Photoelectrochemical Dehalogenation: Bis(cyclopentadienyl)-vanadium Dichloride and -molybdenum Dichloride

Richard G. Compton,* Jonathan Booth and John C. Eklund
Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, UK

The electrochemistry of $[M(cp)_2Cl_2]$ (M = Mo or V, cp = η-C_5H_5) has been investigated in the presence of light of wavelengths between 300 and 400 nm. For both compounds appreciable photocurrents were found to flow at potentials more positive than those required for their oxidation. It is shown that these result from the absorption of light by the cation formed by the one-electron oxidation of $[M(cp)_2Cl_2]$ and that they are mechanistically described by a photo-e.c.e (electrochemical–chemical–electrochemical) process [equations (i)–(iii)].The chemical nature of the photoinduced reaction is discussed. Additionally, in the

$$\text{e. step} \qquad [M(cp)_2Cl_2] - e^- \longrightarrow [M(cp)_2Cl_2]^+ \qquad \text{(i)}$$

$$\text{c. step} \qquad [M(cp)_2Cl_2]^+ + MeCN + h\nu \longrightarrow Cl^\bullet + [M(cp)_2Cl(MeCN)]^+ \qquad \text{(ii)}$$

$$\text{e. step} \qquad [M(cp)_2Cl(MeCN)]^+ - e^- \longrightarrow [M(cp)_2Cl(MeCN)]^{2+} \qquad \text{(iii)}$$

case of $[V(cp)_2Cl_2]$, a parallel c.e. process also occurs as a result of the photofragmentation of the parent molecule [equations (iv) and (v)]. The kinetics and mechanism of this reaction are reported.

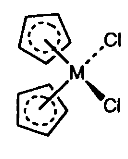
$$\text{c. step} \qquad [V(cp)_2Cl_2] + h\nu \longrightarrow [V(cp)_2Cl] + \tfrac{1}{2}Cl_2 \qquad \text{(iv)}$$

$$\text{e. step} \qquad [V(cp)_2Cl] - e^- \longrightarrow [V(cp)_2Cl]^+ \qquad \text{(v)}$$

It has been previously predicted[1,2] that organometallic compounds should display particularly rich photoelectrochemical properties on account of the ready accessibility of both differing oxidation states and low-lying excited electronic states for the following reasons: (*i*) ligand-loss processes are promoted for organometallic complexes by both photolysis and electron transfer, (*ii*) unusual oxidation states can be attained by electron transfer at an electrode resulting in redox products which have radically differing reactivities to their parent compounds, and (*iii*) excited electronic states achieved by photochemical activation can also have differing properties from those of the parent, resulting in degradation pathways of low-lying excited states which can lead to new species with electrochemical activity.

In this paper we illustrate these predictions with reference to the oxidation of bis(cyclopentadienyl)-vanadium dichloride and -molybdenum dichloride in the presence of light of wavelength greater than 300 nm. Dehalogenation has been previously accomplished *via* joint electrochemical and photochemical activation in the case of organic molecules;[3,4] this work seeks to generalise this potentially useful synthetic process and has the primary aim of establishing the photoelectrochemical mechanism of dehalogenation using channel electrode methodology, including *in situ* electrochemical ESR spectroscopy, as summarised previously.[2,3] Particular use will be made of photocurrent measurements as a function of the rate of mass transport.

Experimental



M = Mo or V

All regular electrochemical, photoelectrochemical, and *in situ* ESR experiments were conducted using a channel electrode made of silica to standard construction and dimensions[3,5] capable of delivering flow rates in the range 10^{-4}–10^{-1} cm^3 s^{-1}. Platinum foils of size *ca.* 4 × 4 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 downstream. Electrochemical measurements were made using an Oxford Electrodes potentiostat modified to boost the counter voltage up to *ca.* 200 V. The reference electrode displayed a steady potential 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 (SCE), +0.20 V being subtracted from the measured values to obtain the potentials quoted. Methodological details were as described previously.[2–5] Irradiation was provided by a Wotan XBO 900 W/2 xenon-arc lamp *via* a Jarrell-Ash 82-410 grating monochromator (incident power 20 mW cm^{-2}) or an Omnichrome continuous-wave 3112XM He–Cd UV laser (λ = 325 nm, incident power 55 mW cm^{-2} after beam expansion). The ESR spectrometer employed has been described elsewhere;[6] 100 kHz field modulation was employed of amplitude 0.5 G (5×10^{-5} T). The UV/VIS measurements were made with a Perkin-Elmer Lamda-5 spectrometer. Rotating-disc measurements were conducted using Oxford Electrodes equipment. Platinum microdisc electrodes of diameter 4.4 µm were supplied by Bioanalytical Systems (West Lafayette).

