Organometallic Photoelectrochemistry: The Photo-oxidation of an (Arene)chromium Tricarbonyl System

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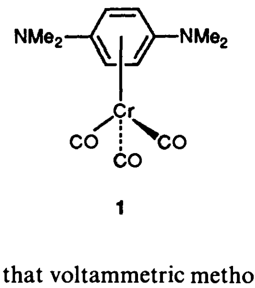
The photoelectrochemical oxidation of the compound tricarbonyl(*N,N,N′,N′*-tetramethyl-1,4- phenylenediamine)chromium **1**, has been studied using a platinum channel electrode. Maximum photocurrents are seen at an irradiation wavelength of 365 nm corresponding to a metal-to-ligand charge transfer absorption. By means of *in situ* electrochemical EPR and quantitative photocurrent/mass transport measurements the process is shown to be of the photo-CE type and a rate constant and approximate quantum yield are reported.

Photochemistry and electrochemistry have each been widely studied and applied separately to bring about reaction of species in fluid solution through electronically excited states and radical ions respectively. Recent work[1–3] has aimed to unify these individual methods with the anticipation that *dual* photochemical and electrochemical activation of species in solution will lead to: (i) novel mechanistic pathways, (ii) the discovery of new chemistry associated with unusual reactive intermediates, and (iii) new synthetic routes. Prior studies have focused almost exclusively on organic compounds. However, in the area of organometallic compounds the ready accessibility of both differing oxidation states and low-lying excited electronic states probably make these the systems-of-choice and should provide the photoelectrochemist with a plethora of new systems for study. In particular, ligand loss processes are promoted for organometallic complexes by both photolysis and electron transfer. Unusual oxidation states can be attained by electron transfer at an electrode; the redox products can have radically differing reactivities to their parent compounds. Excited electronic states achieved by photochemical activation will also have differing properties to the parent and will lead to degradation pathways of low-lying excited states, which may lead to new species with electrochemical activity. With the aim of initiating systematic work in the hitherto sparse and fragmented field of organometallic photoelectrochemistry[4] we report here our investigations on the system tricarbonyl(*N,N,N′,N′*-tetramethyl-1,4-phenylenediamine)chromium **1**, as a model compound. In particular we will show that voltammetric methods may be used to observe the light-induced fragmentation of this molecule, identify the photo-fragments and quantify the kinetics of the reaction. Specifically we will adopt channel electrode methodology for our photoelectrochemical studies since (i) it can be readily adapted for photochemistry[2,5] (ii) it can be coupled with spectroscopic techniques, particularly EPR, UV–VIS[2,5] and fluorescence spectroscopies,[6] and (iii) it permits quantitative mechanistic study *via* photocurrent measurements made as a function of mass transport (solution flow rate).[2,3,5,6]



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Experimental

All regular electrochemical, photoelectrochemical and *in situ* EPR and fluorescence experiments were conducted using a platinum channel electrode made of optical quality synthetic silica to standard construction and dimensions,[2,3,5,6] capable of delivering flow rates in the range 10^{-4}–10^{-1} cm^3 s^{-1}. Foils of size 4 mm × 4 mm, supplied by Goodfellow Advanced Materials (to a purity of 99.95% and thickness 0.025 mm) were used as working electrodes. Precise dimensions were determined using a travelling microscope. A silver wire pseudo-reference electrode was positioned in the flow system upstream of the channel electrode, and a platinum gauze counter electrode was located downstream. Electrochemical measurements were made using an Oxford Electrodes potentiostat modified to boost the counter electrode voltage (up to 200 V). The silver wire reference electrode was found to be steady throughout the period of our experiments: consistent values for the oxidation potential of *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD) were observed. Hence potentials are reported relative to the saturated calomel electrode, +0.20 V being subtracted from the measured values to obtain the potentials quoted. Other methodological details were as described previously.[2,3,5,6] Irradiation was provided by a Wotan XBO 900 W/2 xenon arc lamp *via* a Jarrell-Ash 82–410 grating monochromator (incident power 40 mW cm^{-2}). The EPR spectrometer employed has been described elsewhere.[2] Photochemical EPR experiments used an Omnichrome continuous wave 3112XM He–Cd UV laser (λ = 325 nm, 35 mW, beam diameter 0.64 mm). UV–VIS measurements were made with a Perkin-Elmer Lambda-5 spectrometer and fluorescence data obtained with a Perkin-Elmer LS50 luminescence spectrometer controlled by an Epson PC-AX2e personal computer. Rotating disc measurements were conducted using Oxford Electrodes equipment.

