Photolabilisation of Phosphine Ligands Bound to Iron: Photofragmentation Voltammetry Analysis

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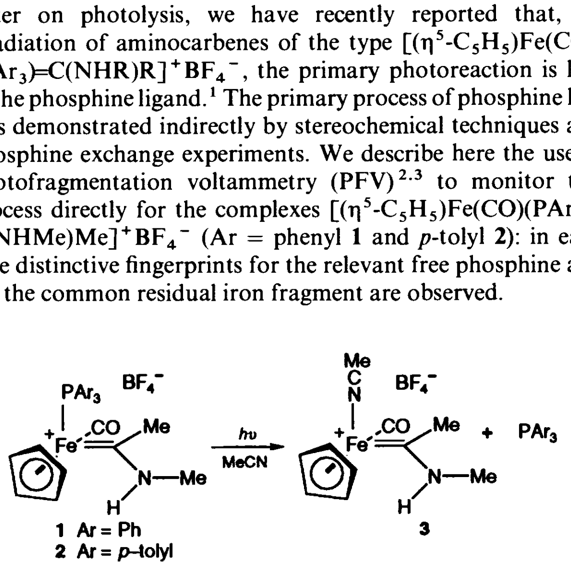
Photofragmentation volammetry is used to demonstrate directly the primary loss of $P(Ar)_3$ from $[(\eta^5\text{-}C_5H_5)Fe(CO)(PAr_3){=}C(NHMe)Me]^+BF_4^-$ (Ar = phenyl **1** and *p*-tolyl **2**) on irradiation with visible light. In contrast, no loss of carbon monoxide is observed.

Contrary to accepted dogma that complexes containing both phosphine and carbon monoxide ligands preferentially lose the latter on photolysis, we have recently reported that, on irradiation of aminocarbenes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(PAr_3){=}C(NHR)R]^+BF_4^-$, the primary photoreaction is loss of the phosphine ligand.[1] The primary process of phosphine loss was demonstrated indirectly by stereochemical techniques and phosphine exchange experiments. We describe here the use of photofragmentation voltammetry (PFV)[2,3] to monitor this process directly for the complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PAr_3){=}C(NHMe)Me]^+BF_4^-$ (Ar = phenyl **1** and *p*-tolyl **2**): in each case distinctive fingerprints for the relevant free phosphine and for the common residual iron fragment are observed.



Experimental

All regular PFV experiments were conducted using a channel electrode made of optical quality synthetic silica to standard construction and dimensions[3,4] capable of delivering flow rates in the range 10^{-4}–10^{-1} cm^3 s^{-1}. Platinum foils (purity 99.95%, thickness 0.025 mm) of approximate size 4 mm x 4 mm, supplied by Goodfellow Advanced Materials, 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, and a platinum gauze counter electrode located downstream, of the channel electrode. 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. 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.[3,4] Irradiation was provided by a Wotan XBO 900 W/2 xenon arc lamp *via* a Jarrell-Ash 82-410 grating monochromator (maximum incident power 40 MW cm^{-2}). Variable light intensity measurements were made by attenuation of the beam as described previously.[3] UV–VIS measurements were made with a Perkin-Elmer Lambda-5 spectrophotometer. Complementary rotating disc measurements were conducted using Oxford Electrodes equipment.

Experiments were performed using solutions of **1** or **2** (*ca.* 10^{-4}–10^{-3} mol dm^{-3}) in dried[3] acetonitrile (Fisons, dried, distilled) solution containing 0.1 mol dm^{-3} (recrystallised) tetrabutylammonium perchlorate (TBAP) (Fluka, *purum*) as supporting electrolyte. Solutions were purged of oxygen by outgassing with prepurified argon prior to electrolysis. **1** and **2** were prepared as described previously.[1]

