# Photoelectrochemical Electron Spin Resonance

## Part 4.—The 'Photo-ECE' Reaction and the Reduction of 1-Halogenoanthraquinones

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The reduction of 1-bromoanthraquinone in acetonitrile solvent in the presence of tetrabutylammonium perchlorate, at irradiated (565 nm) gold electrodes is shown to produce the radical anion of anthraquinone. A combination of photoelectrochemical hydrodynamic voltammetry, *in situ* electrochemical ESR and preparative experiments are used to deduce that the mechanism is a 'photo-ECE' reaction, in which the first electron transfer produces the radical anion of 1-bromoanthraquinone. On irradiation, this anion dissociates. Bromide ions and anthraquinone are formed and the latter undergoes a further one-electron reduction at the electrode resulting in the detection of significant photocurrents. The H atom abstracted in the formation of the anthraquinone is shown to arise from the tetrabutylammonium cations and *not* from the solvent as previously suggested in analogous processes. The related species, the 1-chloroanthraquinone radical anion, is shown to be stable towards irradiation on the electrochemical timescale, whereas 1-iodoanthraquinone is found to undergo reduction at gold in the absence of light in an analogous mechanistic manner to 1-bromoanthraquinone in the light.

In a previous paper<sup>1</sup> we described a flow cell suitable for simultaneous electrochemical electron spin resonance measurements. It was demonstrated that a channel electrode made of synthetic silica could be located at the centre of the cavity of an ESR spectrometer with negligible perturbation of its sensitivity, thus allowing the identification of radical species formed during electrochemical reactions brought about at the electrode. Moreover, the known pattern of convective flow in the channel enabled the calculation of the concentration distributions of electrogenerated radicals under the assumption that they either were stable<sup>1</sup> or else had a defined kinetic mode (1st order, 2nd order, etc) of decay.<sup>2-4</sup> These calculations allowed the steady-state ESR signal to be related to the generating current, the channel geometry and the solution flow rate. In particular, varying the last of these quantities so as to vary the mass transport to the electrode and out of the cavity, was shown to provide a probe for the lifetimes of the radical intermediates and to give mechanistic and kinetic data about the radical decay. This protocol has been validated and exploited in the study of ECE<sup>2,5</sup> and DISP<sup>6</sup> processes, as well as more complicated electrode reactions.<sup>7</sup> The role of ESR in the investigation of dark electrode reaction mechanisms in general has been reviewed recently.<sup>3,4</sup>

We have applied the above methodology to the study of processes taking place at illuminated electrodes where the course of the electrode reaction is altered by the absorption of light by reaction intermediates or products. Thus, firstly, the photo-reduction of crystal violet in acetonitrile solution was shown<sup>8</sup> to have the characteristics of an EC process, the electrode product undergoing a photochemical reaction to form the electrochemically inactive leuco-form of the dye through hydrogen abstraction from the solvent, whereas in the dark a simple kinetically uncomplicated one-electron transfer took place. Secondly, the reduction of fluorescein in aqueous base was shown<sup>9</sup> to be two-electron and produce leuco-fluorescein in the light (390 nm), whereas in the dark the process was a one-electron reduction to the semifluorescein radical. The photoelectrochemical reaction was shown to be a 'photo-DISP2' process with rate-determining disproportionation between ground-state and excited-state semi-fluorescein radicals.

In this paper we continue our search for the photochemical analogues of the familiar mechanistic types of dark electrochemistry and focus on the reduction, at gold, of the 1haloanthraquinones (AQX) in acetonitrile solution:



The reduction of aryl and heteroaryl halides, ArX, in the dark, has been well studied<sup>10-13</sup> and shown to first yield an anion radical, ArX<sup>•-</sup>, which may then decompose according to the nature of the halogen and the aryl/heteroaryl groups. The work described here uses photochemical excitation of AQX<sup>•-</sup> to change the stability and rate of decomposition of the radical anion and thus alter the course of the electrode reaction. In particular, it is shown that in the case of 1bromoanthraquinone the new pathway is that of a 'photo-ECE' reaction in which the final product is the anthraquinone radical anion. This results from excited AQBr<sup>--</sup> rapidly losing bromide to form an aryl radical which abstracts a hydrogen atom from the supporting electrolyte (tetrabutylammonium perchlorate) to form AQH which then undergoes a further heterogeneous one-electron reduction. Negligible H-abstraction from the acetonitrile solvent is observed.

