

Photoelectrochemical reduction of *meta*-halonitrobenzenes and related species

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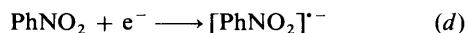
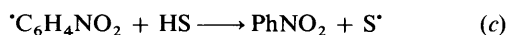
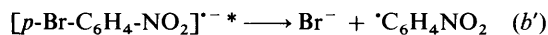
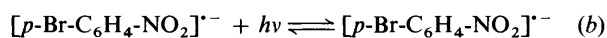
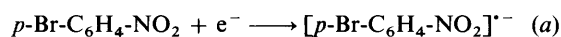
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Dual photo- and electro-chemical activation of *m*-chloronitrobenzene and *m*-bromonitrobenzene in acetonitrile solution leads to halide loss through a photo-ECE mechanism. This proceeds *via* absorption of visible light by the radical anions $[X-C_6H_4NO_2]^{*-}$, which is followed by fragmentation forming the $\cdot C_6H_4NO_2$ aryl radical. The latter reacts with the solvent system forming nitrobenzene which is further reduced at the electrode with the generation of $[C_6H_5NO_2]^{*-}$. Reduction of *m*-iodonitrobenzene leads to iodide loss without the need for irradiation. However, this process is accelerated by visible light. In contrast the dual activation of *p*-cyanonitrobenzene, *p*-dinitrobenzene, phenyl 4-nitrophenyl sulfone, methyl 4-nitrophenyl sulfone, phenyl 4-nitrophenyl sulfoxide or methyl 4-nitrophenyl sulfoxide failed to induce the leaving of any substituent suggesting that the process may be selective to halo-compounds.

In previous publications¹ we have demonstrated that the efficient loss of the halide anion from *p*-chloronitrobenzene and *p*-bromonitrobenzene may be accomplished by dual photochemical and electrochemical activation in acetonitrile solution. Subsequent work² showed that the mechanism by which this process occurs involves the absorption of light by electrogenerated anion radicals $[X-C_6H_4-NO_2]^{*-}$ (X = Br, Cl). This is followed by (reversible) halide loss and, ultimately, the formation of the nitrobenzene radical *via* the following photo-ECE mechanism [eqns. (a)–(d)], where HS represents



the solvent/supporting electrolyte system. The further reduction (e) was shown to be kinetically insignificant on the voltammetric



timescales employed.² A particularly interesting feature of the photoelectrochemical reduction is that excitation of the long wavelength (*ca.* 470 nm) absorption bands of the radical anions is, on a per photon absorbed basis, approximately six times more effective at inducing halide loss than excitation of the higher energy 330 nm transition.

In this paper we seek to generalise these observations with respect to aromatic organic species, while noting that photoelectrochemical dehalogenation has been accomplished from organometallic species,³ and present investigations of the photoelectrochemical reduction of the three *meta*-halonitrobenzenes, *m*-X-C₆H₄-NO₂ where X = Cl 1, Br 2 or I 3. In addition the results are presented of the attempted dual activation of a range of other *para*-substituted nitrobenzenes

including *p*-CN-C₆H₄-NO₂ 4, *p*-NO₂-C₆H₄-NO₂ 5, and several sulfone and sulfoxide compounds: phenyl 4-nitrophenyl sulfone 6, methyl 4-nitrophenyl sulfone 7, phenyl 4-nitrophenyl sulfoxide 8 and methyl 4-nitrophenyl sulfoxide 9.

