Laser Photoelectrochemistry as a Tool for Studies of Metal Complex Excited States

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Summary Photocurrents from argon ion laser irradiation of $[Ru(bipy)_3]^{2+}$ at an SnO_2 electrode in the presence of Fe^{3+} as a scavenger may be analysed to yield the excited state lifetime in a manner which can be extended to non-luminescent excited states.

Gleria and Memming[1] have reported a small anodic photocurrent from irradiation of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) at an SnO_2 electrode. This was attributed to oxidation of the excited state at the electrode and an analysis was presented of the conditions required for such a process. To derive an excited state lifetime directly from such measurements, it is necessary to study competition between relaxation and diffusion to the electrode. For the photocurrent to depart diagnostically from linear dependence on concentration, calculations suggest that a concentration $> 1\ \mathrm{mol\ dm^{-3}}$ would be required for a lifetime of $1\ \mu\mathrm{s}$. (Only at these concentrations would a large fraction of the light be absorbed in the diffusion layer.) The observation by Kobayashi, Furuta, and Simamura[2] of a cathodic current in a similar cell with dioxygen scavenging of the $\mathrm{Ru^{II}}$ excited state suggests an approach to using these cells for measurement of lifetimes of excited states. We have developed and tested this approach.

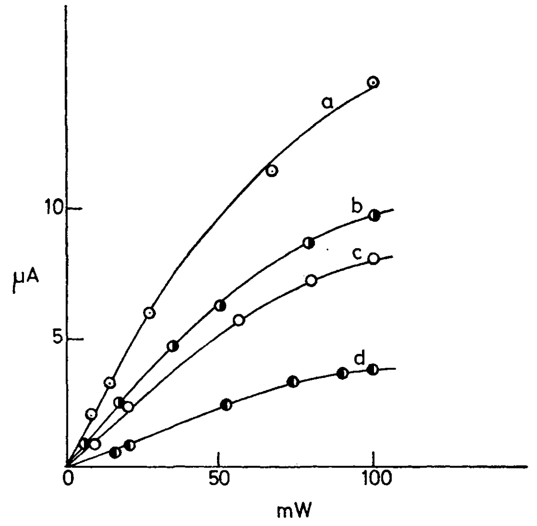

FIGURE 1. The dependence of the cathodic current on the power of the 476 nm laser line. The concentrations of $[\mathrm{Ru(bipy)_3}]^{2+}$ are; (a) 13·3 mM, (b) 8·9 mM, (c) 5·9 mM, and (d) 1·9 mM.

Our experiments have been conducted using a 1 W argon ion laser as a source of radiation at 459, 476, 488, and 514 nm. The radiation entered the solution through a doped $\mathrm{SnO_2}$ electrode (on glass) with a transmittance in the visible region of 80% and a resistance of $80\ \mathrm{ohm\ m^{-2}}$. Solutions of $[\mathrm{Ru(bipy)_3}]\mathrm{Cl_2}$ were prepared in $\mathrm{H_2SO_4}$ and under neutral conditions in the concentration range 1—13 $\times 10^{-3}\ \mathrm{mol\ dm^{-3}}$ (1—13 mM). A solution of $[\mathrm{Fe(bipy)_3}]\mathrm{Cl_2}$ ($1{\cdot}0 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$) was prepared in $0{\cdot}100\ \mathrm{mol\ dm^{-3}}$ $\mathrm{H_2SO_4}$. The potential of the $\mathrm{SnO_2}$ electrode was controlled in a three electrode configuration by a Wenking potentiostat; the counter electrode was Pt wire and the reference electrode an S.C.E. Scavengers observed included $\mathrm{O_2}$ and $\mathrm{Fe^{3+}}$. The latter was studied in a concentration range from 1 to $20 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}$.

In aerated acid solution in the cell, we observed photocurrents several orders of magnitude larger than those of Gleria and Memming[1] and *cathodic* like those reported by Kobayashi, Furuta, and Simamura.[2] In neutral solution (without $\mathrm{Fe^{3+}}$), we observed small *anodic* currents. We suggest mechanisms (1) and (2) for the two cases (an asterisk denotes an excited state). In mechanism (1), X may be either $\mathrm{O_2}$ or $\mathrm{Fe^{3+}}$. When it is $\mathrm{O_2}$, the back reaction (k_{-2}) with $\mathrm{O_2}^{\bullet-}$ (as opposed to $\mathrm{HO_2}^\bullet$) prevents cathodic currents from dominating in aerated neutral solutions and mechanism (2) determines the direction of current flow (the pH dependence is consistent with the acidity of $\mathrm{HO_2}^\bullet$) to yield a residual anodic current of *ca.* 10^{-7} A.