Experiments were performed using solutions of **1** (*ca.* 10^{-4}–10^{-3} mol dm^{-3}) in dried[2] acetonitrile (Fisons, dried, distilled) solution containing 0.1 mol dm^{-3} (recrystallised) tetrabutylammonium perchlorate (TBAP) (Fluka, purum) as supporting electrolyte. $Cr(CO)_6$ and TMPD were obtained from Aldrich (>98%). **1** was prepared according to a literature method,[7] as described below. Solutions were purged of oxygen by outgassing with prepurified argon prior to electrolysis.

Synthesis of Tricarbonyl[(η^6)-N,N,N′,N′*-tetramethyl*-1,4-*phenylenediamine*]*chromium*.—A nitrogen-degassed solution of *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (20 mmol) and chromium hexacarbonyl (30 mmol) in a mixture of THF dibutyl ether (1:10, 50 cm^3 of solvent/1 g arene) was heated to reflux under a nitrogen mixture for 18.5 h. Column chromatography

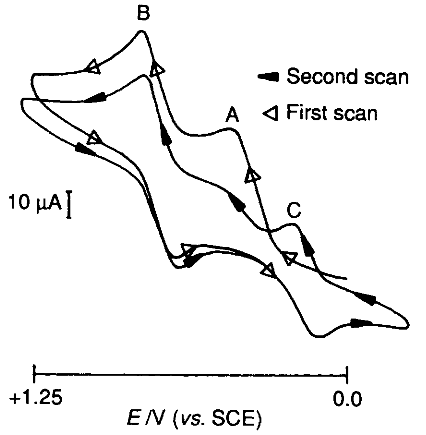

Fig. 1 Cyclic voltammogram obtained from the oxidation of **1** in 0.1 mol dm^{-3} TBAP/acetonitrile solution at a platinum electrode. A voltage scan rate of 200 mV s^{-1} was used.

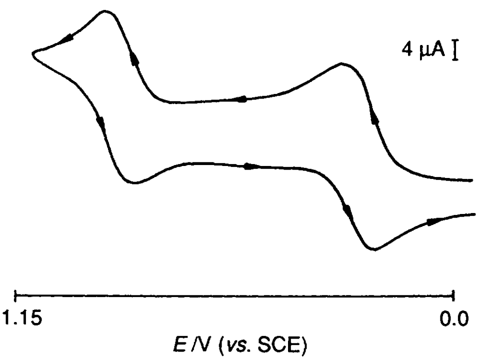

Fig. 2 Cyclic voltammogram obtained from the oxidation of TMPD in 0.1 mol dm^{-3} TBAP/acetonitrile solution at a platinum electrode. A voltage scan rate of 100 mV s^{-1} was used.

on silica gel using light petroleum ether–diethyl ether as eluent, followed by recrystallisation from acetone/hexane afforded the tricarbonyl chromium complex (84%) as yellow prisms m.p. 203–205 °C (lit.,[7] 204–206 °C).

Results and Discussion

Preliminary experiments were performed, in the absence of light, to identify the 'dark' electrochemical behaviour of **1** and the isolated ligand *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD), using a platinum channel electrode. Considering first **1**, concentrations in the range 0.03 mmol dm^{-3} and 0.6 mmol dm^{-3} in TBAP/acetonitrile were used. A typical voltammogram, obtained under no-flow conditions, as shown in Fig. 1. Thorough degassing of the chromium complex solution was required both during the solution preparation and during experiments owing to the oxygen-sensitivity of the system under study. In the voltammogram two peaks (A and B) were observed on the first forward (oxidation) scan with peak potentials, E_p, of +0.45 V and +0.85 V (*vs.* SCE). On the reverse (reduction) sweep following the first scan it was seen that the peak B was reversible but peak A was not. Also a new reduction peak was seen in this scan at $E_p = +0.13$ V (*vs.* SCE). On the second forward scan a third peak (C) was seen at +0.20 V and it was also observed that the current due to peak A dropped but that the current due to peak B was unchanged. It was seen on the second reverse sweep that the reduction peak at +0.13 V was the reverse of peak C.