Experimental

All standard photo-voltammetry experiments were conducted using a platinum channel electrode made of optical quality synthetic silica to standard construction and dimensions.⁴ Solution (volume) flow rates between 10⁻⁴ and 10⁻¹ cm³ s⁻¹ were employed. Working electrodes were fabricated from Pt foils (purity of 99.95%, thickness 0.025 mm) of approximate size 4 × 4 mm, supplied by Goodfellow Advanced Materials. Precise electrode dimensions were determined using a travelling microscope. A saturated calomel reference electrode (SCE) was positioned in the flow system upstream and a platinum gauze counter electrode located downstream, of the channel electrode. In DMF solution the SCE was replaced by a silver pseudo-reference electrode. Electrochemical measurements were made using an Oxford Electrodes potentiostat modified to boost the counter electrode voltage (up to 200 V). Other methodological details were as described previously.⁴ Irradiation was provided by one of two sources: (i) a Wotan XBO 900 W/2 xenon arc lamp used in conjunction with a Jarrell-Ash 82-410 grating mono-chromator (maximum incident power 2.0 mW cm⁻²); this permitted variable light intensity measurements through attenuation of the beam as described previously;⁴ or (ii) an Omnicrome 532MAP argon ion visible laser which could be tuned to different fixed wavelengths in the range 457–514 nm at 90 mW absolute power with a tube current of 10 A and a minimum beam diameter of 0.87 mm. The laser was used in conjunction with a beam expander (Omnichrome, Chino, CA) which gave a 25-fold increase in beam area and a radiative power at the electrode surface of 115 mW cm⁻².

Simultaneous photo-electrochemical EPR experiments used a channel flow cell carefully positioned in the TE₁₀₂ cavity of an X-band (9.0–10.0 GHz) Bruker ER200D spectrometer as previously described.⁵ UV-VIS measurements of electro-generated species were made using an optically transparent thin-layer electrode (OTTLE)⁶ in combination with a Perkin-

Elmer Lambda-5 spectrometer. Rotating disc electrode measurements were conducted using Oxford Electrodes equipment. Platinum micro-disc electrodes of diameter 10–120 μm were supplied by Bioanalytical Systems (West Lafayette, USA).

Experiments were performed using solutions of the electroactive substrate (*ca.* 10^{-4} – 10^{-3} mol dm^{-3}) in dried⁷ acetonitrile (Fisons, dried, distilled) or dimethylformamide (DMF, supplied by BDH, HPLC grade) solution containing 0.1 mol dm^{-3} (recrystallised) tetrabutylammonium perchlorate (TBAP) (Kodak) as supporting electrolyte. Solutions were purged of oxygen by outgassing with pre-purified argon prior to electrolysis.

Nitrobenzene, *m*-iodonitrobenzene, *m*-bromonitrobenzene and *m*-chloronitrobenzene were used as received from Aldrich (>99%).

Methyl 4-nitrophenyl sulfoxide 9⁸

Urea hydrogen peroxide, UHP (4.7 g, 50 mmol) was added slowly to a solution of phthalic anhydride (3.7 g, 25 mmol) in methanol (50 cm^3). The resulting suspension was stirred at room temperature for 15 min then 4-nitrothioanisole (2.12 g, 12.5 mmol) was added with stirring. The reaction mixture was stirred at room temperature for 24 h, then poured onto water (50 cm^3). The aqueous phase was saturated with sodium carbonate and extracted into dichloromethane (3 \times 50 cm^3). The combined extracts were dried (MgSO_4) and concentrated *in vacuo*, to give the sulfoxide in 95% yield (2.2 g, 11.9 mmol) (Found: C, 45.6; H, 3.9; N, 7.6. Calc. for $\text{C}_7\text{H}_7\text{NO}_3\text{S}$: C, 45.4; H, 3.81; N, 7.56%; δ_{H} (CDCl_3) 8.42 (d, 2 H, Ar-H), 7.87 (d, 2 H, ArH) and 2.80 (s, 3 H, OS- CH_3).

Methyl 4-nitrophenyl sulfone 7⁸

The above procedure was repeated using the sulfoxide in place of 4-nitrothioanisole, to give the sulfone in 81% yield (2.0 g, 10.1 mmol) (Found: C, 41.7; H, 3.5; N, 6.9. Calc. for $\text{C}_7\text{H}_7\text{NO}_4\text{S}$: C, 41.79; H, 3.51; N, 6.96%; *m/z* (EI) 201 (M^+), 186, 170, 139 and 122; δ_{H} (CDCl_3) 8.46 (d, 2 H, Ar-H), 8.20 (d, 2 H, Ar-H) and 3.14 (s, 3 H, $\text{O}_2\text{S-CH}_3$).

