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Visible Region Photochemistry of Cu(II) Complexes Adsorbed on Optically Transparent Electrodes

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Introduction

In order to understand the full range of elementary photochemical steps which can follow excitation of metal complexes, it is necessary to find means to detect bimolecular elementary processes arising from short lived excited states. These intermediates are difficult to observe in homogeneous solution because they have a very short diffusion length within their lifetime. Similarly, it is necessary to detect photo processes whose primary products are high energy species which back react rapidly to mask the photochemical event.

Reactions of excited states at transparent electrodes, may confer irreversibility by transporting charge through the external circuit. This is useful for detection of the redox reactions of excited states which are masked in homogeneous media by rapid back reaction. Similarly, reactions of very short lived excited states may be observed when species are adsorbed on an electrode because diffusion need not proceed electron transfer to the electrode. Since photoelectrochemical measurements can be made relatively simply near transparent electrodes with inexpensive and convenient equipment, photoelectrochemistry is an attractive tool for the survey of possible processes. In this communication, we describe the redox photoreactivity of Cu(II) species illuminated in the visible (LF-excitation) region on transparent SnO_2 electrodes.

Experimental

n-doped SnO_2 on glass electrodes were prepared from material supplied by O. H. Johns Ltd. which had a film resistance less than 100 ohm/square. Three versions of the electrode were employed: (1) an untreated electrode; (2) a chemically modified electrode treated with trichlorosilylpropyldiethylenetriamine and; (3) a chemically modified electrode prepared by treating the SnO_2 surface first with $SiCl_4$ and then 3-(3-pyridine)-propanol-1. These electrodes were mounted in a three electrode cell described previously [1] which used an N_2 bubbler to sparge the electrode surface and stir the solution. The lamp was a 1 KW Hg-Xe lamp (Oriel) filtered through 10 cm of H_2O (to limit IR) and a cutoff filter (to remove wavelengths $\leqslant 400$ nm). The effectiveness of the uv cutoff filter was demonstrated by showing that it prevented photocurrents from light absorption by the SnO_2 film itself. The electrochemical processes were monitored with the aid of a PAR 174 polarograph as potentiostat and current monitor.

The small photo effects observed could only be resolved from background thermal currents at potentials near the zero of the 'thermal' background current. To ensure that photoeffects were not related to enhanced convection, photoeffects were recorded at a minimum of three potentials; one at small cathodic background 'thermal' currents, one very near zero 'thermal' current, and one at anodic background current. All reported photocurrents (light currents minus dark currents) were equal in sign and magnitude at all three potentials of measurement. This suggests that potentials are near limiting current values.

Solutions examined included $CuSO_4$ (0.005–1.00 *M*) in 0.65 *M* H_2SO_4 media, $CuSO_4$ (1.00 *M*) in neutral aqueous media, and the glycylglycinate complex of Cu(II) in pH = 9 buffer (Fisher Scientific) with Cu(II) concentrations in the range 10^{-2} to 10^{-1} *M*.

Results and Discussion

Small and similar photocurrents (one to two orders of magnitude below those for the microsecond lifetime $Ru(bipyridine)_3^{2+}$ ion (2) at 10^{-3} *M* concentration) were observed for all solutions examined on all three versions of the electrode. All were found to be *only* weakly dependent upon concentration of Cu(II) in the solution. For example acid (0.05 *M* H_2SO_4) solutions of $Cu^{2+}(aq)$ gave detectable *anodic* currents at 0.005 *M* Cu(II) and reached concentration independent values up to 5 nA between 0.1 and 1.0 *M* $[Cu^{2+}]$. The glycylglycinate complex of Cu(II) in pH = 9 media was studied at lower concentrations because it has much higher optical absorptivity. It gave photocurrents increasing in magnitude by less than a factor of two over the range 2.5×10^{-2} *M* to 1.00×10^{-1} *M* [Cu(II)] (approx. $f([Cu(II)]) = a[Cu^{2+}]^{1/2}$). At a Cu(II) concentration of 0.10 *M*, the photocurrent has a magnitude of approx. 15 nA.

The weak concentration dependence suggest *reaction in an adsorbed layer* at the electrode, although *differences in surface modification were not crucial.* This is confirmed by the observation that steady state

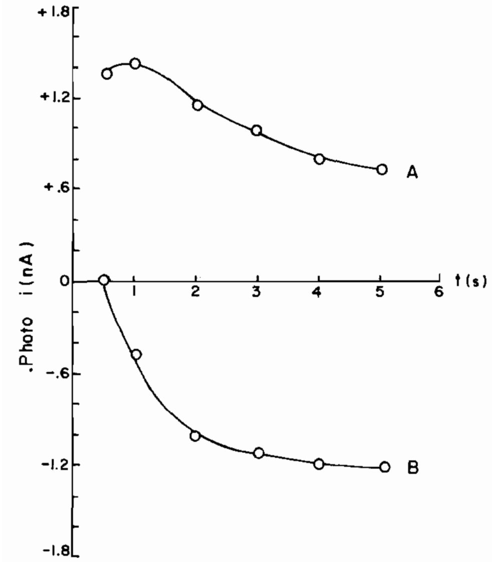

Fig. 1. Transient behaviour of photocurrents following manual opening of a shutter in the light beam as recorded with a recording oscilloscope. Curve A; 1 *M* $CuSO_4$, 0.1 *N* H_2SO_4, 425 mV. Curve B: 1 *M* $CuSO_4$, neutral solution, 420 mV.

currents were not achieved 'promptly' but required relaxation times of the order of 1–2 s. This length of time is appropriate for establishment of a steady state with respect to pore diffusion but not for the polarization of an electrode under the stirring conditions used especially if polarization depends on a short lived excited state.

Examples of the transient behaviour of the photoelectrode are shown in Fig. 1. This figure also indicates the most interesting feature of the results. The *direction* of the net photocurrent is a function of pH. The aquo Cu^{2+} ion in *acid* solution produces *anodic* currents. In *neutral* solution *cathodic* currents are observed and also for the Cu(glygly) complex at pH = 9. This can, no doubt, be related to the shift in the energy levels of SnO_2 surfaces. Clark and Sutin [3] reported that TiO_2 and SnO_2 can oxidize excited $Ru(bipy)_3^{2+}$ ion in acid but not in base and in consequence of a shifting valence band level at the surface. We see parallel behaviour for Cu(II). In acid the hole is sufficiently oxidizing to give Cu(III) as a photoproduct whereas in base the lower energy process of Cu(II) reduction predominates. The experiments do not permit identification of the ultimate fate of the immediate photoproducts. This is mainly because photocurrents were so small.

Acknowledgement

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