Inorganica Chimica Acta, 45 (1980) L37–L38
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Visible Region Photoelectrochemistry of (2,9-dimethyl-1,10-phenanthroline)Cu(I)

A. KIRSCH-DE MESMAEKER*, L. WILPUTTE-STEINERT
and J. NASIELSKI

Université Libre de Bruxelles, Faculté des Sciences, Service de Chimie Organique, Av. F. D. Roosevelt 50, B-1050 Brussels, Belgium

Received March 18, 1980

The usefulness of photoelectrochemistry, to detect redox reactions of excited states, which are masked in homogeneous media by the fast back reaction, has been emphasized recently by Langford and co-workers [1]. We wish to report here our results concerning the photoelectrochemical oxidation of $(dmp)_2Cu(I)$ in aqueous methanol illuminated in the visible region (metal-to-ligand charge-transfer excitation) at a transparent SnO_2 bubbling gas electrode. This contribution is also related to the work of McMillin and Ahn [2] about the rather low-efficient photo-induced reduction of several Co(III) complexes by excited $(dmp)_2Cu(I)$. The authors showed that the redox reaction must be ascribed to an electron transfer directly from the thermally equilibrated excited (thexi) state of $(dmp)_2Cu(I)$ to Co(III); indeed, direct excitation of the cobalt complex did not enhance the efficiency of the photoreaction, suggesting that a mechanism involving prior energy transfer from the excited $(dmp)_2Cu(I)$ species to the cobalt complex, followed by oxidation by a thexi state of Co(III) is not operative.

Experimental

The potentiostatic photoelectrochemical technique and the SnO_2 bubbling gas electrode have already been described elsewhere [3]. The polycrystalline SnO_2 layer deposited on a glass plate is 320 nm thick and has a charge carrier concentration of 10^{20} donors/cm^3. The electrode area is of the order of 16 mm^2. The solutions are 1/1 mixtures of methanol and aqueous acetate buffer (pH 4.5), 5.10^{-4} mol X dm^{-3} in $Cu(dmp)_2NO_3$ and 10^{-1} mol X dm^{-3} in $LiNO_3$ as supporting electrolyte. The $Cu(dmp)_2NO_3$ solution is illuminated through the SnO_2 electrode with a 2000W Osram halogen lamp. Only a fraction of the emitted light is focused with a series of lenses on the electrode surface. The solutions are deoxygenated by bubbling nitrogen during at least 15 minutes before recording the voltammogram.

Results and Discussion

The photovoltammogram and the foot of the dark oxidation wave are given in Fig. 1, curves b and a respectively. The sign of the photocurrent (oxidation current) is obviously to be ascribed to the oxidation of the excited $(dmp)_2Cu(I)$ complex into $(dmp)_2Cu(II)$.

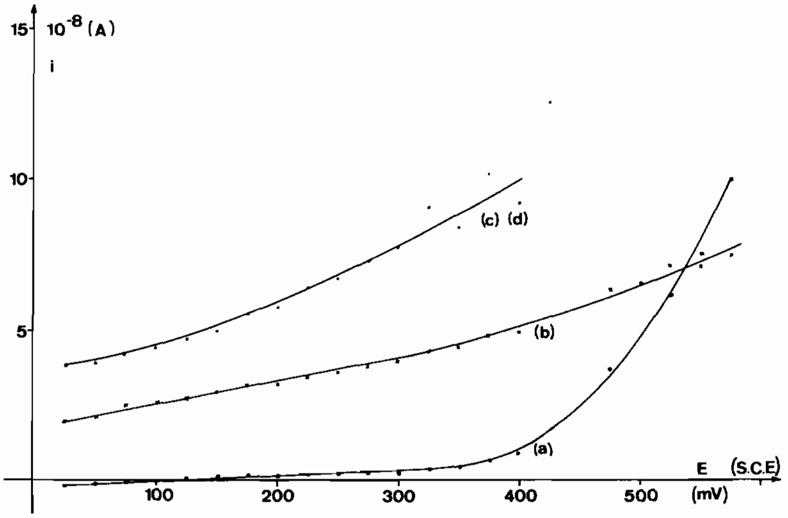

Fig. 1. a: dark voltammogram, b: photovoltammogram in the absence of hydroquinone, c: photovoltammogram with hydroquinone 5 X 10^{-2} mol X dm^{-3}, d: photovoltammogram with hydroquinone 10^{-1} mol X dm^{-3}. Concentration of Cu(I) $(dmp)_2$ = 5 X 10^{-4} mol X dm^{-3}.

