

The Photoelectrochemical Oxidation of Bis(benzylidene)acenaphthene

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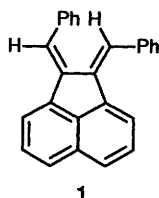
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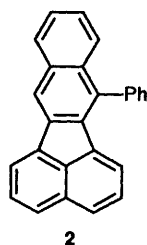
The oxidation of bis(benzylidene)acenaphthene in acetonitrile solution at platinum electrodes irradiated with light (377 nm) has been investigated using a combination of channel electrode and spectrofluorimetric voltammetries. The efficient formation of the highly fluorescent molecule 7-phenylbenzo[*k*]fluoranthene was demonstrated and the electrode reaction mechanism characterised as of the 'photo-CE' type. Kinetic parameters relating to this process are reported.

We have previously shown that photoelectrochemical reactions taking place at metallic electrodes can be mechanistically probed using channel electrodes.¹ In particular, the mass transport dependence of photocurrents measured over a wide range of solution flow rates can effectively discriminate between candidate mechanisms and provide kinetic parameters. This experimental protocol has been successfully applied to demonstrate the existence of photochemical analogues of the familiar mechanistic types of 'dark' electrochemistry such as CE,² ECE/DISP,^{3,4} and EC' (catalytic)⁵ processes. Recently we have extended this general methodology by the addition of *in situ* fluorescence spectroscopy to probe the nature and concentration of reaction intermediates and products.^{6,7}

In this paper we present the first application of this combined strategy, namely, the demonstration and mechanistic investigation of a new photoelectrooxidation, that of bis(benzylidene)acenaphthene (BBAN), drawn as the *E,Z*-isomer in **1**, in aceto-



nitrile solution at platinum electrodes. It will be shown that efficient conversion into the highly fluorescent molecule 7-phenylbenzo[*k*]fluoranthene (**2**) takes place *via* a 'photo-CE' mechanism. Kinetic and other mechanistic parameters will be derived and spectrofluorimetric properties of **2** reported.



Experimental

Platinum foil electrodes (approximate dimensions 4 mm × 4 mm) were supplied by Goodfellow Advanced Materials to a purity of 99.95% and thickness 0.025 mm. Channel flow cells were constructed in optical quality synthetic silica (Suprasil 2) by Heraeus Silica and Metals Ltd, Weybridge, UK. The cover

plates were cemented to the channel units using a low melting wax (Vychem Ltd., Poole, UK) which gives excellent adhesion to silica, melts at 50 °C, dissolves in ethanol for cell dismantling/cleaning and gives a good seal for acetonitrile. Assembled cells had approximate dimensions 6 mm (channel width) × 0.4 mm (depth) × 45 mm (length). There was ample length of cell upstream of the electrode to permit the development of full laminar flow in the region of the electrode and downstream of it. Flow cells were incorporated into a gravity-fed flow system capable of delivering volume flow rates in the range $10^{-4} < V_f/\text{cm}^3 \text{ s}^{-1} < 10^{-1}$. A reference electrode (saturated calomel or a silver wire) was positioned a short distance upstream of the working electrode.

Electrochemical measurements employed a potentiostat and scan generator (Oxford Electrodes, Oxford, UK) modified so that the counter electrode (a platinum gauze located downstream of the electrode) voltage was boosted.⁸ The LS50 luminescence spectrometer was controlled by an Epon PC-AX2e personal computer. Flow cells were located and calibrated in the spectrometer using the methods described previously;^{6,7} the exciting beam of the spectrometer probed an area 1 mm × 9 mm immediately downstream of the electrode surface and entered the cell from the wall opposite that carrying the foil electrode. The system was capable of measuring luminescence induced by excitation between wavelengths 200 and 800 nm. UV-VIS spectra were recorded on a Perkin-Elmer lambda-5 spectrometer. Photochemical conversion of BBAN within the flow system was accomplished by focusing the output of a 20 W mercury lamp on to the glass tubing leading into the flow cell. Mechanistic photoelectrochemical work used the output of a xenon lamp focused onto the channel electrode; the beam intensity was measured using an International Light IL 700 photometer with quartz neutral density filters, and a silicon photo-cell (MS4B, Plessey, UK).