A similar experiment was carried out on the free ligand TMPD (again with careful degassing of the solution) in 0.1 mol dm^{-3} TBAP/acetonitrile. The cyclic voltammogram (Fig. 2) showed two reversible one-electron processes ($E_p = +0.20$ V and +0.85 V, *vs.* SCE) corresponding to the formation of first the radical cation, and second the dication of TMPD. Comparison of Figs. 1 and 2 then led to the assignment that peaks C and B in Fig. 1 were due to the oxidation of the free ligand produced during peak A by the two-electron oxidation of **1**.

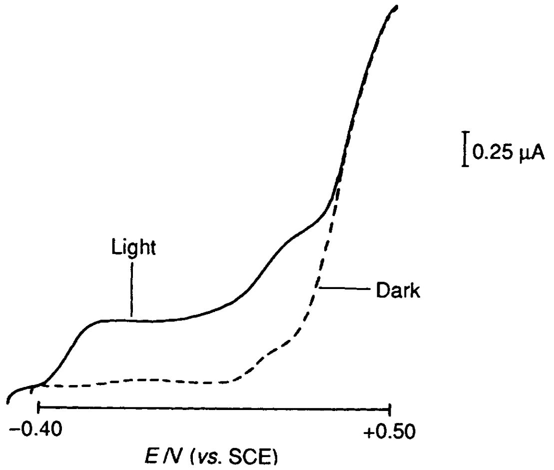

Fig. 3 Hydrodynamic voltammogram obtained at an illuminated (λ = 365 nm; 40 mW cm^{-2}) channel electrode for a solution containing 0.07 mmol dm^{-3} **1**

Peak A: $\mathbf{1} \rightleftharpoons Cr(CO)_3(CH_3CN)_3^{+} + TMPD^{+} + 2e$

Peak B: $TMPD^{+} \rightleftharpoons TMPD^{2+} + e$

Peak C: $TMPD \rightleftharpoons TMPD^{+} + e$

The mechanism of this process will be the subject of a separate paper. For the purposes of the photoelectrochemical study reported here it suffices to know the peak potentials corresponding to dark, as opposed to light, electrochemistry (see below). The identification of the chromium dissociation fragment as $Cr(CO)_3(CH_3CN)_3$ is made on the basis of literature studies[8–15] of the dark electrochemistry of other (arene)chromium tricarbonyls.

We now turn to the photoelectrochemistry of **1**. Initial experiments were carried out with illumination of a platinum channel electrode under electrolyte flow. Fig. 3 shows the resulting hydrodynamic voltammogram obtained at a flow rate of 1.2×10^{-3} cm^3 s^{-1}. Two new features can be seen at potentials less positive than those required for the oxidation of **1** in the dark (+0.45 V). These have half-wave potentials, $E_{\frac{1}{2}}$, of +0.17 V and −0.34 (*vs.* SCE) respectively. Note that the former is close to the peak potential noted above for the oxidation of TMPD to its radical cation.

It was found that with direct illumination electrode passivation was sufficiently significant to preclude quantitative voltammetric measurements. However, this problem was overcome by irradiating immediately upstream of the electrode only, and incorporating a platinum foil (at open-circuit and unconnected with the working electrode) in the zone of irradiation. The latter served to 'mop up' minority species responsible for the electrode passivation and the irradiation products were swept to the unpassivated electrode for interrogation. With this protocol passivation was eliminated and reproducible, quantitative measurements of transport limited current were achieved.

