Tetramethylammonium chloride (Aldrich) and bromide (BDH) were used as supplied.

Oxygen-free nitrogen was purified through a vanadium(II) solution then through water and finally through solvent over molecular sieve (BDH Linde 4A).

Electrochemistry

Cyclic voltammetry was carried out with a Bioanalytical Systems CV1A cyclic voltammeter and recorded on a Gould OS 4200 digital storage oscilloscope, and a Phillips PM 8271 X–Y recorder. Controlled potential electrolysis was carried out with an EG&G PAR 173 potentiostat or a Chemical Electronics 703A potentiostat in a two- or three-compartment cell with compartments separated by a fine porosity frit.

Cyclic voltammetry was performed with a platinum inlaid disc (Corning) of area 0.208 cm^{-2} or a Metrohm hanging mercury drop working electrode (HMDE) with an Orion saturated calomel reference electrode and a platinum coil counter electrode. For controlled potential electrolysis a platinum gauze working electrode was used.

Spectra

Absorption spectra were measured on a Perkin-Elmer Lambda 5 UV–visible spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer PE 204 fluorescence spectrometer.

Experimental Method

In a typical experiment benzoquinone (10^{-3} mol dm^{-3}) and methyl viologen ditetrafluoroborate (2×10^{-3} mol dm^{-3}) in acetonitrile containing TEAP (0.1 mol dm^{-3}) was purged with oxygen-free nitrogen (or argon), electrolysed at -0.35 V *vs.* SCE for 20 min and then irradiated with a medium-pressure mercury arc lamp (Applied Photophysics, 250 W, $\lambda = 250$–580 nm) with a sodium nitrite filter to cut out light below 410 nm. Similarly chloranil (2×10^{-3} mol dm^{-3}) in acetonitrile containing tetramethylammonium tetrafluoroborate (0.1 mol dm^{-3}) was reduced at -0.15 V in the presence of neutral red for 40 min and then illuminated with a medium-pressure arc lamp as before.

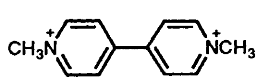
Results and Discussion

Photoelectrochemical Reduction of Viologens and Neutral Red

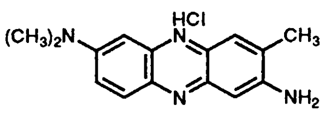
When redox indicators such as methyl viologen (MV^{2+}) (**I**) are reduced they show a marked colour change and characteristic absorption spectra[27,28] such as that shown in Fig. 3.

$$MV^{2+} + e^- \rightarrow MV^{\bullet +} \quad (E^0 = 0.69 \text{ V } vs. \text{ SCE})^{29}$$

Neutral red (**II**) behaves in a similar manner.



I



II

After irradiating the benzoquinone–methyl viologen system for 1 h, the blue colour of the methyl viologen radical cation ($MV^{\bullet +}$) appeared. After 2.5 h the absorption spectrum was measured showing characteristic bands at 395 and 605 nm (Fig. 3). In AN, DMF, AN with 10% water and DMF with 50% water the blue colour of $MV^{\bullet +}$ was observed after electrolysis and photolysis. No formation of $MV^{\bullet +}$ was observed by electrolysis of the quinone at a potential just sufficient to generate the radical anion without photolysis, or with photolysis of MV^{2+} alone, in the absence of the quinone radical anion.

When chloranil and fluoranil were used with the viologens, there was no evidence of the blue $MV^{\bullet +}$ after 2 h. However, after 3 h a purple colour appeared which showed a strong band at 540 nm quite unlike the spectrum of $MV^{\bullet +}$. The band could have arisen from a dimer compound between two $MV^{\bullet +}$ ions, as suggested by Ponjee and van Dam[26] who observed similar bands in the spectrum of reduced ethyl viologen. This could be observed because of the slower rate of electron transfer from the chloranil and fluoroanil radical anions than from benzoquinone.

After irradiating reduced chloranil with neutral red for 1 h the red colour was replaced by a yellow colour. The spectrum showed that the neutral red band at 550 nm had disappeared. It was not possible to observe the 445 nm band for reduced neutral red as it was overlapped by the quinone radical anion band in this region. The green colour of the reduced neutral red was masked by the stronger yellow of the quinone radical anion.