Phenyl 4-nitrophenyl sulfone 6⁹

4-Nitrophenyl phenyl sulfide (1.16 g, 5.02 mmol) was dissolved in AR acetic acid (10 cm^3) and hydrogen peroxide (2 cm^3 , 30 wt% solution in water) added. The mixture was stirred for 3 h at 80 $^\circ\text{C}$. TLC (ethyl acetate–hexane 1 : 3) showed no starting material (R_f 0.75, UV active) and one product (R_f 0.35, UV active). The solvent was removed *in vacuo* and the residue dissolved in ethyl acetate (5 cm^3) and washed with distilled water (5 cm^3), brine (5 cm^3) and dried (MgSO_4). The solvent was removed *in vacuo* and the residue purified by flash chromatography (ethyl acetate–hexane 1 : 3) followed by recrystallisation (EtOH) to give 4-nitrophenyl phenyl sulfone (1.13 g, 86%) as a yellow crystalline solid, mp 137–139 $^\circ\text{C}$ (lit.,⁹ 140 $^\circ\text{C}$) (Found: C, 54.7; H, 3.1; N, 5.3. $\text{C}_{12}\text{H}_9\text{NO}_4\text{S}$ requires C, 54.75; H, 3.45; N, 5.32%).

Phenyl 4-nitrophenyl sulfoxide 8

4-Nitrophenyl phenyl sulfide (1.12 g, 4.84 mmol) was dissolved in freshly distilled THF (20 cm^3) and periodic acid (0.15 g, 5.08 mmol) was added. The mixture was stirred for 6 h at room temp. TLC (ethyl acetate–hexane 1 : 3) showed no starting material (R_f 0.75, UV active) and one product (R_f 0.2, UV active). The mixture was pre-adsorbed onto silica, purified by flash chromatography (ethyl acetate–hexane 1 : 2) and recrystallised (EtOH) to give 4-nitrophenyl phenyl sulfoxide (1.05 g, 88%) as a yellow crystalline solid (Found: C, 58.55; H, 3.4; N, 5.6. $\text{C}_{12}\text{H}_9\text{NO}_3\text{S}$ requires C, 58.29; H, 3.67; N, 5.66%).

Results and discussion

The voltammetric behaviour of **1** and **2** is considered first in the absence of light. Reversible one electron reductions in 0.1

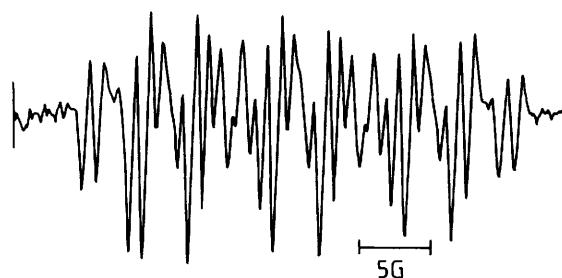


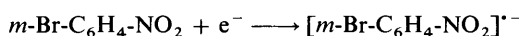
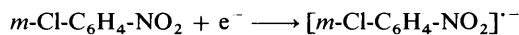
Fig. 1 EPR spectrum recorded simultaneously with electrolysis of **1** (*c.* 1.03 mol dm^{-3}) in acetonitrile–0.1 mol dm^{-3} TBAP solution and attributed to the radical anion $[\text{m-Cl-C}_6\text{H}_4\text{-NO}_2]^{-\bullet}$ formed at a Pt channel electrode whose potential was held at -1.2 V *vs.* an Ag pseudo-reference electrode

mol dm^{-3} TBAP–acetonitrile were observed with half-wave potentials (*vs.* SCE) of -1.08 (± 0.01) V (**1**) and -1.05 (± 0.01) V (**2**), respectively. Measurement of the steady-state transport limited current at a channel electrode as a function of the solution flow rate (V_f) revealed a cube root dependence in accordance with the Levich equation¹⁰ for a one electron reduction [eqn. (1)], where F is the Faraday constant, w is

$$I_{\text{lim}} = 0.925FD^{2/3}c_{\text{bulk}}wx_e^{2/3}(V_f/h^2d)^{1/3} \quad (1)$$