Experiments were performed using solutions of $[M(cp)_2Cl_2]$

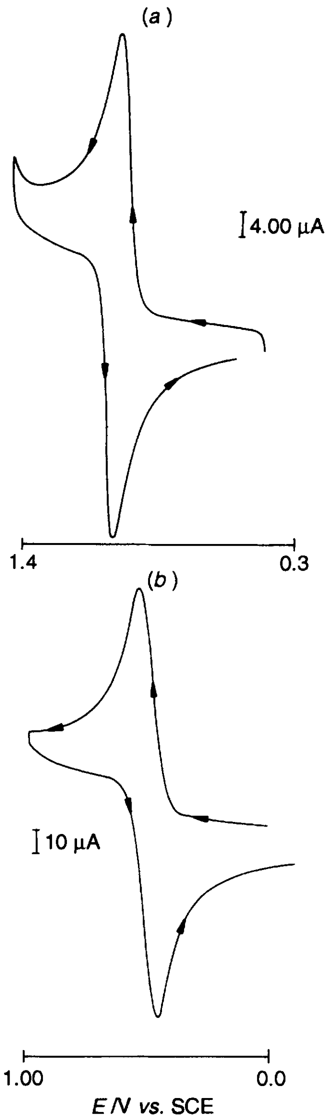


Fig. 1 Cyclic voltammograms for the oxidation of (*a*) [V(cp)$_2$Cl$_2$] (2.15 mmol dm^{-3}) and (*b*) [Mo(cp)$_2$Cl$_2$] (0.68 mmol dm^{-3}) in acetonitrile–0.1 mol dm^{-3} NBu$_4$ClO$_4$ measured under no-flow conditions, using a voltage scan rate of 100 mV s^{-1}