Quinone radical anions with more negative reduction potentials were not appropriate for these reductions as the potential required to reduce the quinone would also reduce the indicators directly. Similarly a solution of quinone radical anions with a more negative reduction potential would reduce the redox indicators directly without photolysis.

Voltammetry

All quinones studied showed typical reversible two-wave voltammograms (Fig. 4), corresponding to two successive one-electron transfers to the radical anion than to the dianion;

$$Q + e^- \rightarrow Q^{\bullet -}$$

$$Q^{\bullet -} + e^- \rightarrow Q^{2-}$$

Traces of water or oxygen made the second (dianion) peak irreversible. It was particularly difficult to obtain two reversible peaks for duroquinone. With methanol and with aqueous–non-aqueous mixtures such as AN with 10% water and DMF with 50% water, it was necessary to add base (tetramethylammonium hydroxide) to give an apparent pH of

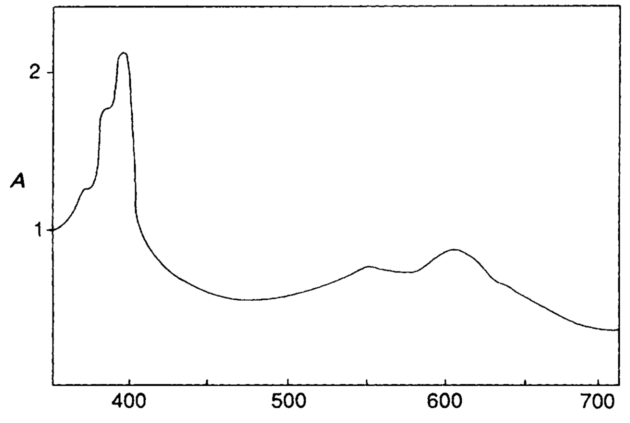


Fig. 3 Absorption spectrum of methyl viologen radical cation

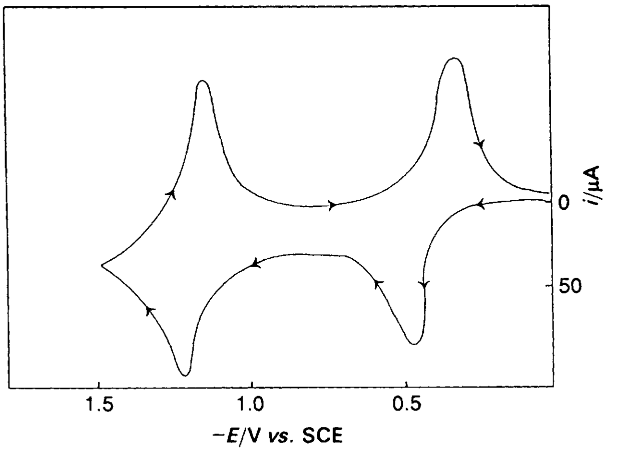


Fig. 4 Cyclic voltammogram of 10^{-3} mol dm^{-3} 1,4-benzoquinone in acetonitrile containing 0.1 M TEAP at 50 mV s^{-1}

Table 1 Cathodic peak potentials of quinones from cyclic voltammetry in acetonitrile containing 0.1 mol dm^{-3} tetramethylammonium tetrafluoroborate on platinum *vs.* SCE

quinone	$E_p(1)$/V	$E_p(2)$/V
1,4-benzoquinone	−0.49	−1.15
duroquinone	−0.85	−1.50
2,6-di-*tert*-butylbenzoquinone	−0.65	−1.30
naphthaquinone	−0.68	−1.23
anthraquinone	−0.90	−1.55
chloranil	+0.05	−1.15
fluoranil	−0.05	−0.75

10 (as indicated on a glass pH electrode) to ensure that all the peaks were obtained.

Results of the voltammetry are shown in Table 1. Reduction peak potentials (E_p) were obtained. It is more relevant to this work to record peak potentials than half-wave potentials as we will be subtracting them from the peak potentials for the reduction of substrates in eqn. (4). The data compared favourably with available literature values,[20a] considering that none of the literature values were obtained using our supporting electrolyte (tetramethylammonium tetrafluoroborate). Also the given literature values are expressed as $E_{1/2}$, which is, for a reversible wave, 28 mV less than E_p. The most negative potential (−0.90 V *vs.* SCE) was for anthraquinone and the most positive (+0.05 V *vs.* SCE) was for chloranil.

