# The Photo-CE Mechanism: the Oxidation of Tris-(*p*-tolyl)amine in Acetonitrile at an Illuminated Platinum Electrode

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The oxidation of tris-(*p*-tolyl)amine (A) has been studied in acetonitrile solution using a channel electrode flow cell. In the dark a simple reversible one-electron oxidation to the corresponding (stable) radical cation is observed. However on irradiation with light of wavelength 300 nm a 'pre-wave' is additionally seen *ca*. 200 mV cathodic of the simple 'dark' process. Action spectrum measurements, preparative experiments and photocurrent/solution flow rate data are used to show that this process has the kinetic characteristics of a 'photo-CE' reaction in which the product of a photochemical pre-equilibrium involving A undergoes a disproportionation reaction forming an electroactive species. The nature of the species involved is deduced and a detailed mechanistic scheme presented. Rate and equilibrium constants are estimated. The 'photo-CE' reaction is shown to have the unusual property for an electrode reaction at a channel electrode that the photocurrents decrease with solution flow rate.

Whilst an extensive literature exists on the separate use of photochemical and electrochemical activation of organic molecules to bring about chemical reaction, reports of their simultaneous use are fragmentary and essentially limited to work on the photochemistry of ion radicals. To date, the best example of the latter is the so-called 'photo-benzidine' rearrangement discovered by Swanholm and Parker<sup>1</sup> who found that cation radicals of tetraphenylbenzidine on irradiation with visible light rearrange into N,N'-diphenylbenzidine, in contrast to the parent molecule which dissociates to form diphenylamine. The remaining examples accrue from, first, the work of Moutet and Reverdy<sup>2</sup> who showed that excited ion radicals can undergo electron transfer reactions and, secondly, from studies by Lund and Carlsson<sup>3</sup> who used a micro-electrode continuously irradiated by a laser to examine the behaviour of the radical anions of pyrene and perylene and the thianthrene radical cation. Further developments in the area have been hampered by suitable methodology: the interpretation of the photocurrent data in Lunds' experiments were hampered owing to contributions from local heating inducing uncertain and unquantifiable thermal convection. This problem has been resolved and we have shown<sup>4-7</sup> that channel electrodes are ideally suited for the mechanistic study of photoelectrochemical reactions at metallic electrodes, particularly via photocurrent/solution flow-rate measurements, combined with action spectra data and sometimes simultaneous electron spin resonance or UV-visible spectroscopic experiments.

In this paper we continue our search for new chemistry and intermediates arising from dual photochemical and electrochemical activation, and focus on the oxidation, at platinum, of tris-(*p*-tolyl)amine (A) in acetonitrile solution:



The oxidation of this molecule in the dark has been fully studied and shown to yield the stable radical cation,  $A^+$ . The work described here shows that on irradiation the reaction pathway is altered resulting in the (partial) oxidation of A at a lower potential than is observed in the dark. This is found to result from a new electroactive species formed in a photochemically driven disproportionation reaction so that overall this low-potential reaction has the kinetic characteristics of what in dark electrochemistry would be regarded as a CE reaction. The work presented in this paper thus constitutes the first reported example of a 'photo-CE' mechanism.

## **Experimental**

The basic apparatus and experimental techniques have been described previously.<sup>3</sup> The silica channel electrode unit was 30 mm long and had approximate cross-sectional dimensions of 0.4 mm  $\times$  6.0 mm. Platinum electrodes, of dimensions 4.0 mm  $\times$  4.0 mm, were cemented to the silica cover plate and polished flat before use, with a succession of finer diamond lapping compounds down to 0.25 µm.

In the particular case of measurements under no-flow conditions the flow cell was modified as previously<sup>4</sup> 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 was either quantitatively electrolysed, for example to provide a large quantity of the stable radical cation,  $A^+$ , or subjected to cyclic voltammetry in the presence or absence of light.

Electrochemical measurements were carried out using an Oxford Electrodes potentiostat modified to boost the counter electrode voltage.<sup>9</sup> A silver wire pseudo-reference electrode, or a saturated calomel electrode was positioned in the flow upstream of the channel electrode and a platinum gauze counter electrode was located downstream. Flow rates in the range  $10^{-4}$ - $10^{-1}$  cm<sup>3</sup> s<sup>-1</sup> were employed.

Photochemical irradiation was provided by a Wotan XBO 900 W/2 xenon arc lamp via a Jarrell-Ash 82-410 grating

UV-visible spectroelectrochemistry was carried out either with an optically transparent thin-layer electrode cell (OTTLE), described fully elsewhere,<sup>7</sup> or with standard silica cells, and spectra were recorded on a Perkin-Elmer Lambda-5 spectrophotometer.

Acetonitrile (Fisons' dried distilled) was refluxed with calcium hydride and fractionally distilled. Tetrabutylammonium perchlorate, TBAP, (Fluka, purum.) was recrystallised once from a mixture of ethanol and petroleum ether. Tris-(p-tolyl)amine was prepared using a literature method.<sup>10</sup> Electrolysis was performed in acetonitrile solution containing 0.1 mol dm<sup>-3</sup> of TBAP as supporting electrolyte. Where necessary, solutions were purged of oxygen by outgassing with nitrogen (prepurified of trace oxygen and dried) prior to electrolysis.