#### Experimental

The basic apparatus and techniques for the *in situ* photoelectrochemical ESR experiments have been described previously.<sup>9</sup> The silica channel electrode unit was 30 mm long and had approximate cross-sectional dimensions of 0.4 mm  $\times$  6.0 mm. Gold foils (4.0 mm  $\times$  4.0 mm), used as electrodes in this unit, were cemented onto the silica cover plates and were carefully polished flat (with a succession of finer diamond lapping compounds down to 0.25 µm before use. In the particular case of photochemically induced ESR transient measurements under no-flow conditions the flow cell was modified as shown schematically in fig. 1 so as to minimise, as far as possible, the loss of material by convection from the electrode zone. This was accomplished by inserting two silica plates (one upstream and one downstream of the electrode) into the channel unit so as to provide connection with the flow system through the very narrow (0.5 mm) ducts between the silica inserts and the edge of the channel unit. With this arrangement, fresh solution could be flowed up to the electrode surface, the flow stopped via Teflon taps, and the solution between the inserts quantitatively electrolysed, for example to provide a large quantity of the stable radical anion, AQX'-, the decay of which could then be monitored by ESR upon exposure to irradiation with the electrode either under potentiostatic control or open-circuited. The ESR spectrometers used were as reported previously.<sup>1,8</sup> Irradiation was provided by a Wotan XBO 900 W/2 xenon arc lamp via a Jarrell-Ash 82-410 grating monochromator. The radiation power incident at the electrode position was typically of the order of 40 mW cm<sup>-2</sup>. Power was varied by attenuating with wire gauzes of differing mesh size. Radiation intensity was measured using an International Light IL700 photometer. A reference electrode was located in the flow system upstream of the cavity. This was either a saturated calomel electrode or a silver wire pseudo-reference electrode. All experiments were carried out at 25°C.

Acetonitrile (Fisons' dried distilled) was refluxed with calcium hydride and then fractionally distilled. Tetrabutylammonium perchlorate, TBAP (Fluka, purum) was recrystallised once from a mixture of ethanol and petroleum ether. Either this, or sodium perchlorate (Aldrich), was used as the supporting electrolyte. Anthraquinone (BDH), 1chloroanthraquinone (Aldrich) and tetrabutylammonium chloride, TBAC (Fluka, purum) were used as received. 1-Bromoanthraguinone and 1-iodoanthraguinone were recrystallised samples prepared for a previous investigation of substitution reactions of 1-halo-anthraquinones catalysed by Cu<sup>I</sup> salts.<sup>14</sup> All solutions were prepared in a dry box and dried with activated Al<sub>2</sub>O<sub>3</sub> (N-Super 1, ICN Biomedicals) before use. Concentrations were measured, spectrophotometrically. Electrolysis was performed in acetonitrile solution containing 0.1 mol dm<sup>-3</sup> of supporting electrolyte. Oxygen was removed by outgassing with nitrogen (prepurified of trace oxygen and dried) prior to electrolysis. Electrochemical measurements were carried out using an Oxford Electrodes potentiostat, modified to boost the counter-electrode

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voltage.<sup>15</sup> Complementary rotating-disc experiments utilised an Oxford Electrodes rotating-disc assembly and motor controller. UV-visible absorption spectra were recorded on a Perkin-Elmer Lambda-5 spectrophotometer, with either a 10 mm × 10 mm silica Perkin-Elmer cuvette cell or, in the case of electrogenerated species, using an optically transparent thin layer electrode (OTTLE) cell described previously.<sup>16</sup> The working chamber of the latter was formed by sandwiching a semitransparent gold minigrid (100 wires in<sup>-1</sup>,‡ 80% transmittance, Buckbee Mears Co., St. Paul, Minnesota, USA) between two silica cell plates (Hellma Ltd., Westcliff-on-Sea, UK). Optical pathlengths of either 150 µm (AQI) or 550 µm (AQCl and AQBr) were used.