Tetrabutylammonium perchlorate (TBAP), (Fluka, purum) and acetonitrile (Fisons, dried, distilled) were used as received. Bis(benzylidene)acenaphthene (BBAN) was prepared by dehydration of the related ditertiary alcohol according to a literature method⁹ m.p. 146–147 °C (lit.,⁹ 142 °C) (Found: C, 94.4; H, 5.5. C₂₆H₁₈ requires C, 94.47; H, 5.53%). The *E,E*-structure is assumed in ref. 10 for a compound m.p. 170–172 °C obtained by hydrogenation of a tris(triphenylphosphine)rhodium complex of 1,8-bis(phenylethynyl)naphthalene. ¹³C NMR spectroscopy at 100.6 MHz on the present compound indicates that it has the *E,E*-configuration, only 12 signals are detected (139.0, 138.4, 137.6, 136.5, 131.1, 128.9, 128.7, 127.7, 127.4, 124.9, 122.8 and 119.2 ppm relative to Me₄Si). Typically, experimental solutions were made up to the desired concentration in acetonitrile solution containing 0.1 mol dm⁻³ TBAP as

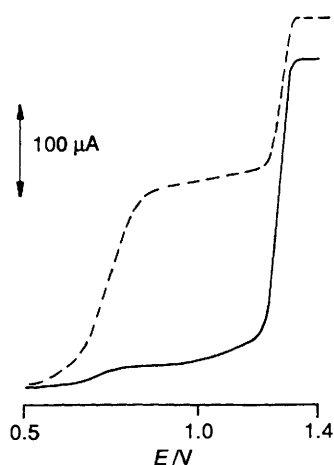


Fig. 1 A channel electrode steady-state voltammogram obtained for the oxidation of BBAN in the absence of light (—) and in the presence of 377 nm radiation (---) of intensity 40 mW cm^{-2} . The flow rate used was $1.5 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ and $[\text{BBAN}] = 0.29 \text{ mmol dm}^{-3}$.

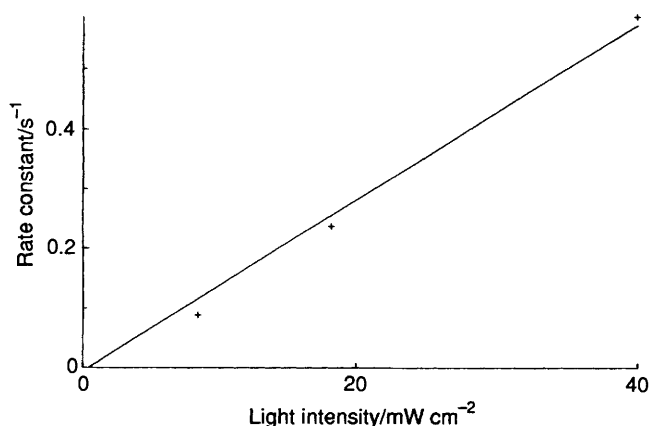


Fig. 2 The linear dependence of the deduced first order rate constant within a CE mechanism, on the light intensity incident on the electrode surface. The error in all three rate constants was estimated as $\pm 10\%$.

supporting electrolyte. Solutions were de-gassed with oxygen-free argon prior to use.