The products of preparative experiments (see below) were isolated by removal of the solvent *in vacuo*, sonication of the residue with ether, filtration and, finally, removal of the ether, also *in vacuo*. Analysis was 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 the identity of the GC peaks was confirmed by mass spectrometry (VG 7070E).

Supporting theory was generated from programs written in FORTRAN 77 on a VAX 11/785 mainframe computer, using NAG 11 library routines.

### **Results and Discussion**

We consider first the behaviour in the dark of a A towards electrochemical oxidation in acetonitrile solution at a platinum electrode. Current-voltage (I/E) curves were recorded at a channel electrode as a function of electrolyte flow rate for solutions  $1 \times 10^{-3}$  mol dm<sup>-3</sup> in A. Analysis of the oxidation waves was consistent with a reversible one-electron oxidation. This was evidenced first by mass-transport corrected Tafel analysis:<sup>11</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 and a standard electrode potential of 0.83 V (vs. saturated calomel electrode; 1.05 V vs. Ag). 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 oxidation),

$$I_{\rm lim} = 1.165 \times (96\,485) D_c^{2/3} U^{1/3} h^{-1/3} w x_e^{2/3} [A]_0 \tag{1}$$

where  $U (\text{cm s}^{-1})$  is the mean solution velocity,  $D_e (\text{cm}^2 \text{ s}^{-1})$  is the diffusion coefficient, h (cm) is the half-height of the cell and w (cm) and  $x_e (\text{cm})$ , respectively, are the width and the length of the electrode. [A]<sub>0</sub> (mol cm<sup>-3</sup>) is the bulk concentration of A. Both the measured standard electrode potential and the diffusion coefficient  $(1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$  were in good agreement with the literature values.<sup>8</sup>

It may therefore be concluded, on the basis of the above and other observations,<sup>8</sup> that the electrode process, in the dark, is:

$$\mathbf{A} - \mathbf{e}^{-} \rightleftharpoons \mathbf{A}^{+} \tag{I}$$

and that under these conditions both A and  $A^+$  are stable.

As a preliminary to the photoelectrochemical experiments the absorption spectrum of A was measured; this is shown in Fig. 1. The spectrum of  $A^+$  was found using an OTTLE as described above and found to be as reported in the literature.<sup>12</sup>

Photoelectrochemical experiments were next conducted using the channel electrode cell modified as described above for no-flow conditions so as to minimise convection in/out of

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the cell. In addition, the cell was masked so that only the electrode area was irradiated. Cyclic voltammetry was then carried out in the presence and absence of light of a wavelength in the range 250-350 nm. Typical results are shown in Fig. 2. In the dark [Fig. 2(a)] a typical reversible oxidation, at 1.05 V (vs. silver pseudo-reference electrode), can be seen (slightly distorted through ohmic drop in the channel cell),



Fig. 2 Cyclic voltammetry, carried out in the modified flow cell, at 50 mV s<sup>-1</sup>, on an acetonitrile solution containing  $1 \times 10^{-3}$  mol dm<sup>-3</sup> A. The different voltammograms correspond to: (a) the first scan, starting from 0.5 V, in the absence of light; (b) the first scan, starting from 0.5 V, in the presence of light of wavelength 300 nm; (c) the last of a large number of scans corresponding to conditions where A has been exhausted



Fig. 3 An 'action spectrum' obtained by measuring the peak current of the 0.85 V oxidation as a function of excitation wavelength. Fresh solution was introduced into the modified channel cell before each measurement

whereas that on photo-excitation [Fig. 2(b)] new peaks are observed at 0.85 V, 1.20 and 1.40 V (vs. silver) and the size of these peaks increases with an increase in the light intensity. The aim of this work is to interpret and explain the prewave at 0.85 V. The new wave at 1.40 V will be shown to be associated with the prewave but also with photochemical reactions of  $A^+$ . The latter, along with its own prewave at 1.20 V, will be discussed elsewhere<sup>13</sup> and no quantitative interpretations of the 1.40 V oxidation wave will be attempted here.

Fig. 3 shows an 'action spectrum' obtained by measuring the peak current of the 0.85 V prewave as a function of the excitation wavelength. Comparison with Fig. 1 shows that there is a close similarity with the UV-visible spectrum of A, but the spectrum is quite different to that of  $A^+$ , <sup>9</sup> so that the prewave would appear to be related to a photochemical reaction of the parent compound, A. The likely nature of this reaction may be inferred from the work of Grellmann and co-workers on related diarylamine systems:<sup>14,15</sup>

$$\mathbf{A} + hv(ca. \ 300 \ \mathrm{nm}) \rightleftharpoons \mathbf{B} \tag{II}$$

$$\mathbf{B} + \mathbf{O}_2 \to \mathbf{C} \tag{III}$$

$$B + B \rightarrow C + D$$
 (IV)