Preparative experiments employed an H-cell electrode assembly with a porous membrane (Nafion 417, ICI) as a separator between the counter- and working-electrode compartments. A graphite rod served as the counter-electrode and a gold wire of area 24  $\text{cm}^2$  as the working electrode. A saturated calomel reference electrode was located ca. 5 mm from the latter. The solution was degassed as described above and stirred continuously by a bar magnet. Typically, a  $5 \times 10^{-3}$  mol dm<sup>-3</sup> solution was almost (90%) exhaustively electrolysed with this arrangement after ca. 2 h. The working compartment was irradiated with light from a 300 W tungsten filament lamp, which was filtered with a Braun ferrous glass filter to remove infrared radiation and an OY4 Chance-Pilkington filter to eliminate light below 490 nm in wavelength. The following analytical procedure was used to identify the products of the preparative photoelectrochemistry. Quantitative mass balances were not possible, probably because of loss of material due to adsorption of reactant on alumina (N-Super 1, ICN Biomedicals) used to keep the solutions dry during electrolysis. Aliquots of the photoelectrolysed solution (10 cm<sup>3</sup>) were combined with a standard solution of benzophenone in acetonitrile (5 cm<sup>3</sup>) and poured into water (ca. 100 cm<sup>3</sup>). Extraction was with methylene chloride  $(2 \times 40 \text{ cm}^3)$ . Combined extracts were washed twice with water, dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed on a rotary evaporator (bath temperature <40 °C). The dark, partly crystalline residue was treated with ether (50 cm<sup>3</sup>) and the mixture sonicated for 60 s. After filtration to remove TBAP, the solution was evaporated to dryness in vacuo and the residue taken up in  $CH_2Cl_2$  (1 cm<sup>3</sup>). This solution was then analysed by capillary gas chromatography [(GC : Dani 3800) stationary phase OV1, program 80°C: (2 min)  $\times 10^{\circ}$ C min<sup>-1</sup> to 250°C] and where appropriate GC/MS (VG 7070E). A modified extraction procedure was adopted in an attempt to detect succinonitrile: aliquots of



Fig. 1. A schematic diagram showing the channel flow cell as modified for photochemically induced ESR transient measurements under no-flow conditions. The length of the electrode,  $x_e$ , is 0.5 cm, and its width, w, 0.5 cm. The electrode is located centrally within the 'electrolysis cavity' of length,  $S_x$ , 0.6 cm, and width, d, 0.6 cm. The solution inlet and outlet are of width  $S_w = 0.05$  cm. The half-height, h, of the cell is 0.02 cm.

reaction mixture and standards were evaporated to dryness on a rotary evaporator (bath temperature <40 °C) and the residue sonicated with ether (50 cm<sup>3</sup>) for 60 s. The filtered solution was again evaporated to dryness and the residue taken up in CH<sub>2</sub>Cl<sub>2</sub> (1 cm<sup>3</sup>). Control experiments showed that succinonitrile was readily detectable by GC in this way; recovery appeared to be *ca*. 65%.

Supporting theory was generated from programs written in FORTRAN on a VAX/VMS computer.

#### **Results and Discussion**

We consider first the behaviour in the dark of AQX (X = H, Cl, Br, I) towards electrochemical reduction in acetonitrile solution at gold electrodes. Current-voltage (*I*-*E*) curves were recorded at a channel electrode as a function of electrolyte flow rate for solutions *ca.*  $1 \times 10^{-3}$  mol dm<sup>-3</sup> in AQX. Analysis of the reduction waves was consistent with a reversible one-electron reduction. This was evidenced first by mass-transport-corrected Tafel analysis:<sup>17</sup> a plot of *E vs.*  $\log[I^{-1} - I_{lim}^{-1}]$ , where  $I_{lim}$  is the transport-limited current, gave a slope of 59 mV per decade. Secondly,  $I_{lim}$  was found to vary with the cube root of the solution flow rate (in the case of channel-electrode data) as predicted by the Levich equation (for a one-electron reduction):

$$I_{\rm lim} = 1.165 \times (96485) D^2 3 U^{1/3} h^{-1/3} w x_{\rm e}^{2/3} [\rm AQX]_0 \quad (1)$$

where U (cm s<sup>-1</sup>) is the mean solution velocity, D (cm<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient, h (cm) is the half-height of the cell,<sup>1</sup> and w (cm) and  $x_e$  (cm), respectively, are the width and the length of the electrode. [AQX]<sub>0</sub> (mol cm<sup>-3</sup>) is the bulk concentration of AQX. In all cases, except for AQI at low flow rates, the data indicated one-electron reductions for all four species and permitted the deduction of the following diffusion coefficients and formal electrode potentials ( $\pm 0.005$  V vs. SCE): AQH 2.20  $\pm 0.10 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, -0.900 V; AQCI  $1.83 \pm 0.10 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, -0.881 V; AQBr  $1.73 \pm$  $0.10 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, -0.878 V; AQI  $1.70 \pm 0.10 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, -0.826 V. Values have previously been reported<sup>18-20</sup> for AQH and are in close agreement with those cited here. For the case of AQI at flow rates below  $5 \times 10^{-3}$  cm<sup>3</sup> s<sup>-1</sup> the voltammetric data indicated an effective number of electrons transferred a little above unity ( $n_{eff} \approx 1.00-1.10$ ) suggesting some decomposition of AQI<sup>--</sup> in the dark (vide infra).