On changing from AN to DMF or DMA a negative shift of around 15 mV was observed for both waves possibly due to the donor–acceptor relationship between the quinone radical anion and the solvent,[30] though it is not possible to eliminate the effects of changes in the liquid junction potentials. A linear relationship has been found between the reduction potential of the quinone and the 'acceptor numbers' of the solvent.[30] A negative shift was found with a decreased acceptor number *i.e.* with decreased Lewis acidity. On changing from aprotic solvents to aqueous mixtures (90% AN–water and 50% DMF–water) and to methanol, there was a positive shift for all the waves, with the largest shift for the dianion wave (the most basic form),[31] due to the proton donor effect of the water.

Analysis of the effects of solvents on physical measurements such as redox potentials and UV–visible absorption spectra are dependent on a number of interacting factors such as solvent polarity and relative permittivity, ion–molecule polarisability, proton–electron and donor–acceptor relationships between solvent and solute.[32] Many single-parameter solvent effect indicators have been proposed and used over the years but one of the better approaches is Taft's[33] multi-parameter correlation which has recently been successfully applied by Fernandez and Zon[34] to the one-electron electrochemical oxidation of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) to the corresponding radical cation $TMPD^{\cdot +}$ on platinum electrodes in ten different protic and aprotic solvents.

We have shown that this approach is applicable to the correlation of the electrode potentials of our seven quinones in four solvents using π^*, an index of polarisability; β, a basicity scale and α, an acidity scale. The correlation coefficient was similar to that obtained by Fernandez and Zon.[34] Details will be reported elsewhere.[35]

The effect of proton donors was in accord with previously reported results.[20c,31,36] However, whereas our previous studies[20c] used fairly strong proton donors such as benzoic acid and perchloric acid, we now report the effects of isopropanol, water and phenol on the voltammetry of three quinones in AN. Isopropanol caused a positive shift of wave 2 by *ca.* 100 mV. Water caused a shift of *ca.* 350 mV in wave 2 but little change in peak currents. These effects are caused by the progressive protonation of the dianion.

$$Q^{2-} + H^+ = QH^-$$

Phenol caused wave 2 to disappear altogether and caused the height of wave 1 to double. This is due to the protonation of the quinone radical anion.

$$Q^{\cdot -} + H^+ = QH^{\cdot}$$

For example with naphthaquinone, $E_p(1)$ remains steady at −0.68 V, while $E_p(2)$ shifts from −1.32 to −1.11 V (with propan-2-ol) to −0.89 V (with water). Peak current functions (i_p/A C v$^{1/2}$) changed from 0.32 to 0.32 (propan-2-ol) to 0.33 (water) to 0.65 (phenol) for wave (1), and from 0.21 to 0.21 (propan-2-ol) to 0.16 (water) to 0.00 (phenol) for wave (2).

Absorption and Fluorescence Spectra of Quinone Radical Anions and Excitation Energies

Absorption spectra of the quinone radical anions were obtained following constant potential electrolysis of the parent quinones under nitrogen or argon in AN, DMF and methanol. The colours of the solutions were deep orange–brown or pinkish red, in contrast to the pale yellow colour of