Results and Discussion

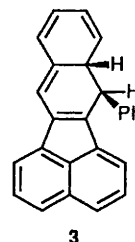
First experiments were conducted on the oxidation of BBAN in the absence of light using a platinum channel electrode. A two-electron oxidation process with a half-wave potential, $E_{1/2} = 1.23 \text{ V}$ (*vs.* silver) was observed. Mass transport variation of the diffusion limited current at the channel electrode enabled the calculation of the diffusion coefficient of BBAN (**1**) as $D = 1.59 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ through application of the Levich equation (1), where F is the Faraday constant

$$I_{\text{lim}} = 0.925nF[\text{BBAN}]_{\text{bulk}}\omega x_c^{2/3}D^{2/3}\left(\frac{V_f}{h^2d}\right)^{1/3} \quad (1)$$

and $n = 2$. Cyclic voltammetry showed the oxidation to be chemically irreversible but that no protons were released during the oxidation in the absence of light. No further investigations into the nature of the 'dark' electrochemistry were conducted.

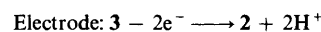
For simplicity in the discussion we shall assume that the structure is as given in **1** and that cyclisation results from irradiation of this form. The arguments that follow are unaffected by the possibility that the starting material is of *E,E*-configuration and that this is first transformed photochemically

into the *E,Z*-form followed by a further photochemical reaction (two successive one-quantum processes). Irrespective of this possibility it is known¹⁰ that irradiation of BBAN (**1**) in the presence of atmospheric oxygen as oxidising agent effects the conversion of **1** to **2**: absorption of light leads to electrocyclic reaction, presumably by conrotation with the formation of **3**, which would be subsequently aerially oxidised to **2**.



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Experiments in which BBAN (**1**) was irradiated in the flow system produced a red colouration—as expected¹⁰ for the conversion of **1** to **2**—which was destroyed on electrolysis. Accordingly, the following mechanism (Scheme 1) was in-



Scheme 1

vestigated as the likely basis for the photoelectrochemical reaction seen when the electrode was irradiated in which the electrode mimics the previously reported behaviour of dissolved oxygen.

Preliminary photoelectrochemical experiments were conducted using monochromated light of 377 nm from a xenon lamp focused onto the electrode within the channel flow cell under de-oxygenated conditions and a 'prewave', cathodic of the voltammetric wave seen in the dark, was observed as shown in Fig. 1. This wave increased in height as the solution flow rate was reduced and/or the light intensity enhanced. Photocurrents corresponding to the transport limited part of the 'prewave' were measured as a function of the mass transport. The latter was analysed in terms of the now well-established theory for a photochemical CE process¹¹⁻¹³ and the mechanism unambiguously determined, provided the possibility of different diffusion coefficients of reactant and product in the chemical step were allowed for. Excellent agreement was found between theoretical and experimental photocurrents for a range of concentrations $0.29 < [\text{BBAN}] < 0.47 \text{ mmol dm}^{-3}$, the range of flow rates specified above and a factor of five-fold in light intensity incident on the flow cell. A single rate constant of 0.59 s^{-1} for the photochemical conversion of BBAN into the electroactive form (light intensity of 39.8 mW) was found to fit all the data, corresponding to a quantum yield of 0.14 ± 0.01 and a diffusion coefficient for the chemical reaction product of $2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was deduced. Fig. 2 shows how the measured first-order rate constant for the preceding chemical step—deduced from our modelling—depended on the light intensity. The excellent straight line graph provides further confirmation of the existence of a CE mechanism in the case under study.

The proposed CE mechanism was additionally supported by the observation that cyclic voltammetry under irradiation, but with no flow, shows the formation of significant levels of protons accompanying the electrooxidation $\mathbf{3} \longrightarrow \mathbf{2}$ as shown in Fig. 3.