Exactly analogous conclusions to the above were drawn from corresponding rotating-disc voltammetric measurements (made as a function of rotation speed). It may thus be concluded that, in the dark, the electrode process is

## $AQX + e^- \rightarrow AQX^{\bullet}$

and that, with the exception of AQI<sup>--</sup>, the radical anion is stable on the electrochemical timescale. These conclusions were confirmed by in situ electrochemical ESR experiments, again conducted in the absence of light, using the channelflow cell technique. For each of AQH, AQCl, AQBr and AQI radical species were detected at potentials corresponding to their one-electron reduction. The spectrum of AQH<sup>•-</sup> (fig. 2) was unambiguously identified by comparison with the literature.<sup>21</sup> The spectra in fig. 3 and 4 were obtained from AQCl and AQBr, respectively, and attributed to AQCl'- and AQBr<sup>--</sup>, although the absence of well defined hyperfine structure precluded detailed spectral assignment. The spectrum shown in fig. 5 was obtained from the reduction of AQI but is identical to that of the AQH<sup>•-</sup> radical anion. This last observation is consistent with the low flow rate voltammetric measurements for AQI and will be discussed further below.



Fig. 2. ESR spectrum obtained by the reduction of a ca.  $0.2 \times 10^{-3}$  mol dm<sup>-3</sup> solution of AQH (in acetonitrile solution containing 0.1 mol dm<sup>-3</sup> TBAP) at a gold channel electrode (flow rate  $4 \times 10^{-4}$  cm<sup>3</sup> s<sup>-1</sup>) and attributed to the radical anion AQH<sup>--</sup>.



Fig. 3. ESR spectrum obtained by the reduction of a  $ca. 0.5 \times 10^{-3}$  mol dm<sup>-3</sup> solution of AQCl (in acetonitrile solution containing 0.1 mol dm<sup>-3</sup> TBAP) at a gold channel electrode (flow rate  $4 \times 10^{-4}$  cm<sup>3</sup> s<sup>-1</sup>) and attributed to the radical anion AQCl<sup>--</sup>.



Fig. 4. ESR spectrum obtained by the reduction of a  $ca. 0.5 \times 10^{-3}$  mol dm<sup>-3</sup> solution of AQBr (in acetonitrile solution containing 0.1 mol dm<sup>-3</sup> TBAP) at a gold channel electrode (3 × 10<sup>-4</sup> cm<sup>3</sup> s<sup>-1</sup>) and attributed to the radical anion AQBr<sup>--</sup>.



Fig. 5. ESR spectrum obtained by the reduction of a ca.  $0.5 \times 10^{-3}$  mol dm<sup>-3</sup> solution of AQI (in acetonitrile solution containing 0.1 mol dm<sup>-3</sup> TBAP) at a gold channel electrode (flow rate  $3 \times 10^{-4}$  cm<sup>3</sup> s<sup>-1</sup>) and attributed (predominantly) to the radical anion AQH<sup>--</sup> formed from the decomposition of AQI<sup>--</sup>.

The ESR signal (S)-current-flow rate behaviour was next examined for the reductions of AQH, AQCl and AQBr. We have shown elsewhere<sup>1</sup> that in the case of a stable radical the following relationship should be obeyed;

$$S = \text{constant} \times I/U^{2/3}.$$
 (2)

For each of the three compounds it was found that a plot of  $\log(S/I)$  vs. log U was linear with a slope close to -2/3 as required by eqn (2). Thus, these experiments again indicate that the radical anions of AQH, AQCl and AQBr are 'stable' on the timescale of the experiment, corresponding to an approximate lifetime of ca. 10 s or longer.

As a preliminary to the photoelectrochemical experiments the absorption spectra of the radical anions AQX<sup>--</sup> were determined using an optically transparent thin-layer cell<sup>16</sup> (stationary solution) in which a semitransparent gold minigrid acted as a working electrode. The latter was potentiostatted at a value corresponding to the one-electron reduction of the species of interest and the resulting UVvisible spectra are shown in fig. 6. The radical anions of AQCI and AQBr are seen to have absorption maxima at 565 and 566 nm, respectively [fig. 6(a) and (b)]. The spectrum shown in fig. 6(c) was obtained from AQI<sup>--</sup> (maximum 566.5 nm). The dotted line was measured within the first 15 s of the electrolysis of AQI under no-flow conditions. After this time, the AQI<sup>--</sup> spectrum was largely swamped by that of AQH<sup>-</sup> [dashed line in fig. 6(c)]. Fig. 6(d) shows the spectrum obtained from the reduction of AOH (to a maximum of 544 nm). An approximate extinction coefficient  $dm^3 cm^{-1} mol^{-1}$ ) was deduced for each radical anion: AQH<sup>-</sup>,  $8.5 \times 10^3$ ; -, 7.0 × 10<sup>3</sup>. AQCI<sup>--</sup>,  $10.8 \times 10^3$ ; AQBr<sup>--</sup>,  $9.2 \times 10^3$ ; AQI<sup>--</sup> The last value represents a lower bound because of the partial decomposition of the radical anion during the experiment.