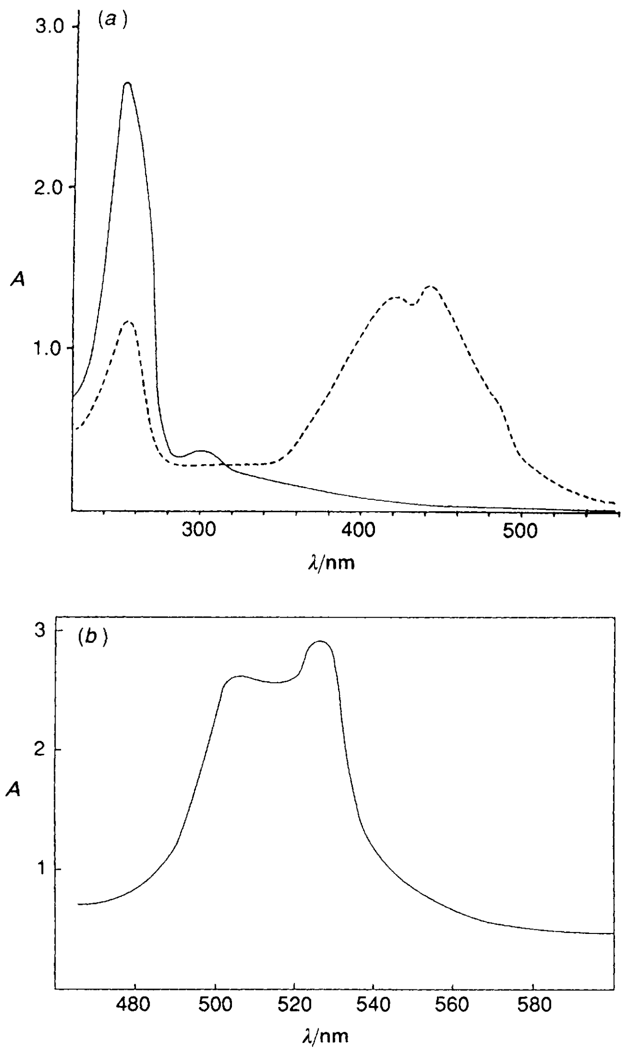


Fig. 5 (*a*) Absorption spectra of 5 × 10^{-4} mol dm^{-3} benzoquinone (——) and benzoquinone radical anions (- - - -) in acetonitrile. (*b*) Absorption spectrum of 5 × 10^{-4} mol dm^{-3} anthraquinone radical anions in acetonitrile.

Table 2 Spectral data for quinone radical anions and calculated excitation energies

	$\lambda_{max}(Q^{\bullet-})$/nm	log ε	τ/ns	$\lambda_{max}(Q^{\bullet-*})$/nm	E_{00}/V	$E^{0\prime}$ $(Q/Q^{\bullet-*})$/V
BQ	415	3.60	22.2		2.71	3.19
	445	3.65				
DQ	420	3.48	27.0			
	450	3.57				
ClQ	420	3.54	24.3		2.66	2.61
	450	3.61				
FQ	415	3.62	20.8		2.74	2.79
	440	3.61				
DBQ	430	3.63	20.4		2.58	3.23
	465	3.69				
NQ	480	3.67	18.8	545	2.32	3.00
	525	3.72		560		
AQ	510	3.70	17.2	520	2.23	3.13
	530	3.76		540		

[a] BQ = benzoquinone, DQ = duroquinone, ClQ = chloranil, FQ = Auoranil, DBQ = 2,6-di-*tert*-butylbenzoquinone, NQ = napthaquinone, AQ = anthraquinone.

the parent quinones. A distinctive visible spectrum with two bands separated by 20–30 nm was observed as shown in Fig. 5(*a*) and (*b*). On changing the solvent from AN to DMF no large change in the quinone radical anion bands was observed. Data are shown in Table. 2.

The transitions are of a π–π* nature and probably involve doublet–doublet transitions.[37,38] Transition to the quartet state is unlikely as it is above the lowest doublet state, so population *via* intersystem crossing would be unlikely.[39] The red shift compared with the spectrum of the parent molecule can be explained by the fact that the HOMO of the radical corresponds to the LUMO of the quinone. Thus there is a much smaller difference in energy between the HOMO and the LUMO for the radical.[39] The double-peaked bands are due to the C—O stretching vibration in the excited state.[40]

In methanol there is a blue shift of *ca.* 20 nm, which could be due to hydrogen bonding to the quinone carbonyl oxygen atom.[37,38]

From the molar absorption coefficients (ε) the mean lifetime of the excited state (τ) could be estimated using eqn. (1):[6]

$$\tau = 10^{-4}/\varepsilon \qquad (1)$$

The lifetimes were of the order of 10 ns (Table 2) in good agreement with the value of 13.7 ns for the fluorescence lifetime of the anthraquinone radical anion obtained by single-photon counting.[9]

Fluorescence spectra were obtained for anthraquinone and naphthaquinone as shown in Fig. 6 and 7. From the wavelength at which the fluorescence and absorption spectra crossed (see Fig. 6 and 7), the values of the excitation energies, E_{00}, can be obtained using eqn. (2),[9,25]

$$E_{00} = \frac{hcN_A}{\lambda_x F}/\text{eV} \qquad (2)$$

where h = Planck's constant, c = velocity of light, N_A = Avogadro's number, F = Faraday's constant and λ_x = wavelength at which fluorescence and absorption spectra cross.