the electrode width, x_e the electrode length, d the channel cell width, $2h$ the cell depth, c_{bulk} the bulk concentration of the electroactive species and D its diffusion coefficient. Analysis of the slope of I_{lim} *vs.* $V_f^{1/3}$ plots gave a value of $(2.1 \pm 0.2) \times 10^{-5}$ $\text{cm}^2 \text{s}^{-1}$ for the diffusion coefficient of both **1** and **2**. The electrochemical reversibility of the electron transfer in each case was demonstrated by Tafel analysis¹¹ which gave values of (59.1 ± 0.3) and (61.9 ± 0.5) mV per decade for **1** and **2**, respectively.

The nature of the electrode process for the reduction of **1** and **2** in the absence of UV–VIS radiation was confirmed as a one-electron reduction leading to the radical anions,



by means of *in situ* electrochemical EPR experiments⁵ in which the channel electrode was located in the TE_{102} cavity of an X-band spectrometer and spectra recorded simultaneously with electrolysis at a potential of -1.2 V (*vs.* SCE). Figs. 1 and 2 show the EPR spectra derived from the electrolysis of **1** and **2** which are attributable to their respective radical anions,¹² as evidenced by measurement of the associated coupling constants. The absence of any signals attributable to the nitrobenzene radical anion, together with the observed agreement with eqn. (1) at all flow rates studied, confirms the stability of the radical anions on the channel electrode timescale; we concur with previous reports stating that any decay of these species must occur with a first order rate constant of *ca.* $5 \times 10^{-3} \text{ s}^{-1}$ or less.¹²

As a final preliminary to the photoelectrochemical work, the UV–VIS spectra of the radical anions of **1** and **2** were recorded in acetonitrile using an OTTL cell.⁶ Two bands were seen in each case in the spectral range 300 to 600 nm as follows: $[\text{m-Cl-C}_6\text{H}_4\text{-NO}_2]^{-\bullet}$; $\lambda_{\text{max}} = 323$ nm ($\epsilon = 8300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and $\lambda_{\text{max}} = 440$ nm ($\epsilon = 1900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$); $[\text{m-Br-C}_6\text{H}_4\text{-NO}_2]^{-\bullet}$; $\lambda_{\text{max}} = 320$ nm ($\epsilon = 2600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and $\lambda_{\text{max}} = 476$ nm ($\epsilon = 1400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The parent molecules display negligible absorption above 300 nm in the case of **1** and **2**.

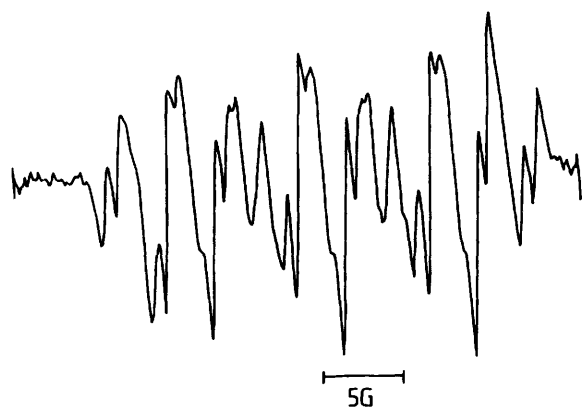


Fig. 2 EPR spectrum recorded simultaneously with electrolysis of **1** (c $0.98 \text{ mmol dm}^{-3}$) in acetonitrile- 0.1 mol dm^{-3} TBAP solution and attributed to the radical anion $[m\text{-Br-C}_6\text{H}_4\text{-NO}_2]^\bullet-$ formed at a Pt channel electrode whose potential was held at $-1.2 \text{ V vs. an Ag pseudo-reference electrode}$

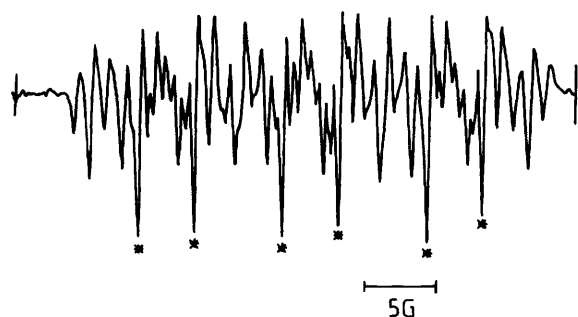


Fig. 3 EPR spectrum recorded simultaneously with electrolysis of **2** (c $0.98 \text{ mmol dm}^{-3}$) using the conditions given above, in the presence of argon ion laser light (488 nm). The asterisks denote the six strongest new lines which, in comparison with Fig. 2, appear as a result of photolysis of the radical anion.