Photoelectrochemical experiments were next conducted on the halides of interest using the channel-electrode flow cell. In each case, the wavelength used corresponded to the absorption maximum cited above and the electrode potential held at a value corresponding to the transport-controlled reduction of AQX. The effect of irradiation on the current and on the ESR signal intensity was then examined. In the case of AQCl, negligible photocurrents were observed and the ESR signal was unchanged on irradiation. It was therefore concluded that AQCl<sup>--</sup> is photochemically stable on the timescale of this experiment (but see below). In contrast irradiation of the AQBr and AQI reductions produced photocurrents and ESR signals attributable to AOH<sup>--</sup>. In both cases the 'action spectrum' i.e. a plot of photocurrent against wavelength closely resembled the corresponding UV-visible spectrum in fig. 6. Fig. 7 shows the action spectrum for AQBr<sup>-</sup>. No photocurrents were observed from irradiation of AQH'- in the wavelength range 500-600 nm. Fig. 8 shows an ESR spectrum obtained by irradiation of AQBr<sup>-</sup> and is seen to be consistent with a combination of the spectra shown in fig. 2 and 4, i.e. with a mixture of AQH<sup>--</sup> and AQBr<sup>--</sup>. At very low flow rates the spectrum was almost entirely that of the AQH radical anion. Under these conditions the currents observed approached twice those seen in the dark. The effect of irradiating AQBr<sup>--</sup> at 566 nm is clearly to cause decomposition with the ultimate formation of AQH<sup>-</sup>. The radical anion of AQI behaved in a similar way. We have seen above that this decomposes in the dark, forming AQH<sup>•-</sup>. However, the rate of this process was greatly increased on irradiation. The rates of decomposition of AQI'- and AQBr'- are quantified below.

Kinetic information about the rates of photodecay of AQB<sup>•-</sup> and AQI<sup>•-</sup> was obtained under no-flow conditions using the channel ESR cell modified as described in the

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Fig. 6. The UV-visible spectra of (a) AQCI<sup>-</sup>, (b) AQBr<sup>-</sup>, (c) AQI<sup>-</sup> and (d) AQH<sup>-</sup> measured using an OTTLE. In each case the solid line represents the spectrum of the parent material *i.e.* AQCI, AQBr, AQI or AQH, and the dotted line that of the radical anion. For the case of AQI (c) the radical anion spectrum was obtained within the first 15 s of electrolysis, and the dashed line represents a spectrum showing the build-up of AQH<sup>-</sup> at longer times (see text). A pathlength of 550  $\mu$ m was used for (a), (b) and (d); 150  $\mu$ m for (c).

Experimental section so as to minimise natural convection. Under this protocol, solutions of AQBr and AQI were exhaustively electrolysed in the dark at the gold electrode to provide a large concentration of the corresponding radical anion. The electrode was then open-circuited and irradiated with light of wavelength corresponding to the absorption maximum of AQX<sup>--</sup>, and the radical concentration moni-

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Fig. 7. The action spectrum obtained by irradiating the AQBr<sup>-</sup> radical anion. Concentration of AQBr =  $5 \times 10^{-4}$  mol dm<sup>-3</sup>; flow rate =  $1.8 \times 10^{-4}$  cm<sup>3</sup> s<sup>-1</sup>; light intensity = 47.4 mW cm<sup>-2</sup>.

tored through the intensity of the ESR signal. The resulting transients were analysed successfully by treating the decay as a simple first-order process. Fig. 9 shows the observed behaviour and analysis in the case of AQBr<sup>-</sup>. The slopes of such plots as fig. 9(b) allowed the deduction of the first-order rate constant for the photo-decay of AQBr<sup>-</sup> as a function of light intensity. This is shown in fig. 10 where the rate constants have been adjusted for the observed loss of AQBr<sup>-</sup> in the dark due to slight loss of radical out of the cavity arising from unavoidable small amounts of natural convection. This latter process was found to be satisfactorily modelled by first-order kinetics with a rate constant of  $4.2 \times 10^{-3} \text{ s}^{-1}$ , which is substantially smaller than the measured values in the presence of light.