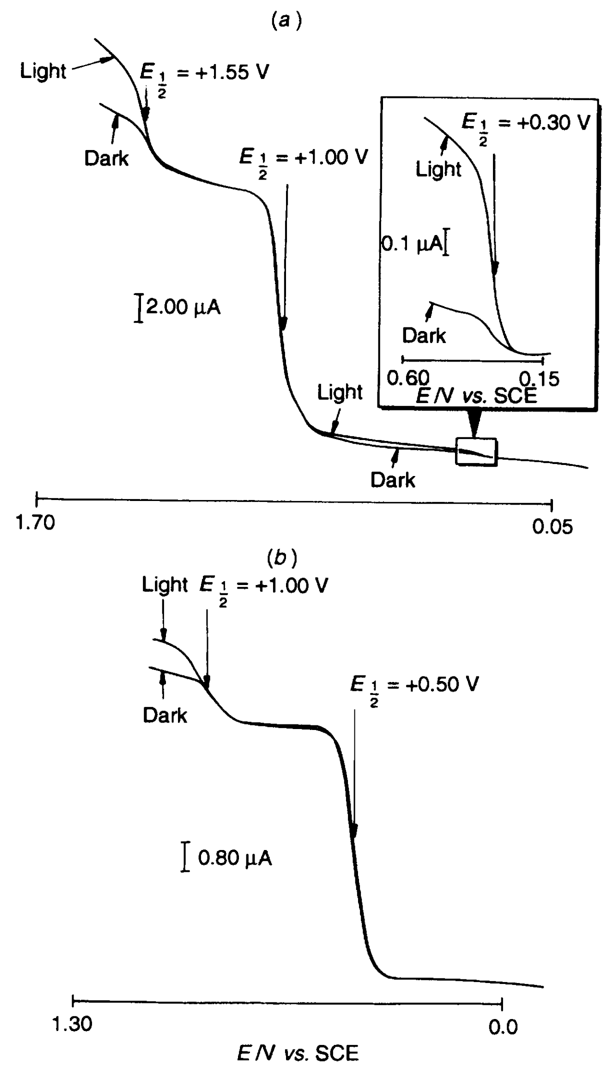


Fig. 2 Steady-state hydrodynamic voltammograms measured at a channel electrode (flow rate 1.1 × 10^{-3} cm^3 s^{-1}) for the oxidation of (*a*) [V(cp)$_2$Cl$_2$] (0.70 mmol dm^{-3}) and (*b*) [Mo(cp)$_2$Cl$_2$] (0.36 mmol dm^{-3}) in acetonitrile–0.1 mol dm^{-3} NBu$_4$ClO$_4$ for dark conditions and for the electrode uniformly irradiated by light of wavelength 325 nm and intensity 20 mW cm^{-2}

(M = V or Mo, cp = η^5-C$_5$H$_5$) (*ca.* 10^{-4}–10^{-3} mol dm^{-3}) in dried,[6] distilled acetonitrile (Fisons) containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (Fluka, purum) as supporting electrolyte. The complexes were obtained from Aldrich (> 98%) and used as received. Solutions were purged of oxygen by outgassing with prepurified argon prior to electrolysis.

Results and Discussion

We consider first the anodic voltammetry of [M(cp)$_2$Cl$_2$] (M = V or Mo) in the absence of light. Fig. 1 shows typical cyclic voltammograms measured at a stationary platinum electrode. Both display characteristics expected from an electrochemically reversible one-electron oxidation process. A combination of rotating-disc and channel-electrode voltammetry permitted the deduction of the following parameters: [V(cp)$_2$Cl$_2$], halfwave potential + 1.00 V (*vs.* SCE), diffusion coefficient (1.40 ± 0.20) × 10^{-5} cm^2 s^{-1}; [Mo(cp)$_2$Cl$_2$], half-wave potential + 0.50 V (*vs.* SCE), diffusion coefficient (1.45 ± 0.10) × 10^{-5} cm^2 s^{-1}. The near-equality of the anodic and cathodic peak heights in the cyclic voltammetry suggests that the cations [M(cp)$_2$Cl$_2$]$^+$ have some kinetic stability on the voltammetric time-scale. However Fig. 2(a) and 2(b) show hydrodynamic voltammograms recorded at a channel electrode and a small wave at potentials anodic of the [M(cp)$_2$Cl$_2$] oxidation is apparent in each case. The half-wave potentials of these post-waves are + 1.55 V (*vs.* SCE) for M = V and + 1.00 V for M = Mo. The size of these waves decreased relative to that of the [M(cp)$_2$Cl$_2$] wave as the solution flow rate was increased. This effect was quantitatively modelled in terms of an electrochemical–chemical–electrochemical (e.c.e.) process in which the cations [M(cp)$_2$Cl$_2$]$^+$ undergo slow first-order decomposition into products which are themselves oxidised at the higher potentials.

The necessary theory for the interpretation of such processes at channel electrodes has been given previously[6,7] and is directly applicable to the case studied here. Analysis proceeds *via* the generation of a 'working curve' relevant for the particular cell geometry employed experimentally. This predicts the ratio of the transport-limited current of the post-wave to that of the simple one-electron oxidation of the parent molecule as a function of a 'normalised' rate constant K^*, defined as in equation (1) where V_f is the volume flow rate, h is the half-height

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

of the cell, x_e is the electrode length, d is the channel width and D is the diffusion coefficient of $[M(cp)_2Cl_2]$ {assumed equal to that of the cation $[M(cp)_2Cl_2]^+$ and its electroactive decomposition product}; k is the first-order rate constant for the chemical step in the e.c.e. scheme above. Note that K^* is a dimensionless quantity. Theory thus facilitates the deduction of K^* for each experimental flow rate measured since each value of the ratio alluded to above gives a value of K^* from the working curve. If the correct mechanism has been selected for the theoretical generation of the latter than a plot of K^* against $V_f^{-\frac{1}{3}}$ should give a straight line through the origin. This was found to be the case for both systems studied and permitted the deduction of values for k experimentally of 0.09 ± 0.03 s^{-1} for M = V and 0.05 ± 0.01 s^{-1} for M = Mo.