The effect of light on the electro-reduction of **1** and **2** was first investigated by means of *in situ* electrochemical EPR experiments in which the channel electrode was irradiated with laser light (488 nm). Fig. 3 shows that the introduction of light depletes the intensity of the $[m\text{-Br-C}_6\text{H}_4\text{-NO}_2]^\bullet-$ radical anion whilst new spectral signals become evident. In particular six strong new lines (marked * in Fig. 3) become apparent. These were attributed to the radical anion $[\text{Ph-NO}_2]^\bullet-$ as was confirmed by the electrogeneration of this species directly from nitrobenzene in a separate experiment by electrolysis at -1.20 V vs. SCE . The coupling constant to the nitrogen atom measured in both cases was found to be 10.3 G , in good agreement with that quoted in earlier work.¹³ It may be concluded that, as in the case of the *para*-isomer, the photoelectrochemical reduction of **2** leads to the formation of $[\text{Ph-NO}_2]^\bullet-$. In contrast the EPR spectrum of the radical anion electrogenerated from **1** showed little change when compared to that observed in the dark.

Next current-voltage curves were recorded in the presence of light and the magnitude of the transport limited current was found to be enhanced in comparison with eqn. (1). Action spectra were measured by potentiostatting the channel electrode at a value corresponding to the transport limited reduction of **1** or **2** and recording the photocurrent as a function of excitation wavelength in the range 300 to 600 nm using a monochromated xenon arc lamp source at a fixed electrolyte flow rate of $2.3 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ in acetonitrile media. The results are shown in Figs. 4 and 5 which reveal that wavelengths corresponding to the absorption bands of the radical anions of **1**

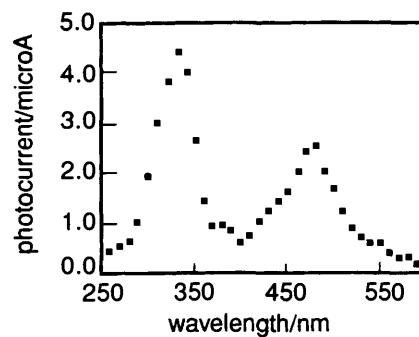


Fig. 4 Photocurrent spectrum for the reduction of **1** (c $0.96 \text{ mmol dm}^{-3}$) in 0.1 mol dm^{-3} TBAP-acetonitrile measured at a Pt channel electrode. The current scale represents the extra current seen under conditions of irradiation.

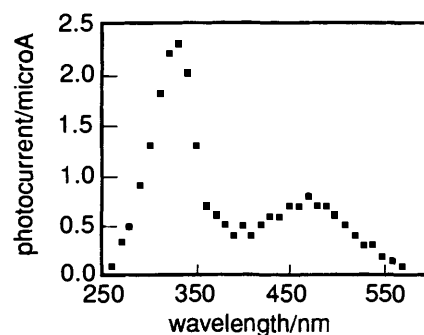


Fig. 5 Photocurrent spectrum for the reduction of **2** (c 1.04 mol dm^{-3}) in 0.1 mol dm^{-3} TBAP-acetonitrile measured at a Pt channel electrode. The current scale represents the extra current seen under conditions of irradiation.