An 'action spectrum' (a plot of photocurrent against wavelength) was first recorded with the electrode potential fixed at +0.20 V (*vs.* SCE) corresponding to the 'second' prewave *i.e.* that closest to the dark oxidation wave. This is shown in Fig. 4 and corresponds to a clear shoulder on the highest wavelength peak in the UV–VIS spectrum of **1**. The action spectrum had a

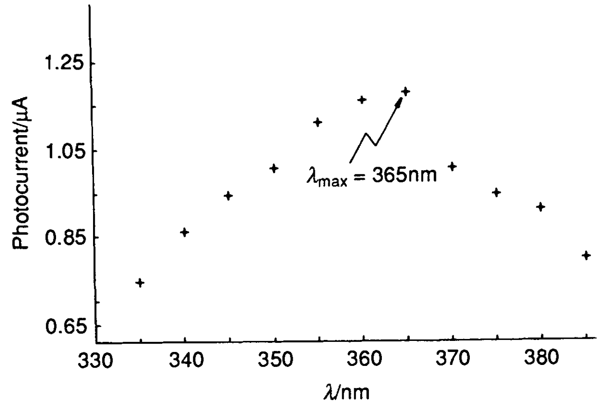

Fig. 4 Action spectrum showing the wavelength dependence of the measured photocurrents

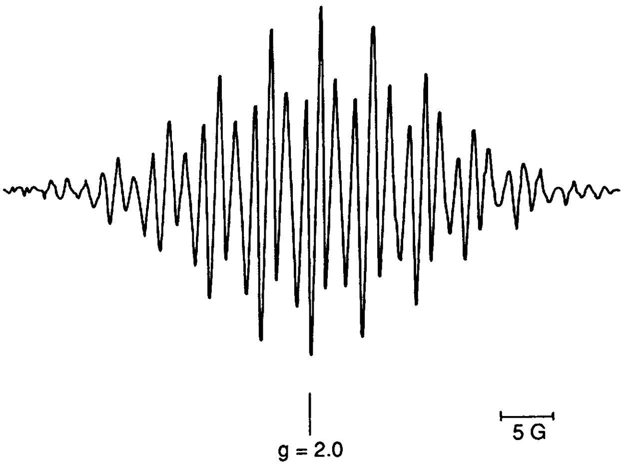

Fig. 5 EPR spectrum obtained at a channel electrode potentiostatted at +0.20 V whilst being irradiated with a He–Cd UV laser (λ = 325 nm). The spectrum was deduced to be that of the radical cation of TMPD.

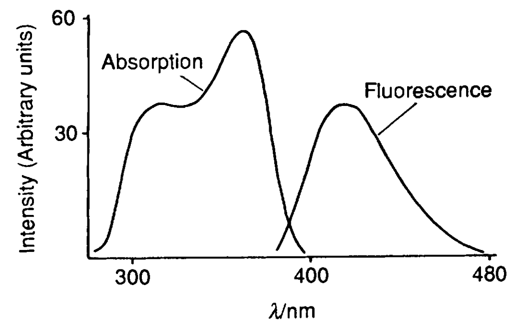

Fig. 6 Fluorescence spectrum obtained after irradiation of **1** for a period of 30 min and shown to be identical to that of a solution of TMPD