Hence the redox potential of the photoexcited quinone radical anion could be estimated using eqn. (3),[3]

$$E^0(Q/Q^{\bullet-*}) = E^0(Q/Q^{\bullet-}) + E_{00}$$
$$E^{\bullet 0}(Q/Q^{\bullet-*}) = E_p(Q/Q^{\bullet-}) + E_{00} \qquad (3)$$

The radical anions without detectable fluorescence were probably quenched by a non-radiative process since phosphorescence was most unlikely. This could have involved a radiationless internal conversion from the excited state to a higher vibrationally excited ground state.[10] In order to calculate the excitation energies for these ions one can estimate the likely position at which the fluorescence spectra would have crossed the absorption spectra if they existed.[25] This value would have an error of ± 4 nm (± 50 mV). This technique has been used before in calculations of non-fluorescent molecules.[25]

Calculated and estimated values of E_{00} and $E^{0\prime}$ $(Q/Q^{\bullet-*})$ are shown in Table 2.

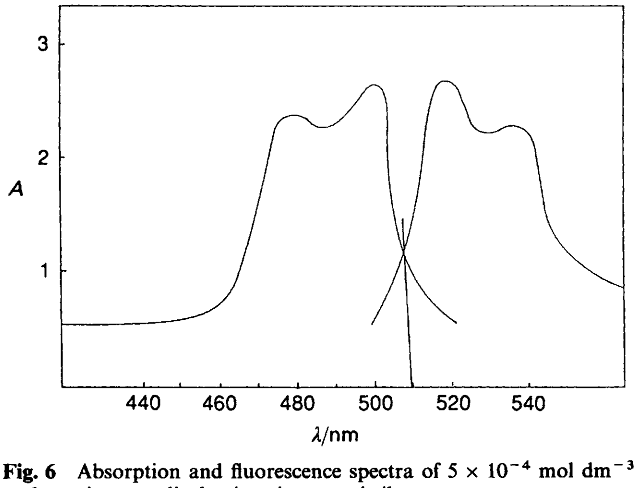


Fig. 6 Absorption and fluorescence spectra of 5×10^{-4} mol dm^{-3} anthraquinone radical anions in acetonitrile

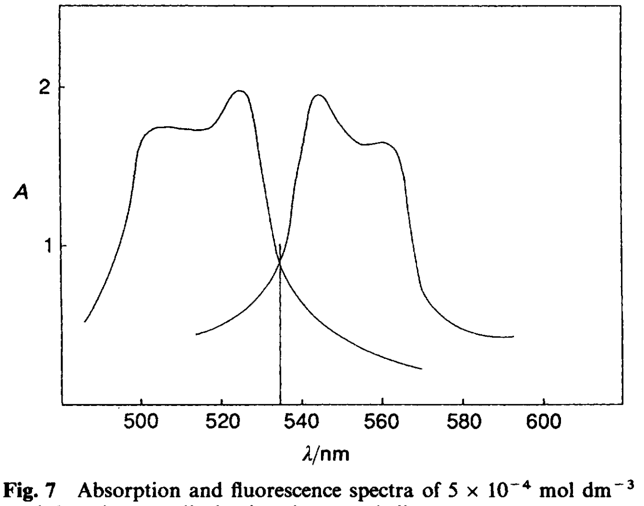


Fig. 7 Absorption and fluorescence spectra of 5×10^{-4} mol dm^{-3} naphthaquinone radical anions in acetonitrile

Application of Marcus Theory

From these data and the reduction potentials of the various substrates (5), Gibbs energies for the quenching of the excited quinone anion radicals can be calculated for use in deriving Marcus theory data. Using the excitation energies, the Gibbs energy of the electron transfer reaction can be calculated using eqn. (4).[9,17]

$$\Delta G(\text{kJ mol}^{-1}) = 96.49(E^0_{S/S^-} - E^0_{Q/Q^-} - E_{00})$$
$$\Delta G = F(E^{0\prime}_{S/S^-} - E^{0\prime}_{Q/Q^{\cdot-}}) \quad (4)$$