Results and Discussion

Preliminary experiments were first performed, in the absence of light, to identify the 'dark' electrochemical behaviour of **1** and **2**, and of the free phosphines PAr_3. Considering first **1**, voltammetry under no-flow conditions using a scan rate of 100 mV s^{-1} revealed an electrochemically reversible one-electron feature with peak potentials of +1.135 V (forward scan) and +1.085 V (reverse scan). Next, the corresponding measurements for **2** again showed a reversible one-electron oxidation (peak potentials of +1.10 and +1.02 V). For both **1** and **2** the ratio of anodic to cathodic peak currents was close to unity suggesting that the dication resulting from the oxidation is stable on the voltammetric timescale although at low scan rates ($\leqslant$ 100 mV s^{-1}) there was a suggestion in the reverse (cathodic) scan for both species of an additional voltammetric feature with a peak potential near +0.920 V which may arise from slow decomposition of the dication *via* an EC route. However this process was not kinetically significant on the timescale of the PFV experiments reported below and so was not investigated further.

The voltammetry of the free phosphines, PAr_3, was then re-examined for comparison with literature reports. Separate voltammetric experiments on PPh_3 in 0.1 mol dm^{-3} TBAP–acetonitrile using both a channel electrode and a platinum rotating disc showed a reproducible (irreversible) one-electron oxidation with a half-wave potential of +1.55 (+/−0.10) V in rigorously dry solvent in agreement with the general consensus of opinion from previous studies.[5,6] Analogous behaviour was seen for the case of tris(*p*-tolyl)phosphine except that the half-wave potential was lowered to +1.41 (+/−0.10) V.

We turn now to the voltammetric behaviour observed for the oxidation of **1** and **2** at an illuminated channel electrode. Fig. 1 shows the photofragmentation voltammogram measured in a solution containing 5.1 x 10^{-4} mol dm^{-3} **1** in 0.1 mol dm^{-3} TBAP–acetonitrile at λ = 390 nm. For comparison the corresponding 'dark' hydrodynamic voltammogram is also displayed. Two new voltammetric signatures, in addition to that of the simple oxidation of **1**, may be deciphered in the presence of light. First the wave at 1.65 (+/−0.10) V may, on the basis of the results presented above for the oxidation of the free phosphines, be attributed to the oxidation of PPh_3, and second,

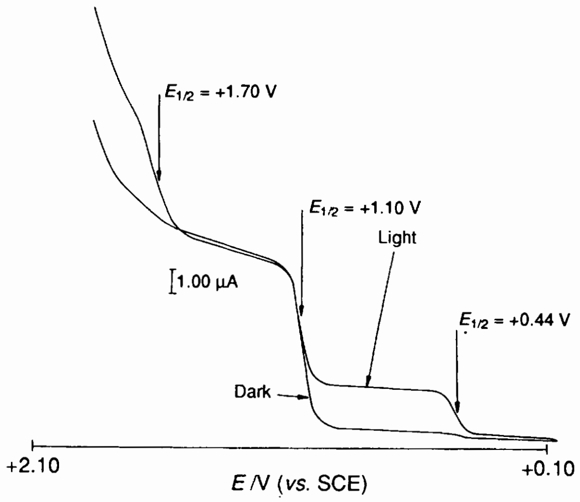


Fig. 1 Photofragmentation voltammogram for the oxidation of **1** measured at a platinum channel electrode using a flow rate of 1.3×10^{-3} cm^3 s^{-1}

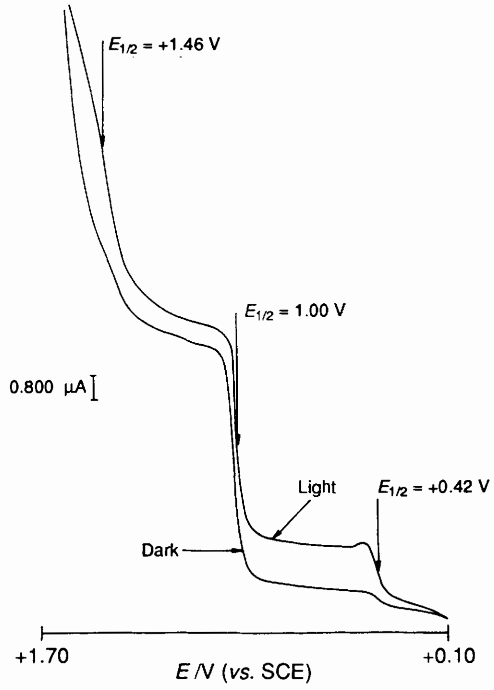


Fig. 2 Photofragmentation voltammogram for the oxidation of **2** measured at a platinum channel electrode using a flow rate of 1.2×10^{-3} cm^3 s^{-1}