and **2** correspond to maximum photocurrent. Qualitatively the action spectra reflect the measured absorption spectra of the two radical anions so confirming that the photocurrent results from the absorption of light by these species. Mechanistic insight was pursued by means of measurements of the photocurrent as a function of electrolyte flow rate through the channel electrode under conditions where the electrode was irradiated with light of wavelength either 330 or 480 nm corresponding to photocurrent maxima (Figs. 4 and 5). Experiments were carried out in the flow rate range 10^{-4} to $10^{-1} \text{ cm}^3 \text{ s}^{-1}$ and for varying concentrations of electroactive substrate between 0.6 and 2.0 mmol dm^{-3} . The data were analysed in terms of an ECE mechanism, as is known to operate for the corresponding *para*-isomers and which is consistent with the observations reported above. The theoretical basis for such analysis has been developed¹⁴ and the effective number of electrons transferred under irradiation, defined in eqn. (2) is a unique function of the

$$N_{\text{eff}} = \frac{\text{Total limiting photocurrent}}{\text{Total dark limiting current}} \quad (2)$$

dimensionless rate constant [eqn. (3)], where k is the first-order

$$K = k\{4h^4x_e^2d^2/9V_f^2D\}^{1/3} \quad (3)$$

rate constant which describes the C-step—steps (b) and (b')—of the ECE process. Established theory¹⁴ permits the generation of 'working curves' which facilitate the analysis of the photocurrent-flow rate data by relating N_{eff} to K . Thus, experimental photocurrents are thus first converted into N_{eff} values which are then used to deduce corresponding values of K . Finally K is plotted against $(\text{flow rate})^{-2/3}$, as suggested by the form of eqn. (3). If a good linear dependence is observed, then

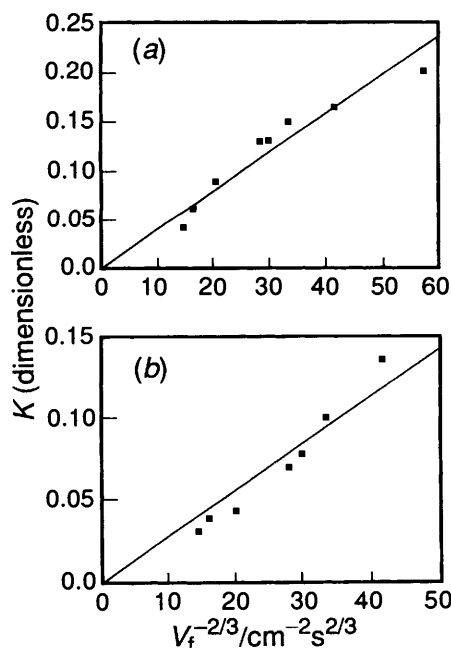


Fig. 6 Plots of the dimensionless rate constant, K , against $(\text{flow rate})^{-2/3}$ for the analysis of photocurrent data obtained for **1** at wavelengths of (a) 330 and (b) 480 nm. The concentration of **1** was $1.91 \text{ mmol dm}^{-3}$ (in 0.1 mol dm^{-3} TBAP-acetonitrile solution) and the cell geometry defined by $h = 0.0405 \text{ cm}$, $x_c = 0.386 \text{ cm}$, $d = 0.6 \text{ cm}$ and $w = 404 \text{ cm}$.

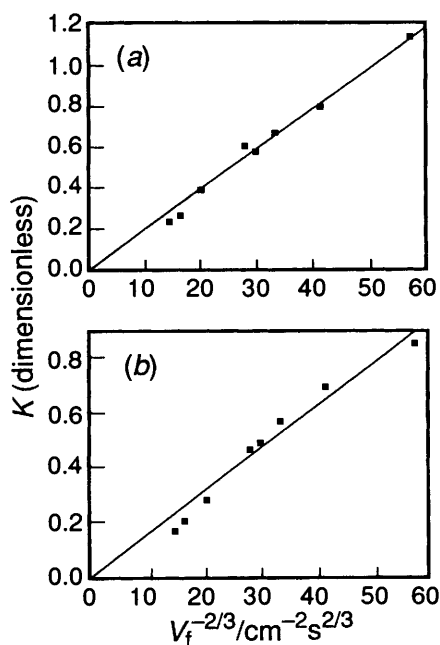


Fig. 7 Plots of the dimensionless rate constant, K , against $(\text{flow rate})^{-2/3}$ for the analysis of photocurrent data obtained for **2** at wavelengths of (a) 330 and (b) 480 nm. The concentration of **1** was $0.847 \text{ mmol dm}^{-3}$ (in 0.1 mol dm^{-3} TBAP-acetonitrile solution) and the cell geometry defined by $h = 0.0400 \text{ cm}$, $x_c = 0.386 \text{ cm}$, $d = 0.6 \text{ cm}$ and $w = 0.404 \text{ cm}$.