Species **2** was found to be highly fluorescent as shown by the spectra in Fig. 4. Under extreme conditions of very slow flow and ultra-high light intensity, quantitative conversion under the *ex situ* experimental conditions could be accomplished (but not

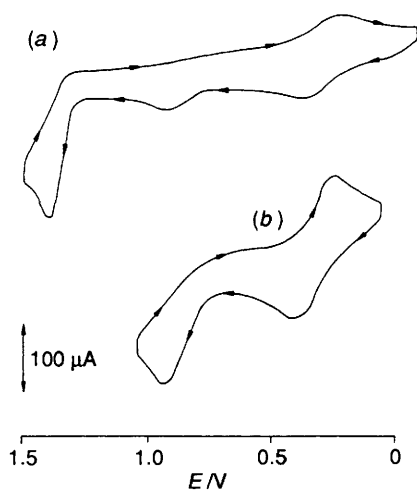


Fig. 3 Cyclic voltammograms for the oxidation of BBAN in (a) the absence of light and (b) the presence of light showing the formation of protons (H^+) which are electroreduced at ca. $+0.2$ V (vs. Ag). Note that (a) suggests a small extent of photochemical reaction: this arises from slight adventitious illumination of the flow system upstream of the channel electrode cell.

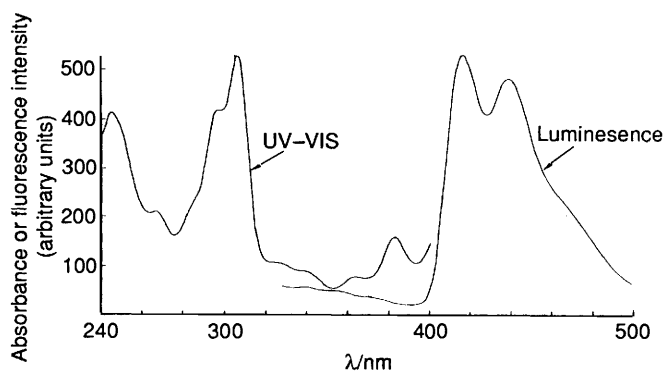


Fig. 4 The fluorescence spectrum of **2** obtained by excitation at 307 nm. Also shown is the UV-VIS absorption spectrum.

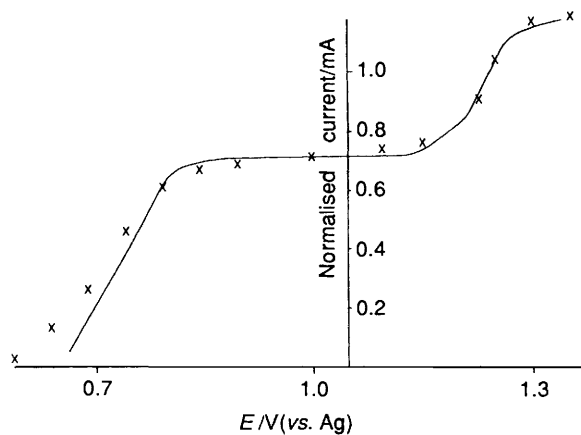


Fig. 5 Simulated channel electrode voltammograms for the oxidation of BBAN in the presence (—) of light (377 nm). The crosses (x) represent experimental data points for $[BBAN] = 0.476$ mmol dm^{-3} and a flow rate of 0.00133 cm^3 s^{-1} as used in the simulation. The current has been normalised relative to that found for the dark electrochemical wave.

in the fluorescence work described below) from which it could be deduced, *via* eqn. (1), that D had a diffusion coefficient of 2.3×10^{-5} cm^2 s^{-1} in complete agreement with that deduced separately from the modelling of the experimental data measured at faster flow rates and lower light intensities.

As a sensitive test of our reaction model the voltammetric

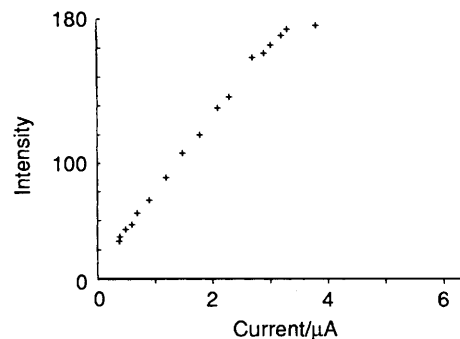


Fig. 6 The variation of the fluorescence intensity (arbitrary units) as a function of current as the electrode potential is swept through the 'prewave' and onto the voltammetric oxidation seen in the dark