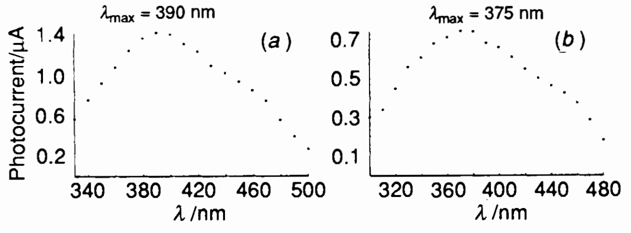


Fig. 3 Action spectra showing how the prewave photocurrent (measured at +0.60 V) varies with wavelength for the irradiation of (*a*) **1** measured at a flow rate of 2.3×10^{-3} cm^3 s^{-1} and (*b*) **2** measured at a flow rate of 1.2×10^{-3} cm^3 s^{-1}. λ_{max} refers to the maximum photocurrent flowing.

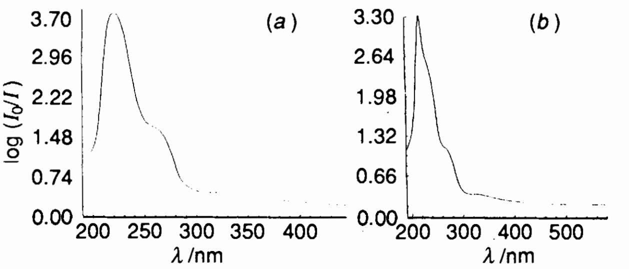


Fig. 4 UV–VIS spectra measured for (*a*) **1** where the extinction coefficient at 390 nm (corresponding to maximum photocurrent) is 2.2×10^3 dm^3 mol^{-1} cm^{-1} and (*b*) **2** where the extinction coefficient at λ = 375 nm (corresponding to maximum photocurrent) is 2.5×10^3 dm^3 mol^{-1} cm^{-1}

the prewave [$E_{\frac{1}{2}}$ = 0.44 (+/−0.05) V], may be inferred to result from the oxidation of the iron-containing photofragment formed through the loss of PPh$_3$. Fig. 2 shows the analogous photofragmentation voltammogram for **2** (3.3×10^{-4} mol dm^{-3}) under identical conditions except that a wavelength of 375 nm was required to induce fragmentation. Again two new voltammetric waves result: one attributable to free phosphine, P(*p*-tolyl)$_3$, [$E_{\frac{1}{2}}$ = 1.46 (+/−0.10) V] and the second—the prewave—to the residual photofragment [$E_{\frac{1}{2}}$ = 0.42 (+/−0.05) V]. Notice that comparison of Figs. 1 and 2 shows (*i*) that the prewave occurs at an essentially identical halfwave potential for both **1** and **2** suggesting the formation of a common species from the two precursors, and (*ii*) the voltammetric fragment seen in each case at potentials more positive than the 'dark' electrooxidation, in each case, is observed at a half-wave potential consistent with that expected for the relevant free phosphine. We therefore suggest that the photofragmentation voltammograms shown in Figs. 1 and 2 constitute direct evidence for the photofragmentation scheme suggested in the introduction. Note additionally that Figs. 1 and 2 show no voltammetric evidence of any other photo-fragment such as might result from the loss of carbon monoxide. Moreover, the fact that the sum of the currents due to the prewave and to the direct oxidation of the precursor material (*i.e.* **1** or **2**), is in each case, very close to that observed in the dark for the latter process, enables us to deduce that any other process is relatively kinetically insignificant (< 5%) on the PFV timescale.