In the case of AQI the ESR photo-transient experiments were further complicated by the decay of the radical in the dark. No-flow experiments using the modified flow cell to generate AQI<sup>•-</sup> radical anions, followed by open-circuiting of the electrode, suggested a first-order rate constant,  $k_d$ , of  $(1.43 \pm 0.20) \times 10^{-2} \text{ s}^{-1}$  for the dark reaction. Phototransient experiments were then conducted as before, except that rather than employing exhaustive reduction of AQI the reduction period was kept to a minimum (ca. 15 s) before open-circuiting the working electrode and switching on the light so as to prevent any significant build up of AQH<sup>•-</sup>. Again, a first-order decay was observed and fig. 11 shows

Fig. 8. The ESR spectrum obtained by irradiation (566 nm, 47.4 mW cm<sup>-2</sup>) of a gold channel electrode at which AQBr ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>) is undergoing reduction. A solution flow rate of  $1.8 \times 10^{-4}$  cm<sup>3</sup> s<sup>-1</sup> was employed. The spectrum is consistent with a mixture of AQBr<sup>•-</sup> and AQH<sup>•-</sup>.



Fig. 9. (a) The ESR transient measured for the photodecay of AQBr<sup>-</sup> (566 nm, 21.4 mW cm<sup>-2</sup>) under no-flow conditions (see text), and (b) its analysis as a simple first-order process. The ESR signal intensity, S, is displayed normalised to its initial value,  $S_0$ .

that the photochemical decay-rate constant,  $k_{obs}$ , deduced from the slope of a plot such as fig. 9(b), uncorrected for the dark reaction ( $k_{obs} = k_1 + k_d$ ), is a linear function of the light intensity. The intercept of fig. 11 corresponds to  $k_d$ .

Phototransient experiments were also performed on  $AQCI^{-}$  and  $AQH^{-}$ . In the former case, the results were analogous to those found for  $AQB^{*-}$ ; first-order kinetics were again found, except that the rate of decay was very much slower, so that the correction for the loss of the radical from the ESR cavity by natural convection was comparable in magnitude to the rate of photodecay. Accordingly, no further kinetic analysis was possible. Experiments with  $AQH^{*-}$  showed this radical anion to be stable with respect to irradiation at wavelengths between 500 and 600 nm, in agreement with the observed corresponding lack of photocurrents in this range (vide supra).



Fig. 10. The measured first-order rate constant,  $k_1$ , for the photodecay of AQBr<sup>-</sup> as a function of light intensity (565 nm).





Fig. 11. The observed first-order rate constant,  $k_{obs} (=k_1 + k_d)$ , for the photodecay of AQI<sup>-</sup> as a function of light intensity (565 nm).

The above phototransient experiments show that the lightinduced decomposition of  $AQX^{-}$  is a first-order process. We have also seen that, in the cases of AQBr and AQI, channelelectrode flow cell experiments indicate that, when the electrode is potentiostatted at a value corresponding to the transport-limited current, irradiation produces both ESR signals attributable to  $AQH^{-}$  and also appreciable photocurrents. We may thus suggest the following general mechanistic scheme for the process:

$$AQX + e^- \rightarrow AQX^{-}$$
 (i)

$$AQX^{-} + hv \rightarrow AQ^{+} + X^{-}$$
(ii)

$$AQ' + H'' \rightarrow AQH$$
 (iii)

$$AQH + e^- \rightarrow AQH^{--}$$
 (iv)

$$AQH + AQX^{-} \rightleftharpoons AQH^{-} + AQX.$$
 (v)

Reaction (iii) implies hydrogen atom abstraction from a suitable donor, the identity of which is discussed below. In the case that (iii) is 'fast' then reactions (ii) and (iii) can be simply written as the following first-order process:

$$AQX^{-} + hv + H^{+} \rightarrow AQH + X^{-}.$$
 (vi)

Given that we have shown that the photochemical step is rate-determining (fig. 10 and 11) the above scheme allows for two extreme mechanistic types, 'photo-ECE' and 'photo-DISP1', named by analogy with familiar dark processes. Reactions (i)-(iii) are common to both these mechanisms. However, they differ in the nature of the second electron transfer, which either takes place heterogeneously at the electrode surface [reaction (iv), 'photo-ECE'], or homogeneously through disproportionation [reaction (v), 'photo-DISP1'].<sup>22,23</sup> In both mechanisms reaction (vi) may be considered as being the slowest step. We consider next the analysis of the channel flow cell photocurrent data in terms of the above scheme.