Our observations on the dark electrochemistry of $[Mo(cp)_2Cl_2]$ are entirely consistent with a previous report[8] in which the post-wave is demonstrated to result from the oxidation of $[Mo(cp)_2Cl(MeCN)]^+$ formed through the oxidatively induced reductive elimination of a chlorine atom *via* the overall mechanism[8] in equations (2)–(4). The expulsion of atomic

$$\text{e. step} \quad [Mo(cp)_2Cl_2] - e^- \longrightarrow [Mo(cp)_2Cl_2]^+ \qquad (2)$$

$$\text{c. step} \quad [Mo(cp)_2Cl_2]^+ + MeCN \longrightarrow Cl^{\bullet} + [Mo(cp)_2Cl(MeCN)]^+ \qquad (3)$$

$$\text{e. step} \quad [Mo(cp)_2Cl(MeCN)]^+ - e^- \longrightarrow [Mo(cp)_2Cl(MeCN)]^{2+} \qquad (4)$$

chlorine *via* a corresponding mechanism has also been reported in the structurally related compound $[Ti(cp)_2Cl_2]$.[9] We are unaware of any previous work on the *oxidation* of $[V(cp)_2Cl_2]$ although its reduction has been extensively examined.[10] We speculate that the above mechanism is also applicable to the oxidation of $[V(cp)_2Cl_2]$.

We next examine the behaviour of the two complexes in the presence of light of wavelength greater than 300 nm. Fig. 2 shows hydrodynamic voltammograms measured at a channel electrode in the presence of continuous-wave laser light of wavelength 325 nm. Considering initially the vanadium species, two new features were observed in the voltammetry. First a 'pre-wave' is evident at potentials less positive than those required to oxidise the parent species in the absence of light. This had a half-wave potential of +0.30 V (*vs.* SCE). Secondly an enhancement of the post-wave with a half-wave potential of +1.55 V (*vs.* SCE) is seen. Turning now to the voltammogram of the molybdenum-containing species shown in Fig. 2(*b*) and comparing it with the vanadium case, we see that there is *no* pre-wave, but again an increased post-wave appears after the dark oxidation with a half-wave potential of +1.00 V (*vs.* SCE).

We focus first on the light-induced post-wave of $[V(cp)_2Cl_2]$. First the photocurrent spectrum, *i.e.* the variation of photocurrent with wavelength, was recorded (Fig. 3). The maximum photocurrent for the post-wave occurs with light of wavelength 335 nm. Fig. 4 shows the UV/VIS absorption spectrum of the parent, $[V(cp)_2Cl_2]$, compound. Absorption maxima were noted at the following wavelengths: 220 (ε = 7500 ± 300), 280 (5500 ± 200) and 380 nm (2400 ± 100 dm^3 mol^{-1} cm^{-1}). We assign the transition at 380 nm to be of d–d character.[11] The other two are probably charge-transfer bands.[11] Comparison of the photocurrent spectrum with Fig. 4 suggests that the post-wave must derive from light absorbed by some species other than the parent; in particular the cation resulting from the oxidation of $[V(cp)_2Cl_2]$ is a plausible candidate.

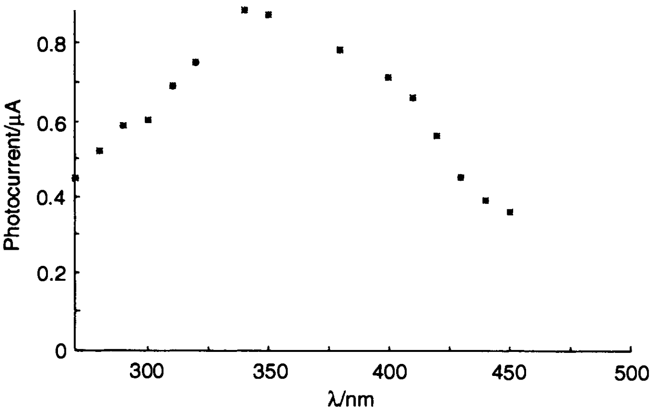


Fig. 3 Photocurrent spectrum measured for $[V(cp)_2Cl_2]$ using the transport-limited currents related to the post-wave with a half-wave potential of +1.55 V (the electrode was potentiostatted at +1.70 V)