The basic mechanism for the process can be written as:

$$Q + e^- \rightleftharpoons Q^{\cdot -}$$
$$Q^{\cdot -} + h\nu \rightarrow Q^{\cdot -}*$$
$$Q^{\cdot -}* \rightarrow Q + h\nu$$
$$Q^{\cdot -}* + S \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [Q \ldots S]^{\cdot -} \rightarrow Q^{\cdot -} + S^{\cdot -}$$

The last step is the quenching step, for which the overall Gibb's Energy is ΔG, from eqn. (4). ΔG^{+}, the Gibbs energy of activation can be calculated from Marcus theory[7] which is based on an outer-sphere adiabatic electron-transfer theory equation, eqn. (5).

$$\Delta G^{*} = \Delta G^{\ddagger}_{(0)}[1 + \Delta G/4\Delta G^{\ddagger}_{(0)}]^2 \quad (5)$$

where $\Delta G^{\ddagger}_{(0)}$ is the zero point (intrinsic) free energy of activation when $\Delta G = 0$.

Rehm and Weller[8] derived an empirical expression for ΔG^{+}:

$$\Delta G^{+} = [(\Delta G/2)^2 + (\Delta G_{(0)})^{2+}]^{1/2} + \Delta G/2 \quad (6)$$

They also derived an empirical equation for the quenching electron transfer rate constant, k_q:

$$k_q = \frac{k_d}{1 + 0.25[\exp(\Delta G^{+}/RT) + \exp(\Delta G/RT)]} \quad (7)$$

k_d is the diffusion limited rate constant, usually taken as 2×10^{10} dm^3 mol^{-1} s^{-1} (for DMF). It is dependent on solvent viscosity according to the approximate equation:[41]

$$k_d = \frac{8RT}{3\eta}$$

which is approximately independent of the reacting species.[42]

The value originally suggested by Rehm and Weller[8] for $\Delta G^{\ddagger}_{(0)}$ was 10.04 kJ mol^{-1}.[8] Using this value in the Marcus equation,[7] eqn. (5) or the Weller equation,[8] eqn. (6) together with eqn. (7) good agreement has been obtained with experimental data for neutral molecules.[8,30] However, for radical anions[9,17] and cations neither the Marcus curve nor the Weller curve fitted the data with this value of $\Delta G^{\ddagger}_{(0)}$.[9,17] However, by varying the values of $\Delta G^{\ddagger}_{(0)}$, Eriksen and co-workers[9,17] obtained good fits for their data for fluorescence quenching of excited radical anions and cations.

For the Marcus equation, the quenching data for $AQ^{\cdot -}$ fitted with $\Delta G^{\ddagger}_{(0)} = 41.8$ kJ mol^{-1} and for thianthrene radical cation the data fitted with $\Delta G^{\ddagger}_{(0)} = 64$ kJ mol^{-1}. But the

Table 3 Gibbs energy changes and calculated quenching rate constants for excited quinone radical anions

Substrate	G/kJ mol^{-1}	E_{red}/V[a]	k_q/10^9 dm^3 mol^{-1} s^{-1}
(*a*) with 2,6-di-*tert*-butylbenzoquinone			
1 acetophenone	118.3	−2.02	9.81
2 benzophenone	132.8	−1.85	13.27
3 benzaldehyde	137.6	−1.80	14.07
4 acetone	79.9	−2.40	0.81
5 acetaldehyde	65.4	−2.55	0.16
6 cinnamaldehyde	140.5		14.46
(*b*) with benzoquinone			
7 methyl viologen	240.2	−0.70	2.84 (20.0)[b]
(*c*) with chloranil			
8 methyl viologen	184.0	−0.70	15.44 (20.0)[b]
10 neutral red	216.6	−0.36	9.65 (20.0)[b]
(*d*) with fluoranil			
9 methyl viologen	201.2	−0.70	13.35 (20.0)[b]
11 neutral red	233.9	−0.36	4.39 (20.0)[b]
(*e*) with anthraquinone			
12 1,2-dibromobenzene	118.3	−1.88	10.26
13 1,4-dibromobenzene	93.3	−2.16	2.62
14 4-chlorobenzonitrile	110.7	−1.98	7.46
15 acetophenone	108.7	−2.02	6.84
16 benzophenone	123.1	−1.85	11.14
17 benzaldehyde	128.0	−1.80	12.31
18 acetone	70.3	−2.40	0.29
19 acetaldehyde	55.8	−2.55	0.049
20 cinnamonitrile	130.9		12.91
21 methylcinnamonitrile	123.2		11.15
(*f*) with naphthaquinone			
22 1,2-dibromobenzene	105.8	−1.88	5.95
23 acetophenone	95.26	−2.02	3.09
24 benzaldehyde	115.5	−1.80	8.95
25 acetone	57.7	−2.40	0.063
26 acetaldehyde	43.3	−2.55	0.0085
27 cinnamonitrile	118.4		9.83
28 methylcinnamonitrile	110.6		7.45