$$[\mathrm{Ru(bipy)_3}]^{2+} \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} [{}^*\mathrm{Ru(bipy)_3}]^{2+} + \mathrm{X} \xrightarrow{k_2} [\mathrm{Ru(bipy)_3}]^{+} + \mathrm{X}^\bullet$$
$$\mathrm{Ru(bipy)_3}]^{3+} + \mathrm{X}^\bullet \xrightarrow{k_{-2}} [\mathrm{Ru(bipy)_3}]^{2+} + \mathrm{X} \qquad (1)$$
$$\mathrm{Ru(bipy)_3}]^{3+} + \mathrm{e}^- \xrightarrow[\text{(cathodic)}]{\text{electrode}} [\mathrm{Ru(bipy)_3}]^{2+}$$

$$\mathrm{Ru(bipy)_3}]^{2+} \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} [{}^*\mathrm{Ru(bipy)_3}]^{2+} \xrightarrow[\text{(anodic)}]{\text{electrode}} [\mathrm{Ru(bipy)_3}]^{3+} + \mathrm{e}^- \qquad (2)$$

A particularly convincing and novel indication of the operation of mechanism (1) to produce cathodic currents is the evidence of intensity saturation of photocurrents shown in Figure 1. At constant scavenger concentration, the limit on the photocurrent is imposed by the efficiency of the k_{-2} process. Since both $[\mathrm{Ru(bipy)_3}]^{3+}$ and $\mathrm{X}^\bullet$ are photogenerated, the rate of this reaction will depend on the square of the intensity and limit the increase of photocurrent with intensity arising from k_2. This non-linear intensity dependence is revealed by laser irradiation.

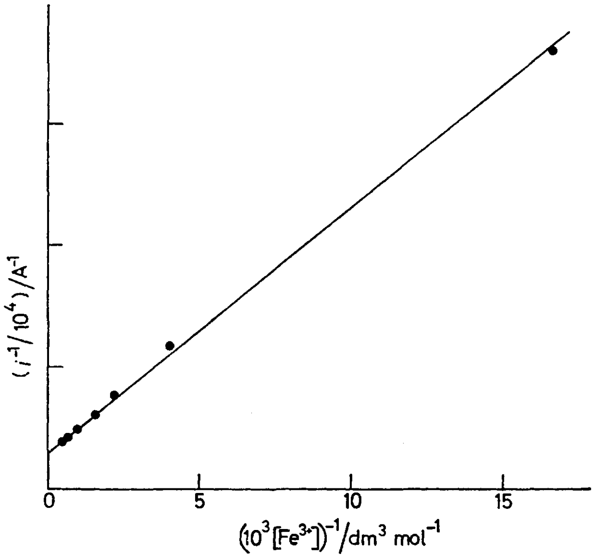

FIGURE 2. The dependence of the reciprocal of the photocurrent on the reciprocal of the $\mathrm{Fe^{3+}}$ concentration for a potential of 0·7 V and a $\mathrm{Ru^{II}}$ concentration of 6 mM. From the values of the slope and the intercept, it is possible to derive a value of $1{\cdot}5 \times 10^3$ for the ratio k_2/k_{-1} defined by equation (1).

With mechanism (1), the dependence of the photocurrent on scavenger concentration is a consequence of competition between the excited state reaction with the scavenger (k_2) and relaxation (k_{-1}). This suggests use of the scavenger concentration dependence to estimate k_{-1} (hence excited state lifetime), if k_2 can be estimated. Figure 2 shows the dependence of photocurrent on $\mathrm{Fe^{3+}}$ concentration at a potential of 0·70 V and a $\mathrm{Ru^{II}}$ concentration of 6 mM. The curve is presented in reciprocal form. The intercept represents complete $\mathrm{Fe^{3+}}$ scavenging. In conjunction with the slope, it allows assignment of $k_2/k_{-1} = 1{\cdot}5 \times 10^3$.

We need only estimate k_2. The best approach is to choose a scavenger to which a diffusion limited rate constant may be confidently assigned. Since the reaction in question is an outer sphere reduction process, rate constant correlations of the Marcus theory[3] may be used to identify scavengers which react at diffusion limited rates. A main factor making many reactions diffusion controlled is the large exothermicity of reaction from the excited state.[4]

Assigning a diffusion limited rate constant as k_2 with a value of $2{\cdot}4 \times 10^9$ mol^{-1} dm^3 s^{-1} following a discussion by Caldin,[5] we find a value of $1{\cdot}6 \times 10^6$ s^{-1} for k_{-1}. We have chosen, here, to attempt the estimation of an excited state constant, k_{-1}, that is already known from luminescence lifetime studies[6] to be $1{\cdot}7 \times 10^6$ s^{-1}. Our method is seen to be as successful as can be expected where the estimation of a diffusion limited rate constant is required. The method has two strengths, however. First, since scavenger concentration did not exceed millimolar levels, it is clear that much shorter lifetimes are accessible. Second, there is no requirement for luminescence which holds out hope for study of a range of previously inaccessible excited states. A photocurrent has also been observed in the solution of the non-luminescent $[\mathrm{Fe(bipy)_3}]^{2+}$ ion.

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