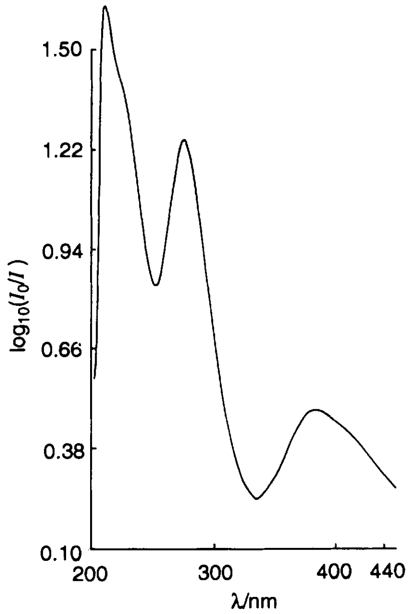


Fig. 4 The UV/VIS spectrum of $[V(cp)_2Cl_2]$ in acetonitrile solution

Next the post-wave was mechanistically examined again using the mass-transport dependence of the photocurrents flowing when the electrode was irradiated with light of 325 nm, noting as suggested above that the likely cause of the photo-effect is absorption of light by the cation formed upon one-electron oxidation of the parent compound. Hence the measured photocurrent *vs.* flow rate data were again interpreted using the e.c.e. scheme proposed above except that the dechlorination is light induced, equations (5)–(7). As

$$\text{e. step} \quad [V(cp)_2Cl_2] - e^- \longrightarrow [V(cp)_2Cl_2]^+ \qquad (5)$$

$$\text{c. step} \quad [V(cp)_2Cl_2]^+ + h\nu + MeCN \longrightarrow Cl^{\bullet} + [V(cp)_2Cl(MeCN)]^+ \qquad (6)$$

$$\text{e. step} \quad [V(cp)_2Cl(MeCN)]^+ - e^- \longrightarrow [V(cp)_2Cl(MeCN)]^{2+} \qquad (7)$$

summarised above, if an e.c.e. mechanism correctly describes the process then a plot of K^* against $V_f^{-\frac{1}{3}}$ should give a straight line through the origin. As can be seen from Fig. 5 this is the case. The slope of the plot permits the deduction of a value for k relating to the laser light intensity used experimentally: 0.40 ± 0.01 s^{-1}.

We next investigate the post-wave seen under irradiation of $[Mo(cp)_2Cl_2]$ using an analogous procedure to that for the corresponding vanadium case. Fig. 6 shows the resulting analysis of the experimental data obtained with light of

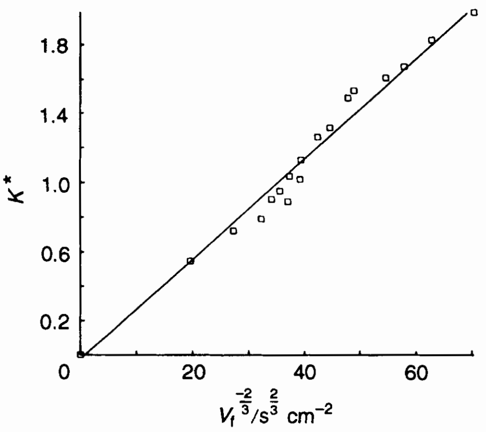


Fig. 5 The e.c.e. analysis (see text) of photocurrent *vs.* flow rate data obtained at +1.70 V, for the [V(cp)$_2$Cl$_2$] post-wave. [V(cp)$_2$Cl$_2$] = 0.58 mmol dm^{-3}. Laser light of wavelength 325 nm was used (see Experimental section)

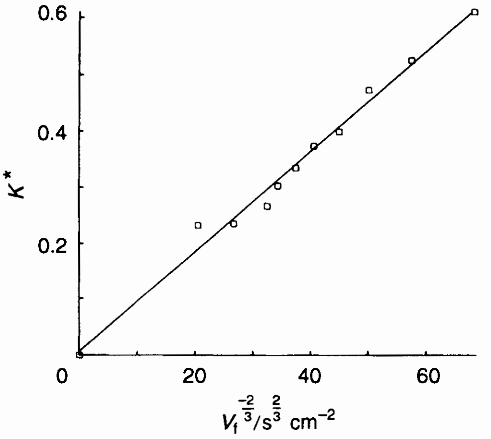


Fig. 6 The e.c.e. analysis (see text) of photocurrent *vs.* flow rate data obtained at +1.20 V, for the [Mo(cp)$_2$Cl$_2$] post-wave. [Mo(cp)$_2$Cl$_2$] = 0.29 mmol dm^{-3}. Laser light as in Fig. 5