[a] E_p for reduction of substrate in AN containing 0.1 mol dm^{-3} tetramethylammonium tetrafluorborate on platinum *vs.* SCE. [b] Rehm–Weller value.

Weller curve required different values for a good fit, *viz.* 31.8 kJ mol^{-1} for $AQ^{\bullet -}$ and 40.1 kJ mol^{-1} for thianthrene. Since then various workers have used several different values to fit their data to Marcus or Weller curves. Soumillion *et al.*[14] used a mean value of 23.5 kJ mol^{-1} for naphthoate ions. They also obtained a better fit of Rehm and Weller's original data[8] for 60 compounds using 22.9 kJ mol^{-1} (and with $k_d = 1.6 \times 10^{10}$ dm^3 mol^{-1} s^{-1} in AN). Kemp *et al.*[43] studied nucleic acid bases in AN and used values of 6.7, 16.5 and 19.1 kJ mol^{-1}.

The most relevant literature value for our work with quinone radical anions is clearly the value used by Eriksen *et al.* for $AQ^{\bullet -}$ [17] of $\Delta G^{\ddagger}_{(0)} = 41.8$ kJ mol^{-1}. We therefore used this value to calculate $\Delta G^{\ddagger}$ from the eqn. (5) and hence rate constants, k_q using eqn. (7).

Marcus–Rehm–Weller

The rate constants and ΔG values are given in Table 3 and are plotted in Fig. 8. The values of k_q calculated for methyl viologen and neutral red reductions fall in the Marcus inverted region. This is a region at very negative ΔG values where rate constants decrease with more negative ΔG according to Marcus theory [eqn. (5)]. With the Rehm–Weller equation, eqn. (6), there is no such decrease. There is much controversy about the existence of the inverted region.[14] It has been confirmed in several cases such as when donor and acceptor are held at fixed distances[44] or in electron back-transfer.[45] However, with freely diffusing species it still needs confirmation.[42]

The electron transfer mechanism in a quenching reaction may be considered in three ways:[14] (1) Charge separation from neutral starting materials, (2) charge shift between an ion and a neutral molecule and (3) charge recombination. The second is the relevant case in this work. The products of the electron transfer are free of electrostatic attraction and may diffuse more freely. A photoinduced electron transfer leading to high-energy ions will give a photoreaction leading to isolable products. This may be very restricted by reverse electron transfer. However, with excited anions the forward electron transfer may be very efficient as the charged species is a better electron donor than the neutral molecule. Kakitani and Mataga[46] suggested that in this case of a charge shift, the Marcus inverted region may exist. Hence we may be justified in plotting Fig. 8 with the inverted region. Only the MV^{2+} and NR reactions with benzoquinone and halogenated quinone radical anions fall in this region. Soumillion and co-workers'[14] recent work with naphthoate ions did not however show an inversion effect at the most negative Gibbs energies which extend to -180 kJ mol^{-1}. All our results which fit into the inverted region, however, had ΔGs from -184 to -242 kJ mol^{-1}.

Observed quenching rate constants have been shown to decrease with the accepting power of the quencher (reduction potential).[14] Our calculated values follow this trend. These values reach a diffusion limit at around -2 V. Our value of k_q for benzophenone with anthraquinone excited radical anions of 11.14×10^9 dm^3 mol^{-1} s^{-1} compares favourably with Eriksen's experimental value of 12.0×10^9 dm^3 mol^{-1} s^{-1}.[17]

Conclusions

Reactions of photoexcited benzoquinone radical anions with methyl viologen and of chloranil radical anions with neutral red demonstrated the photoelectrochemical effect of quinone radical anions visually.