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In this scheme the dipolar species, B, can thermally revert to the parent tris-(*p*-tolylamine), react with oxygen (if it is present) with the formation of C, 3,6-dimethyl, N-(*p*-tolyl) carbazole, or else disproportionate producing C and a tetrahydro-derivative of the carbazole, D. The precise location of the four labile hydrogens in D is uncertain but the structure shown corresponds to the final product observed by Grellman.<sup>15</sup>

We have independently synthesised the compound 3,6dimethyl, N-(p-tolyl)carbazole (C) and found it to have a cyclic voltammogram as shown in Fig. 2(c) {oxidation potential of 1.40 V (vs. silver)} so that the scheme can explain the appearance of a peak at this potential: we suggest that the peak at 0.85 V may be attributed to the electro-oxidation of B, analogous to the chemical oxidation by  $O_2$ :

$$B - e^- \rightarrow \text{products}$$
 (V)

These suggestions were supported first by preparative experiments; irradiation of an argon-purged acetonitrile solution of A (4.2 mmol dm<sup>-3</sup>) in a Pyrex cell of 1 cm optical path with light from a Xe source (Applied Photophysics model 4960) for 7 h led to 86% conversion into the carbazole (by GC analysis). Introduction of a filter (1 cm pathlength of acetophenone) which eliminates all radiation of wavelength below 390 nm gave no carbazole formation after a similar time period. Similar preparative experiments using a solution of A<sup>+</sup> irradiated at the same wavelengths also revealed the slow formation of the carbazole. It is apparent that the new 1.40 V peak is attributable to the oxidation of C formed photochemically from both A and A<sup>+</sup>.

A second verification of the proposed scheme was obtained from the observation that the prewave vanished if the solution was saturated with oxygen prior to electrolysis. In this situation the loss of B through reaction (III) is far greater than through reaction (V) so no photocurrents will be seen.

In order to verify the kinetic scheme presented above we conducted quantitative photocurrent/solution flow rate measurements on the 0.85 V oxidation wave using a channel electrode and incident light intensity in the range 4.4-47.4 mW  $cm^{-2}$ . The cell was masked so that only the electrode was illuminated and no conversion of A into B, C or D took place upstream of the electrode, and the solution was rigorously degassed to eliminate reaction (III). Under flow cell conditions a well defined limiting current was observed for the prewave and the height of this was found to depend on the electrolyte flow rate. Fig. 4 shows typical results. Note that the photocurrent decreases with flow rate. This most unusual observation can be explained by the fact that the solution arriving at the upstream edge of the electrode (where the illumination starts) contains only A. The observed photocurrent (the limiting current of the prewave) depends on the amount of conversion of A into B as the solution flows over the surface of the electrode. At slow flow rates this conversion is efficient, whereas at fast flow rates this conversion is efficient, whereas at fast flow rates A is swept off the surface of the electrode before it has chance to react to form B and consequently the photocurrents are lower.

In further support of the proposed mechanism it was found that the sum of the limiting currents of the waves at 0.85 and 1.05 V was constant at a given flow rate (throughout the range  $10^{-4}$ – $10^{-1}$  cm<sup>3</sup> s<sup>-1</sup>) and equal to the current found in the dark for the simple oxidation of A to A<sup>+</sup> which is required by the above scheme if A and B have similar diffusion coefficients.

The limiting current data were modelled using the backwards implicit finite difference method<sup>16</sup> to describe the (spatially variant) concentration profiles throughout the channel cell on the basis of the following kinetic scheme:



Fig. 4 Typical photocurrent/solution flow-rate data obtained for the 0.85 V prewave at a channel electrode with light intensities of: ( $\square$ ) 4.4; ( $\triangle$ ) 9.9; ( $\times$ ) 21.4; ( $\triangle$ ) 47.4 mW cm<sup>-2</sup>. The lines drawn through the experimental data correspond to the photocurrent behaviour calculated using the model and rate constants specified in the text

$$A + hv \rightleftharpoons B \qquad K_{II} = [B]/[A]$$
$$B + B - k_{IV} \rightarrow C + D$$
$$B - e^{-} \rightarrow \text{products}$$

The model predicted the dependence of the prewave limiting current on flow rate for a known electrode and flow-cell geometry.<sup>16</sup> It was assumed that B, C and D had diffusion coefficients similar to that of A. A highly satisfactory fit with the experimental data was found at all light intensities and over the entire flow-rate range using the parameters  $k_{IV} = 10^6$  mol<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup> and  $K_{II} = 0.042 \times I$  where I is the incident light intensity (mW cm<sup>-2</sup>). Notice that these two parameters give an excellent agreement with all four light intensities over the entire flow-rate range. This constitutes strong evidence in favour of the proposed kinetic model.

In conclusion, we have shown that the oxidation of tris-(*p*-tolyl)amine under irradiation with 300 nm light proceeds *via* a 'photo-CE reaction' and that this mechanism has the unusual feature that photocurrents decrease as the electrolyte flow rate is increased.

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