wavelength 325 nm; the parent compound [Mo(cp)$_2$Cl$_2$] shows negligible absorption above 300 nm. Again a photo-e.c.e. mechanism was clearly indicated and a pseudo-first-order rate constant of 0.12 ± 0.01 s^{-1} deduced. It is inferred that the effect of light is to induce the e.c.e. reaction known[8] to occur in the dark, as in equations (8)–(10).

$$\text{e. step} \quad [\text{Mo(cp)}_2\text{Cl}_2] - e^- \longrightarrow [\text{Mo(cp)}_2\text{Cl}_2]^+ \qquad (8)$$

$$\text{c. step} \quad [\text{Mo(cp)}_2\text{Cl}_2]^+ + h\nu + \text{MeCN} \longrightarrow [\text{MoCl(MeCN)}]^+ + \text{Cl}^\bullet \qquad (9)$$

$$\text{e. step} \quad [\text{Mo(cp)}_2\text{Cl(MeCN)}]^+ - e^- \longrightarrow \text{products} \qquad (10)$$

We now return to the pre-wave observed for [V(cp)$_2$Cl$_2$]. Fig. 7 shows the photocurrent spectrum observed for this case. It can be seen that this has a maximum at 385 nm close to an absorption maximum in the UV/VIS spectrum of [V(cp)$_2$Cl$_2$] and we therefore suggest that the photocurrent derives from absorption by the parent compound. To pursue the nature of the photoprocess in greater detail, measurements were made of the mass-transport dependence of the pre-wave. It was observed that the photocurrent *fell* as the rate of mass transport was *increased* and this is characteristic of a c.e. mechanism. Accordingly the experimental data were then compared with theoretical predictions based on the model in equations (11) and (12) using the measured diffusion coefficient of [V(cp)$_2$Cl$_2$],

$$\text{c. step} \quad [\text{V(cp)}_2\text{Cl}_2] + h\nu \longrightarrow \text{X} + \text{Y} \qquad (11)$$

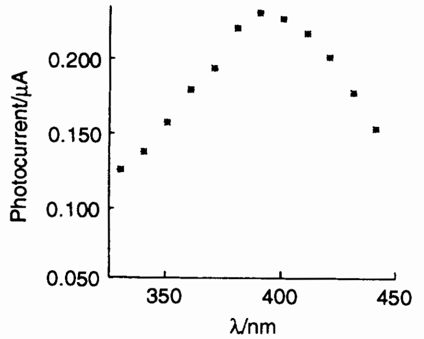


Fig. 7 The photocurrent spectrum measured for [V(cp)$_2$Cl$_2$] using the transport-limited currents related to the pre-wave with a half-wave potential of +0.30 V (the electrode was potentiostatted at +0.60 V)