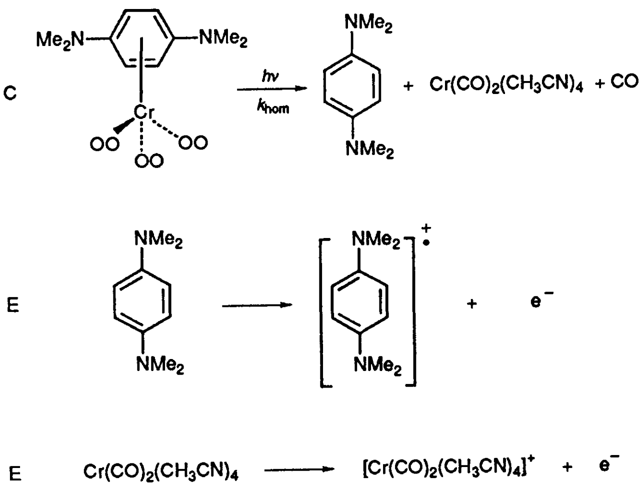

Fig. 7 The photochemical CE mechanism for the decomposition of **1**

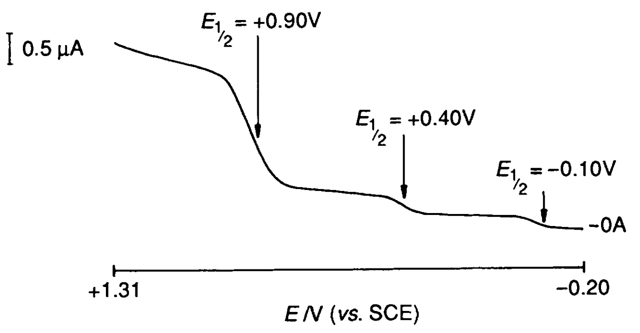

Fig. 8 A hydrodynamic voltammogram obtained for the oxidation of $Cr(CO)_6$ in 0.1 mol dm^{-3} TBAP/acetonitrile obtained at a channel electrode directly irradiated at 320 nm (40 mW cm^{-2})

maximum at 365 nm and this wavelength was used for all subsequent quantitative measurements.

Further insight into the nature of the prewaves was gleaned first by conducting *in situ* electrochemical EPR experiments with the electrode illuminated by an Omnichrome continuous wave He–Cd UV laser (λ = 325 nm, 35 mW) directed through the irradiation port of the spectrometer onto the electrode surface. Under flow conditions, and with the electrode potentiostatted near the transport-limited current of the second prewave, at +0.20 V (*vs.* SCE), the spectrum shown in Fig. 5 was observed. No spectrum was seen in the dark for the second prewave, or under any conditions, light or dark, flow or no flow, for the first prewave. The spectrum in Fig. 5 was shown to be identical to that seen on electrolysis (in the dark) of TMPD at potentials corresponding to the formation of its radical cation.

Second, fluorescence spectra of a sample of **1** were recorded over a period of 30 min during which the sample was continuously irradiated. Negligible fluorescence was detected before irradiation. After irradiation fluorescence, with maximum emission at λ = 405 nm (λ_{exc} = 360 nm) was seen, as shown in Fig. 6, and the intensity of fluorescence steadily increased during the period of irradiation. The fluorescence behaviour was found to be identical with that measured for a solution of free TMPD in acetonitrile suggesting that the effect of irradiation is to eject the neutral ligand.

The above observations suggest that the second prewave is due to the oxidation of free TMPD ligand released by irradiation of the complex. The process is thus classified as of the CE type and the first prewave is then attributed to the oxidation of the chromium fragment formed on photo-dissociation. The proposed mechanistic scheme is summarised in Fig. 7.

We next consider the identity of the chromium species, thought responsible for the first prewave. It is believed[8–15] that oxidation of (arene)chromium tricarbonyls in the dark results in the formation of $Cr(CO)_3(CH_3CN)_3$. However the oxidation potential of this species is thought to be −0.18 V (*vs.* SCE)[16] which is appreciably cathodic of the halfwave potential of the first prewave. Accordingly we sought to verify the literature value. A solution of $Cr(CO)_6$ in acetonitrile was allowed to flow through the channel electrode and an oxidation wave found at +1.55 V (*vs.* SCE). The electrode was then irradiated at 320 nm and the resulting hydrodynamic voltammogram is shown in Fig. 8. Under illumination three new (electrochemically reversible) prewaves appeared with halfwave potentials, $E_{\frac{1}{2}}$, of +0.90 V, +0.40 V and −0.10 V (*vs.* SCE). Photolysis of

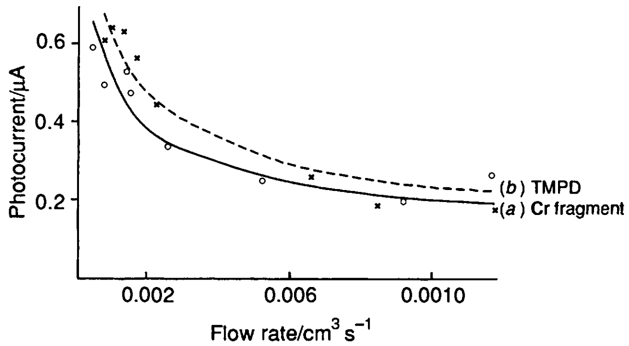

Fig. 9 Photocurrent/flow rate data for the two prewaves corresponding to the oxidation of (*a*) the chromium containing photofragment, and (*b*) the TMPD fragment. The concentration of **1** used was 0.06 mmol dm^{-3}. The lines are those calculated theoretically for a photo-CE mechanism with a rate constant of 0.05 s^{-1}.