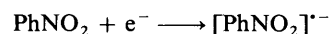
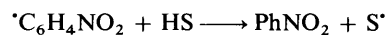
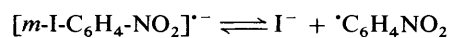
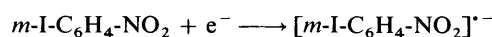
the data is consistent with the operation of an ECE mechanism. Figs. 6 and 7 show representative data at the two wavelengths studied. The required linear dependence is seen and a photo-ECE mechanism may be inferred to operate. The gradient of plots such as Figs. 6 and 7 permit the deduction of rate constants for the light induced dehalogenation at the light intensity studied (20 mW cm^{-2}). These are given in Table 1.

Table 1 Dehalogenation rate constants

| Species | $k(\lambda = 330 \text{ nm})/\text{s}^{-1}$ | $k(\lambda = 480 \text{ nm})/\text{s}^{-1}$ |
|---|---|---|
| <i>m</i> -Cl-C ₆ H ₄ -NO ₂ | $(3.2 \pm 0.5) \times 10^{-2}$ | $(2.2 \pm 0.4) \times 10^{-2}$ |
| <i>m</i> -Br-C ₆ H ₄ -NO ₂ | $(1.2 \pm 0.2) \times 10^{-1}$ | $(1.0 \pm 0.3) \times 10^{-1}$ |
| <i>m</i> -I-C ₆ H ₄ -NO ₂ ^a | $(3.7 \pm 0.05) \times 10^{-1}$ | $(4.0 \pm 0.05) \times 10^{-1}$ |

^a The rate constants for the iodo-species are a composite of the dark and light induced dehalogenation.

We next consider the reduction of **3**. In 0.1 mol dm^{-3} TBAP-acetonitrile solution a reduction potential of -1.09 V (vs. SCE) was observed in the dark. However, rather more than one electron was passed per molecule as assessed by eqn. (1). *In situ* electrochemical EPR experiments clearly demonstrated the formation of the nitrobenzene radical anion so it was inferred that **3** undergoes an ECE-type reduction analogous to that proposed above for the elimination of halide from the bromo- and chloro-isomers but without the need for photochemical activation:



p-Iodonitrobenzene is known¹⁴ to undergo a similar reaction. The kinetics of this process were investigated using a channel electrode by means of current-flow rate analysis and the same procedure as given above and the rate constant for the 'dark' dehalogenation of **3** was found to be $(3.0 \pm 0.05) \times 10^{-1} \text{ s}^{-1}$ using an assumed diffusion coefficient of $2.1 \times 10^{-5} \text{ s}^{-1}$. This value was checked by independent experiments using platinum microdisc electrodes of different radii (5, 13, 30 and $60 \mu\text{m}$) under diffusion-only conditions for which it has been shown that an ECE process is characterised by the approximate eqn. (4),¹⁵ where Δn (< 1) represents the increase in the effective

$$(\Delta n)^{-1} = (4/\pi)\{D/kr^2\}^{1/2} + 1 \quad (4)$$

number of electrons passed over and above unity, as a result of the ECE process. The rate constant so-determined was in exact agreement with the value of $3.0 \times 10^{-1} \text{ s}^{-1}$ deduced from channel electrode measurements.

When the reduction of **3** was studied under conditions where the electrode was irradiated with light in the wavelength range 300–600 nm, increased currents were observed to flow and the action spectrum shown in Fig. 8 resulted. This is qualitatively similar to that seen for **1** and **2** and it may be indirectly inferred that the radical anion of **3** has absorption bands close to 330 and 480 nm. Note that since the radical anion decays in the absence of light, the OTTLE technique cannot be used to record the absorption spectrum directly. The kinetics of the light assisted process was investigated by means of photocurrent-flow rate studies and the resulting data successfully analysed in terms of a photo-ECE process. Table 1 shows the size of the rate constant (at a light intensity of 20 mW cm^{-2}) inferred for the joint 'dark + light' dehalogenation process.