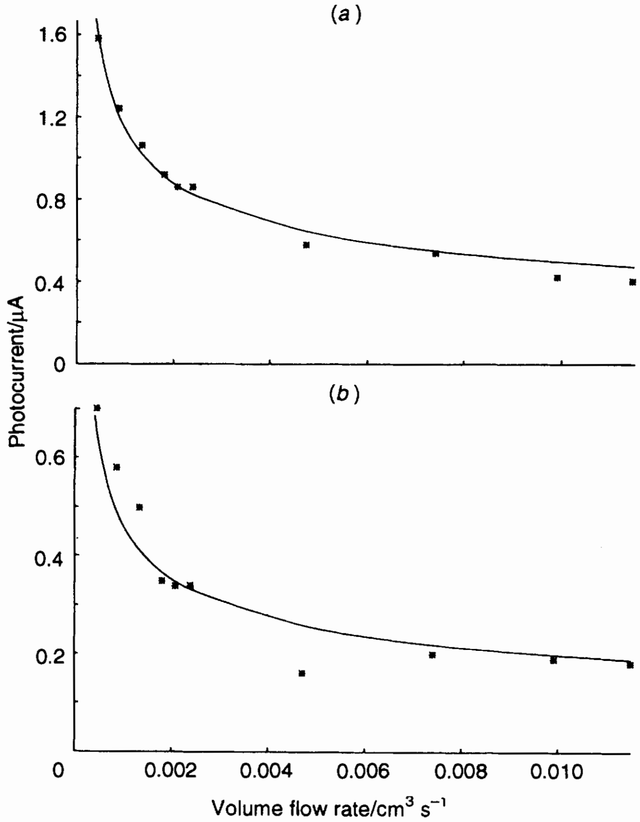


Fig. 8 Photocurrent *vs.* flow rate data obtained at +0.60 V, for the [V(cp)$_2$Cl$_2$] pre-wave at light intensities of (*a*) 20 and (*b*) 9 mW cm^{-2}. In both cases [V(cp)$_2$Cl$_2$] = 1.98 mmol dm^{-3}. The solid lines shown are those calculated theoretically using the photo-c.e. model specified in the text with the first-order rate constants cited

$$\text{e. step} \quad \text{X} - e^- \longrightarrow \text{X}^+ \qquad (12)$$

assuming that of X is comparable, and using the rate constant for the chemical step as an adjustable parameter. The necessary theory for computing the theoretical behaviour for this model is well established and the interested reader is directed towards the literature for the details.[7,12,13] No new computational or conceptual problems emerge in their application to the present work.

Fig. 8 shows the experimental photocurrent *vs.* flow rate data measured at two separate light intensities (9 and 20 mW cm^{-2}). Also shown are the theoretical fits deduced from the mathematical model presented above. Very good agreement between theory and experiment was found across the entire flow rate range when first-order rate constants of (5.2 ± 0.3) × 10^{-3} (20) and (2.0 ± 0.1) × 10^{-3} s^{-1} (9 mW cm^{-2}) were assumed. This agreement, together with the fact that the two best-fit rate constants are approximately in the ratio of the two light intensities used, further indicates the veracity of the assumed c.e. mechanism. We next consider the identity of the species X and Y implicated in the kinetic scheme given above.

To seek insight into the nature of X and Y we first conducted voltammetry in a range of solvent–background electrolyte systems using either a platinum channel electrode (where background electrolyte was present) or a platinum microdisc electrode (no background electrolyte) as follows: (*i*) MeCN–NBu_4ClO_4, (*ii*) MeCN–NBu_4PF_6 (*iii*) MeCN alone, (*iv*) CH_2Cl_2–NBu_4ClO_4, (*v*) CH_2Cl_2–NBu_4PF_6, (*vi*) CH_2Cl_2 alone, and (*vii*) tetrahydrofuran (thf) alone. In all cases a pre-wave was found with a half-wave potential between +0.20 and +0.30 V. This insensitivity to solvent and background electrolyte strongly suggests that the photolysis causing the pre-wave involves purely photofragmentation without substitution. Moreover the oxidation potential measured in thf is identical to that reported by Laviron and co-workers[10] for the oxidation of bis(cyclopentadienyl)vanadium monochloride in this solution. Finally we used ESR spectroscopy to monitor the paramagnetic $[V(cp)_2Cl_2]$ (17-electron species) whilst irradiated (325 nm) with laser light. The intensity of the eight-line spectrum observed dropped steadily when light was applied. This is not inconsistent with the formation of a diamagnetic product.

All of these observations lead us to suggest that X is $[V(cp)_2Cl]$. Accordingly we infer that the effect of photolysis is thus the dehalogenation of the parent material [equations (13) and (14)]. Thus the photoexcitation leads to homolysis

$$\text{c. step} \qquad [V(cp)_2Cl_2] + h\nu \longrightarrow [V(cp)_2Cl] + \tfrac{1}{2}Cl_2 \tag{13}$$

$$\text{e. step} \qquad [V(cp)_2Cl] - e^- \longrightarrow [V(cp)_2Cl]^+ \tag{14}$$

of the metal–chlorine bond as seen in various related species.[14]

Conclusion

We have shown that joint photo- and electro-chemical activation of both $[Mo(cp)_2Cl_2]$ and $[V(cp)_2Cl_2]$ leads to their efficient dechlorination *via* an oxidatively induced reductive elimination. Additionally, for the vanadium compound, reductive elimination of chlorine is induced by the absorption of light alone.

Acknowledgements

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