Voltammetric and spectroscopic data were combined, using the Marcus and Rehm–Weller equations, to give excita-

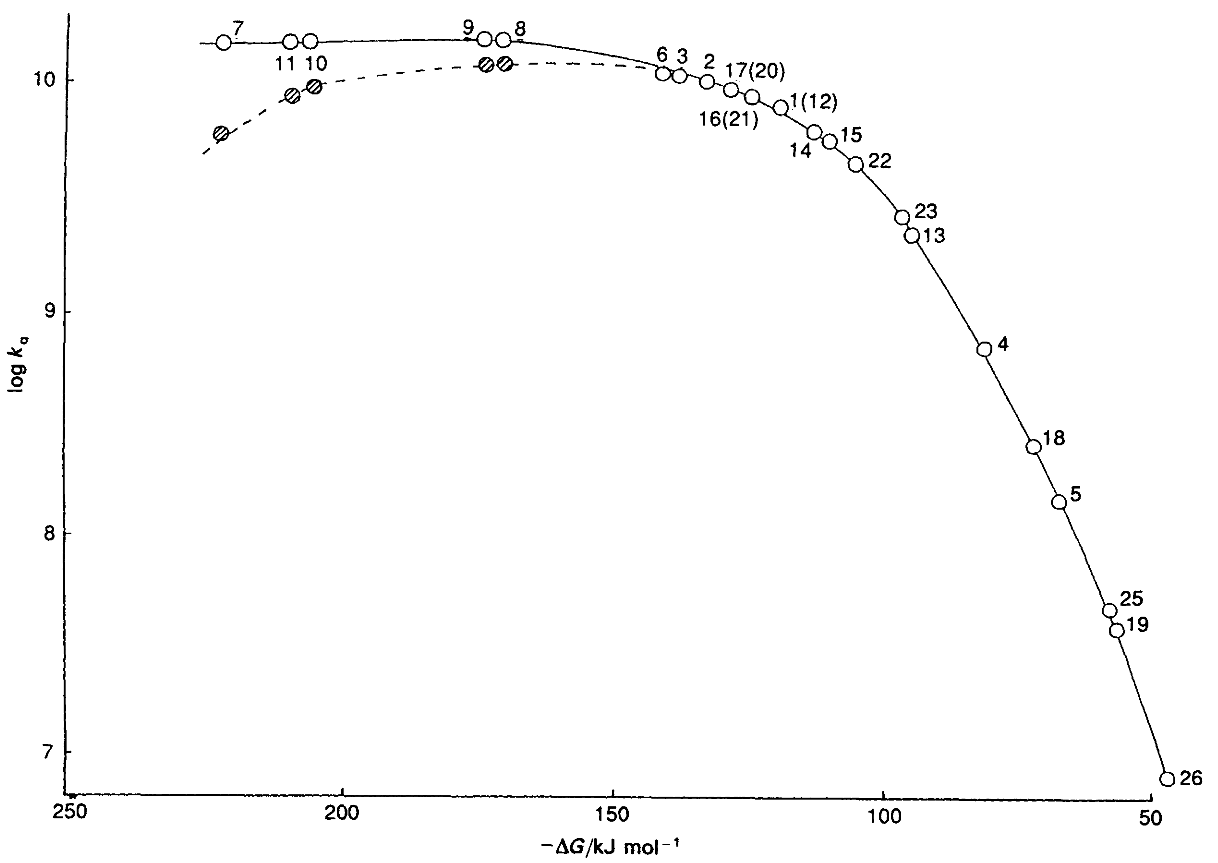


Fig. 8 Marcus–Rehm–Weller plot for quinone radical anions. (- - - -) Marcus inverted region, (——) Rehm–Weller plot. Point numbers refer to pairs of reactants listed in Table 3 under substrate.

tion energies for six quinone radical anions. We obtained electron transfer Gibbs energies of reaction from the voltammetric reduction peak potentials of 12 different substrates and then calculated quenching rate constants for 28 pairs of reactants. When the logarithms of these rate constants were plotted against the Gibbs energies of reaction, a typical Marcus curve was obtained. The quenching rate constants compared favourably with published data. Some of the values fell in the Marcus inverted region thus favouring the existence of the inverted region for ion–molecule electron transfers.

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