chromium hexacarbonyl is known to result in the partial substitution of CO by solvent, CH_3CN,[17,18] and the three prewaves can therefore be assigned to $Cr(CO)_5(CH_3CN)$, $Cr(CO)_4(CH_3CN)_2$ and $Cr(CO)_3(CH_3CN)_3$, respectively. Note the respectable agreement with the literature value[16] for the latter. It follows that the first prewave cannot be due to the oxidation of $Cr(CO)_3(CH_3CN)_3$. However, given the trend in oxidation potential between the mono-, di- and tri-substituted chromium carbonyls it is not unreasonable to assign the prewave to the oxidation of $Cr(CO)_2(CH_3CN)_4$. This will be discussed further below.

The veracity of this mechanism was then examined by measurement of the photocurrents associated with each prewave as a function of electrolyte flow rate (mass transport). It has been established that such data, taken over a wide flow rate range, provides a sensitive method for resolving between different candidate mechanisms for electrode processes.[2,3,5,19] The experimental data was then compared with the theoretical CE model outlined above using the rate constant for the chemical step as an adjustable parameter. The necessary theory for computing the theoretical behaviour for this, or any other chemical model, is well established and the interested reader is directed towards the literature for the necessary details.[5,20,21] No new computational or conceptual problems emerge in their application to the present work.

The modelling took account of the fact that irradiation was confined to immediately upstream of the electrode for this quantitative work and used, for diffusion coefficients, values of 2.2×10^{-5} cm^2 s^{-1} (TMPD) and 1.35×10^{-5} cm^2 s^{-1} (**1**) deduced from conventional dark platinum rotating disc measurements on the substrates. The diffusion coefficient of $Cr(CO)_2(CH_3CN)_4$ was assumed to be identical to that of $Cr(CO)_6$, (1.6×10^{-5} cm^2 s^{-1}) measured in the same way.

Both prewaves were found to give excellent agreement with the photo-CE mechanism summarised in Fig. 7. The mechanism is entirely consistent with the action spectrum, the EPR and fluorescence spectroscopic evidence, and the voltammetric data. Moreover, as can be seen from the representative photocurrent–flow rate data shown in Fig. 9 quantitative agreement, across the entire flow rate range used, was found with the proposed mechanism using the same effective first-order rate constant, 0.05 ($\pm$0.02) s^{-1}, for the photochemical decomposition of **1** at the light intensity employed. The quality of fit between theory and experiment in the two plots is typical of that found across the full concentration range studied (0.03–0.07 mmol dm^{-3}) modelled using the same rate constant specified for both prewaves. We note an approximate estimate for the quantum yield, Φ, of the photodissociation may be found from eqn. (1)

$$k_{hom} = \Phi n_o \varepsilon \qquad (1)$$

where k_{hom} is the first-order rate constant deduced from the modelling, n_o (mol cm^{-2} s^{-1}) is the photon flux incident on the cell and ε is the extinction coefficient (mol^{-1} cm^2) for the transition studied. With a value of $n_o = 1.15 \times 10^{-7}$ mol cm^{-2} s^{-1} for our system[2] this gives a value of $\Phi = 0.12$.

Finally, we need to explain why photodissociation leads to loss of arene *and* CO, unlike the fragmentation induced by electrooxidation where simply the arene is expelled. The optical transition studied, which was that of highest wavelength, has been suggested to be of the charge transfer (metal-to-ligand) type.[22] In benzene(tricarbonyl)chromium the transition is between Cr and arene but, with substituted arenes of reduced symmetry, as in the example studied here, it can take on some Cr-to-CO character as well as Cr-to-ring[23] and expulsion of CO might be anticipated.

Conclusions

It may be concluded that the photoelectrooxidation of **1** proceeds *via* a photo-CE mechanism and that channel electrode voltammetry can quantify the rate of this process.

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