We have shown elsewhere<sup>24</sup> that ECE and DISP1 processes may be characterised by means of the effective number of electrons,  $n_{eff}$ , transferred during the electrode reaction. Fig. 12 displays 'working curves' showing how  $n_{eff}$  depends on  $K_1^*$ , which is a normalised rate constant defined as

$$K_1^* = k_1 (h^2 x_e^2 / 9U^2 D)^{1/3}$$
(3)

where  $k_1$  is the rate constant (s<sup>-1</sup>) describing reaction (vi).<sup>24</sup> Theory has also been presented for the 'mixed' mechanism, *i.e.* where both ECE and DISP1 processes are proceeding simultaneously.<sup>24</sup>

The photoelectrochemical reduction of AQBr (566 nm, light intensity  $4.74 \times 10^{-2}$  W cm<sup>-2</sup>) produced large photo-



Fig. 12. Working curves computed for (a) ECE and (b) DISP1 processes at a channel electrode showing the effective number of electrons transferred as a function of the normalised rate constant (see text).

currents  $(1.0 < n_{\rm eff} < 1.7$  over the flow range  $10^{-4}-10^{-1}$  cm<sup>3</sup> s<sup>-1</sup>) which were analysed according to both ECE and DISP1 mechanisms using the working curves in fig. 12. Fig. 13 shows  $K_1^*$ , deduced in this way, plotted against  $U^{-2/3}$  as suggested by eqn (3). The expected first-order behaviour is superimposed, deduced from the no-flow ESR transient experiments performed at the corresponding light intensity. It can be seen that the best fit straight line through the experimental data, analysed according to a 'photo-ECE' mechanism produces a value of  $k_1$  in excellent agreement with the ESR transient data.

Further evidence in favour of the ECE route is found from examination of the current-voltage waveshape for the reduction of AQBr at the channel flow cell in the presence and absence of irradiation. Fig. 14 shows that appreciable photocurrents pass only near the top of the voltammetric wave. This is incompatible with a DISP1 mechanism since, in that case, the extra current arises from regeneration and further reduction of AQBr. Thus, the current-voltage wave would be proportionately equally amplified compared with the dark wave, at all potentials.<sup>24</sup> In contrast, the proposed



Fig. 13. Analysis of the photocurrent data in terms of (a) ECE ( $\bigcirc$ ) and (b) DISP1 (×) pathways. Superimposed on the plot is a solid line representing the behaviour expected on the basis of the first-order rate constant for the decomposition of AQBr<sup>--</sup> measured under no flow conditions at the same light intensity (47.4 mW cm<sup>-2</sup>).



Fig. 14. A voltammogram measured at the channel flow cell for the reduction of AQBr in acetonitrile/TBAP at a flow rate of  $1.1 \times 10^{-2}$  cm<sup>3</sup> s<sup>-1</sup> in the (*a*) presence (upper curve), and (*b*) absence (lower curve) of light (565 nm, 47.4 mW cm<sup>-2</sup>).

ECE mechanism results in the formation of AQH and it is this which undergoes further heterogeneous electron transfer. We have seen above that this is reduced at potentials slightly negative to those at which AQBr undergoes reduction and thus photocurrents are only seen near the 'top' of the voltammetric wave in fig. 14 where the electrode potential is sufficiently negative to reduce AQH.

It is clear that both the photocurrent and waveshape data point unambiguously to a 'photo-ECE' pathway for the reduction of AQBr. This suggests that reaction (v) is kinetically insignificant. Further modelling was carried out in order to place an upper limit on the rate of this reaction in the forward direction using the Backwards Implicit method for modelling the transport and kinetic processes within the channel electrode.<sup>24</sup> In particular, the equilibrium constant for reaction (v) was calculated as being 0.42 (25 °C) from the reduction potentials quoted above. This allowed values of the rate of reaction (v) in the back direction to be established for different assumed forward rate constants and thus the 'mixed' ECE/DISP1 pathway to be modelled allowing for the reversibility of reaction (v). In this way, an upper limit of  $10^4$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for the rate constant of reaction (v) in the forward direction was established. This value corresponded to the DISP1 path contributing no more than 0.025 to the overall effective number of electrons transferred in the reaction at any flow rate.

