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Photoelectrochemistry of Tris(bipyridine)chromium (III) at a Transparent Tin Oxide Electrode

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Tris(bipyridine)chromium(III) ($Cr(bipy)_3^{3+}$) luminescence at 727 nm may be quenched by, *e.g.*, Fe(II) [1]. An electron transfer mechanism was assigned as shown in equation (1) (X = excited state):

$$\begin{gathered} Cr(bipy)_3^{3+} \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} {}^*Cr(bipy)_3^{3+} \\ {}^*Cr(bipy)_3^{3+} + Fe(II) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cr(bipy)_3^{2+} + Fe(III) \end{gathered} \qquad (1)$$

We have shown that transparent semiconducting electrodes are useful for electrochemical monitoring of excited state electron transfer processes [2, 3]. In this communication, we report the behaviour of $Cr(bipy)_3^{3+}$ in O_2 free acid solution (0.1 *M* H_2SO_4) under monochromatic laser (Ar-ion) and broad band visible (Xe lamp filtered to exclude wavelengths $\leqslant$ 400 nm) at an n-doped SnO_2 on glass electrode (O. H. Johns Glass, Ltd.). The cell consisted of the transparent (approx. 80% T in the visible) working electrode, a Pt counter electrode and an SCE reference. Potential was controlled with a Wenking potentiostat and current was monitored by lock in amplification (PAR HR-8) of the output across a 1K resistor when the light beam was chopped at 10–35 Hz.

The results confirm electron transfer to the low lying doublet ligand field excited state usually labelled ^2E (approximate O_h symmetry) as reported in ref. [1]. This is significant for two reasons. First, the literature has emphasized the role of charge transfer excited states in photo redox; excitation to ^2E involves only minimal rearrangement of either radial or angular electron distribution. Second, the photo product $Cr(bipy)_3^{2+}$ is capable of reducing water [4] (although not in a closed catalytic cycle).

Under laser irradiation using Ar lines between 457 and 514 nm and a constant $Cr(bipy)_3^{3+}$ concentration of 1.79×10^{-2} *M* a cathodic photocurrent was observed at potentials $\leqslant$ 100 mv anodic which increased on changing to more cathodic potentials up to a limit near –250 mv where electrode reduction interferes. Current also increase with absorptivity at shorter wavelength (normalized for laser power). Action spectra for photocurrents which match absorption spectra have been taken as an indication of reactive species [5]; but it should be remembered that this results mainly from the changing population of excited states near the electrode. Experiments at 488 nm and 514 nm with chromium concentrations chosen to match absorptivity, and therefore create equivalent excited state distributions, resulted in indistinguishable photocurrents within the precision of measurement. This implies no wavelength dependence on crossing from a spectral region, 488 nm, where change transfer excitation is important [6] to ligand field excitation [6] at 514 nm. The ligand field state is reactive.

When a scavenger is added to the solution, a potential between 200 and 800 mv anodic may be chosen where the process in equation (2) competes with the reverse reaction labelled by k_{-2} in equation (1) since the Cr(II) is rapidly oxidized at the electrode. The photocurrent becomes *anodic*:

$$Cr(bipy)_3^{2+} \xrightarrow[\text{electrode}]{k_3} Cr(bipy)_3^{3+} \qquad (2)$$

As shown previously [2, 3] at low light intensity (corresponding to low Fe(III) concentration), the dependence of the photocurrent on scavenger concentration is given by $1/i \propto (k_{-1}/[Fe(II)] + k_2)$. A reciprocal plot allows calculation of the ratio k_{-1}/k_2 from the ratio of the slope to the intercept. We used Fe(II) EDTA as prepared from mixing equal concentrations of Fe^{2+} and EDTA as a scavenger; $Fe^{2+}(aq)$ was unsatisfactory because it reacts with $Cr(bipy)_3^{2+}$ to give $Fe(bipy)_3^{2+}$. In the concentration range 3.97×10^{-4} *M* to 2.49×10^{-3} *M*, a plot of the reciprocal of *anodic* photocurrent *vs.* 1/[Fe(II)] gives $k_{-1}/k_2 = 4.39 \pm 0.76 \times 10^{-4}$ *M*. The value of k_2 may be found from quenching of 727 nm luminescence [1]. In our medium, a Stern–Volmer plot [7] for luminescence in a proportional quencher concentration range gave $k_2 = 3.60 \pm 0.27 \times 10^7$ M^{-1} S^{-1}. Combining this with the above result, the lifetime ($1/k_{-1}$) of the photoreactive excited state is found to be 63 μs, a result in excellent agreement (probably fortuitously precise) with the value obtained for the doublet from luminescence decay measurements [7]. We can therefore summarize as follows. Illumination of $Cr(bipy)_3^{3+}$ in the visible produces a cathodic photocurrent corresponding to reduction to $Cr(bipy)_3^{2+}$. Wavelength dependence shows ligand field states to be reactive. Using Fe(II) as a reducing scavenger converts the cathodic current to anodic and analysis of scavenging kinetics show the reactive state to have the lifetime of the doublet ligand field excited state. This state is,

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therefore, susceptible to photochemical reduction. If an analog of the ligand bipy which did not produce a labile Cr(II) complex could be found, a catalytic cycle for photo assisted electrolysis of water could be envisioned.

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