The results reported above demonstrate that the halide anions Cl^- , Br^- and I^- can be removed from the corresponding *meta*-halonitrobenzenes in a fashion analogous to that found to operate for the corresponding *para*-isomers.^{1,2} It is of interest to ask whether other groups may be encouraged to leave substituted nitrobenzenes by means of dual photochemical and

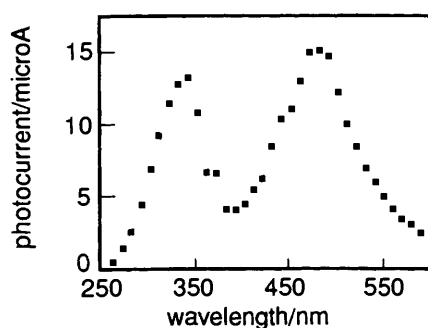


Fig. 8 Photocurrent spectrum for the reduction of **3** (c 1.02 mmol dm⁻³), in 0.1 mol dm⁻³ TBAP-acetonitrile solution, measured at a Pt channel electrode. The current scale represents the extra current seen under conditions of irradiation.

electrochemical activation. We consider first species **4** and **5**. These were found to undergo one-electron reduction in acetonitrile-0.1 mol dm⁻³ TBAP with half-wave potentials (*vs.* SCE) of -0.90 and -0.80 V, respectively. In both cases a stable radical anion was generated. The absorption spectra were measured using an OTTLE cell. The following absorption bands above 300 nm were recorded: [*p*-NC-C₆H₄-NO₂]^{-•}; $\lambda_{\max} = 334$ nm ($\epsilon = 17\,000$ dm³ mol⁻¹ cm⁻¹) and $\lambda_{\max} = 558$ nm ($\epsilon = 3100$ dm³ mol⁻¹ cm⁻¹); [*p*-NO₂-C₆H₄-NO₂]^{-•}; $\lambda_{\max} = 454$ nm ($\epsilon = 31\,000$ dm³ mol⁻¹ cm⁻¹).

However, attempts to induce photocurrents by means of irradiation using either the xenon arc lamp source or the argon ion laser were entirely unsuccessful; no photocurrents were observed to flow at any solution flow rate (in the range 10⁻⁴ to 10⁻¹ cm³ s⁻¹) or excitation wavelength (in the range 300 to 600 nm) employed. It was concluded that the radical anions of **4** and **5** were much more stable to photolysis than the corresponding radical anions of **1-3**.

Finally we consider the sulfones and sulfoxides **6-9**. These were studied in DMF-0.1 mol dm⁻³ TBAP solution since surface/adsorption effects were found to interfere with the voltammetry in acetonitrile solution. The half-wave potentials (measured *vs.* Ag) required to reduce these species were -0.8 V (**6**), -0.45 V (**7**), -0.8 V (**8**) and -0.55 V (**9**). Eqn. (1) suggested in each case that the electrode process at these voltages corresponded to a one electron process and the formation of the radical anions was inferred. However photoelectrochemical experiments in which the electrode was irradiated by light of wavelengths between 300 and 600 nm failed to observe any photocurrents whatsoever.

In conclusion the results given above and elsewhere¹ demonstrate that the dehalogenation of halonitrobenzenes may be efficiently achieved by means of dual photo- and electrochemical activation. The process appears specific to the loss of halide; the groups -CN, -NO₂, -SO-R or -SO₂-R cannot be lost in an analogous fashion. This may reflect interaction of

the lone pair of electrons on the halogen substituent with the π -electron system of the molecule possibly reducing the energy difference between the π^* orbital in which the odd electron resides in the radical anion and the σ^* antibonding C-Hal orbital to which the electron has to be transferred to stimulate fragmentation. We presume that in the cases where no fragmentation occurs, the excitation energy of the radical anion is lost through collisional deactivation by the solvent.

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