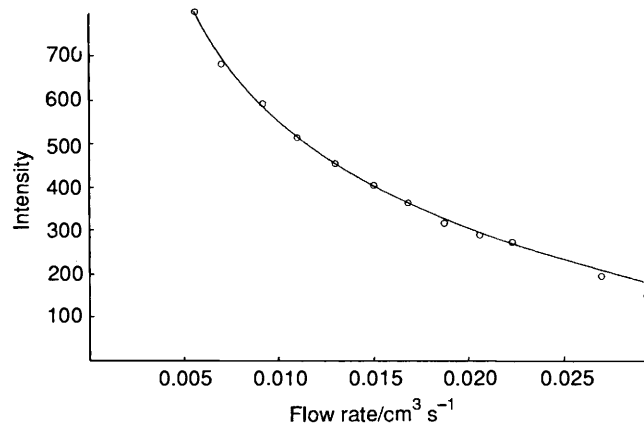


Fig. 7 The dependence of the fluorescence intensity (arbitrary units) on the electrolyte flow rate. The solid line (—) shows the expected behaviour computed using the mechanism outlined in the text and the circles (○) the experimental points for $[BBAN] = 0.124$ mmol dm^{-3} , $x_c = 0.451$ cm, $w = 0.268$ cm and $2h = 0.032$ cm.

wave shapes in the presence and absence of light were simulated at various flow rates using existing theory¹⁴ and the rate constant and diffusion coefficients given above. Fig. 5 shows the excellent agreement obtained and further confirms our mechanistic conclusions.

We turn now to spectrofluorimetric voltammetry in which partial conversion of BBAN into **3** was accomplished by irradiation of the flow system prior to entry into the fluorescence flow cell. The current flowing at the electrode was used to determine the extent of photochemical conversion using eqn. (1). The amount of **2** leaving the electrode surface was then detected *via* fluorescence measurements. Fluorescence intensity for electrode potentials corresponding to the 'prewave' were recorded as a function of mass transport and of the electrode current. Fig. 6 shows how, for a fixed flow rate, the fluorescence intensity varies with generating current. It can be seen that for currents between 0 and 6.2 μA a linear relationship is observed but that at higher currents a plateau is reached. The former corresponds to currents on the prewave and the latter to currents on the voltammetric wave seen in the dark. Fig. 6 clearly shows that whilst the photochemically-induced prewave generates the fluorescent material **2**, the nature of the dark electrode process is qualitatively different and that no **2** is generated. Fig. 7 shows the variation of the fluorescence signal intensity as a function of flow rate for the case where the electrode potential is held at a value corresponding to the transport limited conversion of **3** \rightarrow **2**. Also shown is the theoretically computed behaviour calculated using the Backwards Implicit Finite Difference method¹⁴ outlined above for the experimental cell geometry, the diffusion coefficient of **3** as deduced above, the known extinction coefficient of **2** and its

quantum yield for fluorescence,⁷ and the electrode current observed for the conversion of **3** to **2**. Concentrations of BBAN up to 0.19 mmol dm⁻³ were employed and the excellent agreement shown in Fig. 7 is typical. It will be apparent from that figure which relates to a concentration of BBAN of 0.13 mmol dm⁻³ that the fluorescence experiment is capable of detecting very small amounts of electrogenerated material leaving the electrode surface. In particular, quantitative results were found to be possible for electrode currents as low as 0.2×10^{-6} A corresponding to concentrations of **3** as little as 0.5 mmol dm⁻³ at the electrode surface.

The simultaneous fluorescence/voltammetry experiment thus provides excellent confirmation that the deductions made from the channel electrode work are correct.

Conclusions

The photoelectrooxidation of BBAN proceeds through a 'photo-CE' mechanism and produces the highly fluorescent material **2**.

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