We consider next the nature of step (iii) in more detail, and, in particular, the origin of the hydrogen atom abstracted by the aryl sigma radical AQ'. Such processes have been ascribed previously to reaction with the acetonitrile solvent, with consequent formation of succinonitrile (by dimerisation of cyanomethyl radicals) suggested but not confirmed.11,13,25,26 To clarify the origin of the H atom, preparative scale experiments were carried out in an H cell and the products analysed. The reduction of AQBr (in the light) and AQI (in the dark) gave very large yields of AQH in comparison with other materials formed in the reductions. Tributylamine was observed (initially formed in the same quantities as AQH). When a background electrolyte containing no protons (NaClO<sub>4</sub>) was substituted for TBAP, negligible yields of AQH were obtained. GC/MS analysis revealed no evidence of acetonitrile breakdown products (e.g., succinonitrile) in any analysis. Moreover, channel flow cell experiments showed no photocurrents when NaClO<sub>4</sub> replaced TBAP as supporting electrolyte. The evidence suggests that the H is abstracted from the tetrabutylammonium ion to give tributylamine as a side product. Trace quantities of butylbromoanthraquinone (four isomers detected) and of butylanthraquinone were also detected and clearly arise from the decomposition of the supporting electrolyte.

In a further preparative experiment with AQBr, TBACL was used in equivalent amounts with TBAP (0.1 mol dm<sup>-3</sup>). This was to test whether Cl<sup>-</sup> could intercept the AQ<sup>+</sup> radical. GC/MS analysis revealed negligible, though detectable, yields of AQCl but large quantities of AQH. Clearly, Cl<sup>-</sup> is not a very good competitor with NBu<sub>4</sub><sup>+</sup> for AQ<sup>+</sup> so that there is no light-induced  $S_{RN}$  1-chain formation of chloroanthraquinone.

The above demonstrates that H abstraction is from the counter-ion and involves the AQ<sup>+</sup> radical, whereas previous workers have suggested that the solvent is the major H donor, in the form of H<sup>+</sup> to further reduced AQ<sup>+</sup>, *i.e.* AQ<sup>-.11,13,25,26</sup> This factor and the apparent stability of AQBr<sup>-</sup> and AQ<sup>+</sup> to attack from Cl<sup>-</sup> may indicate an ion pairing of AQBr<sup>+-</sup> with NBu<sub>4</sub><sup>+</sup> so that on irradiation reaction with the cation is strongly favoured:

$$AQBr + e^{-} \rightarrow AQBr^{*-}$$

$$AQBr^{*-} + NBu_{4}^{+} \rightarrow \{AQBr^{*-} \cdot NBu_{4}^{+}\}$$

$$\{AQBr^{*-} \cdot NBu_{4}^{+}\} + hv \rightarrow AQH + Bu_{3}N + Bu^{*}$$

$$AQH + e^{-} \rightarrow AQH^{*-}.$$

The observed production of butylanthraquinone and butylbromoanthraquinones may then arise from the formation of Bu' radicals.

Having considered in detail the photoreduction of AQBr we finally consider further the reduction of AQI. No mechanistic photocurrent measurements were carried out on the reduction of AQI in the light. However, the dark current-flow rate data were analysed as ECE or DISP1 along the above lines. Fig. 15 shows the analysis in terms of eqn (3) where values of  $K_1^*$  have been deduced from measured values of  $n_{\text{eff}}$ and the working curves in fig. 12. It can be seen that the ECE mechanism gives a better fit with the rate constant deduced from the ESR transient data. That is the dark reduction of AQI follows the same mechanism as the photoreduction of AQBr. Since the rate-determining step in the former is the dissociation of the AQI<sup>\*-</sup> radical anion it is likely that the photoreduction of AQI also follows the ECE route, the light simply increasing the rate of decomposition of the anion.



Fig. 15. Analysis of the dark current-flow rate data for the reduction of AQI in terms of either an ECE ( $\times$ ) or a DISP1 ( $\bigcirc$ ) process. The solid line drawn shows the expected behaviour calculated from the first-order rate constant for the dark decay measured from the ESR transient data [(1.43 ± 0.20) × 10<sup>2</sup> s<sup>-1</sup>]. The dotted lines represent the error in this rate constant.

Indeed, preparative experiments again indicated that no succinonitrile was formed, giving confirmation that the chemistry following the dissociation of the radical anion is analogous to the AQBr case.

## Conclusions

The photoreduction (560 nm) of 1-bromoanthraquinone in acetonitrile and TBAP supporting electrolyte, at gold, with light proceeds via a 'photo-ECE' mechanism, producing the radical anion of anthraquinone. In contrast, firstly, the reduction of 1-chloroanthraquinone is unaffected by light of a frequency corresponding to an absorption band in the radical anion and, secondly, the reduction of 1-iodoanthraquinone proceeds in the dark via an ECE route again to the radical anions towards halide loss are clearly in the order AQCl > AQBr > AQI. The source of the H abstracted by the reacting radical anion is from the tetrabutylammonium ions present as supporting electrolyte, and not from the solvent.

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