Confirmation of the suggested scheme was next pursued through the quantitative interpretation of photocurrent/flow rate dependences. First, however, the photocurrents seen for the prewave in each case were optimised by varying the wavelength of the light used to induce the fragmentation. The resulting 'action spectra' are shown in Fig. 3 from which it can be seen that the wavelengths selected to record Figs. 1 and 2 correspond to the maximum photocurrent seen above 300 nm in each case. Fig. 4 shows UV–VIS spectra recorded for **1** and **2**. Comparison with Fig. 3 indicates that the photochemical activity responsible for the dissociation of **1** and **2** arises from absorption in the visible region of their absorption bands. We now return to the quantitative mechanistic/kinetic considerations as revealed by the mass transport (flow rate) dependence of the photocurrents seen in Figs. 1 and 2 due to the oxidation of the iron-containing photofragment inferred, as above, to be [(η^5-C$_5$H$_5$)Fe(CO)(CH$_3$CN)=C(NHMe)Me]$^+$ (**3**). Fig. 5 shows the observed behaviour seen for **1** and **2**, respectively. Also shown is the theoretical behaviour calculated by established procedures[2,3,7,8] for a 'photo-CE' process:

$$\text{C} \quad \mathbf{1} + \text{CH}_3\text{CN} \xrightarrow{k} \text{PAr}_3 + \mathbf{3}$$

$$\text{E} \quad \mathbf{3} - e^- \rightleftharpoons \mathbf{3}^+$$

where the product of the 'E' step has been inferred to be the dication, **3**$^+$, on the basis of the measured chemical and electrochemical reversibility of the prewave as evidenced by (*i*)

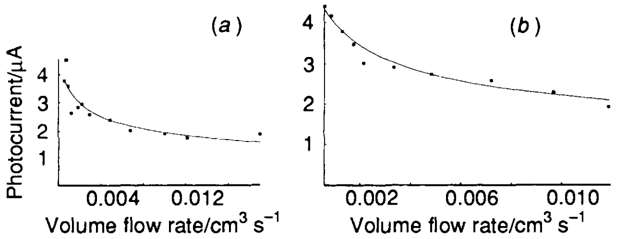


Fig. 5 Photocurrent/volume flow-rate behaviour measured for (*a*) **1** (8.9×10^{-4} mol dm^{-3}) and (*b*) **2** (7.1×10^{-4} mol dm^{-3}) using a platinum channel electrode and a light intensity of 39 mW cm^{-2}. The solid lines are those calculated using standard theory[2,3,7,8] with rate constants of (*a*) 0.05 s^{-1} and (*b*) 0.08 s^{-1}.

cyclic voltammetry under illuminated conditions, and (*ii*) mass transport corrected Tafel analysis[9] (62 mV decade^{-1}).

Experiments such as those shown in Fig. 5 were repeated for various concentrations of **1** and **2** in the range 10^{-4}–10^{-3} mol dm^{-3} and for different light intensities. In all cases excellent agreement between experiment and theory was found confirming the veracity of the 'photo-CE' process suggested. The best-fit rate constants, *k*, deduced for each species, **1** and **2**, showed no systematic dependence on concentration, and, at the maximum light intensity used (39 mW cm^{-2}), the mean values were found to be $k = 0.055$ (+/−0.007) s^{-1} (**1**) and 0.075 (+/−0.004) s^{-1} (**2**). For both species the rate constant, *k*, showed a direct proportionality to the light intensity used which again confirms our choice of mechanism.

In conclusion we have used PFV to demonstrate directly and unambiguously the preferential light-induced expulsion of phosphine over carbon monoxide from **1** and **2**. The mean rate constants given above enable us to estimate the quantum yields (at the optimal visible wavelengths of 390 and 375 nm) for light-induced phosphine expulsion of 0.09 (**1**) and 0.11 (**2**) which are closely similar values to those reported for the loss of phosphines from derivatives of hexacarbonylmolybdenum.[10] The capability of PFV for sensitive and quantitative kinetic and mechanistic studies has again been demonstrated. These results are entirely consistent with our previously reported stereochemical and phosphine exchange experiments and substantiate our hypothesis of photoinduced selective phosphine loss.

Acknowledgements

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