The dark back electron transfer, from the SnO_2 to the resulting $(dmp)_2Cu(II)$, is also possible. Indeed,

---

*Qualified researcher of the Belgian Fonds National de la Recherche Scientifique.

it has been shown [4, 5] that with highly doped semi-conductor, the photooxidation products can be recycled by a reduction current consisting of tunneling conduction electrons. The observed photooxidation would then result from the following reaction steps:

$$\mathrm{Cu(I)} \xrightarrow{h\nu} \mathrm{Cu^*(I)} \qquad (1)$$

$$\mathrm{Cu^*(I)} \longrightarrow \mathrm{Cu(I)} \qquad (2)$$

$$\mathrm{Cu^*(I)} \longrightarrow \mathrm{Cu(II)} + 1\mathrm{e}, i^+ \qquad (3)$$

$$\mathrm{Cu(II)} \longrightarrow \mathrm{Cu(II)\,(bulk)} \qquad (4)$$

$$\mathrm{Cu(II)} + 1\mathrm{e} \longrightarrow \mathrm{Cu(I)}, i^- \qquad (5)$$

$$\mathrm{Cu(II)} + \mathrm{HQ} \longrightarrow \mathrm{Cu(I)} + \mathrm{HQ_{ox}} \qquad (6)$$

where all species are considered to be very close to the electrode; step 4 stands for the diffusion of the oxidized complex from the electrode to the bulk of the solution. Reaction (5) would limit intensity of the resulting photooxidation current. This led us to dry to supersensitize the photocurrent by the addition of hydroquinone (HQ) 5×10^{-2} and 10^{-1} mol X dm^{-3}; reaction (6)* would then compete with reaction (5), leading to a photooxidation increase. But, as shown in Fig. 1 (curves b, c and d), the extent of supersensitization, less then a two-fold increase of the photocurrent, is markedly lower than in the case of several dyes [3, 7] with the same SnO$_2$ electrode, where twenty-to hundred-fold increases of photocurrents could be reached. This poor supersensitization could be ascribed to a particularly weak contribution of the reduction step (reaction 5), compared to that operating with adsorbed dyes [4]; this seems possible because the complex does not seem to adsorb and thus does not interact strongly enough to allow the back reaction. This adsorption effect on the efficiency of the tunnelling electron transfer had already been pointed out by Gerischer and coworkers [8], to explain the poor tunnelling oxidation of hydroquinone at highly doped ZnO electrodes compared to adsorbed rhodamine B.

The slight photocurrent increase observed with HQ would then originate from a regeneration of the Cu(I) complex at the electrode (reaction 6), knowing that the main fate of Cu(II) is step (4). On the contrary, using Ru(bpy)$_3^{2+}$ which is claimed to be adsorbed on the semi-conductor, Memming and coworkers have observed an important decrease of the anodic photocurrent at high-conducting SnO$_2$ (in anaerobic conditions) compared to the photocurrent at poorly doped SnO$_2$ [9]; the decrease of the anodic current was ascribed to the existence of an efficient back-reaction by tunnelling electrons. The short lifetime of (dmp)$_2$Cu*(I), estimated to 1–2 ns [2] in solution, is most probably responsible of the moderate extent of the photocurrent.

We have to mention however, that the thermal back reaction has been detected as a very weak reduction current after cutting off the light, when hydroquinone was basent from the solution (see Fig. 2, curve e); in the presence of the reductant, the oxidation photocurrent drops straightforward to zero as one would expect for a solution containing no (dmp)$_2$Cu(II) (see Fig. 2, curve f).

As a conclusion, our photoelectrochemical results bring confirmation to the assumption of McMillin and Ahn according to which the excited (dmp)$_2$Cu(I) species (MLCT state) operates as an outer-sphere reducing agent.

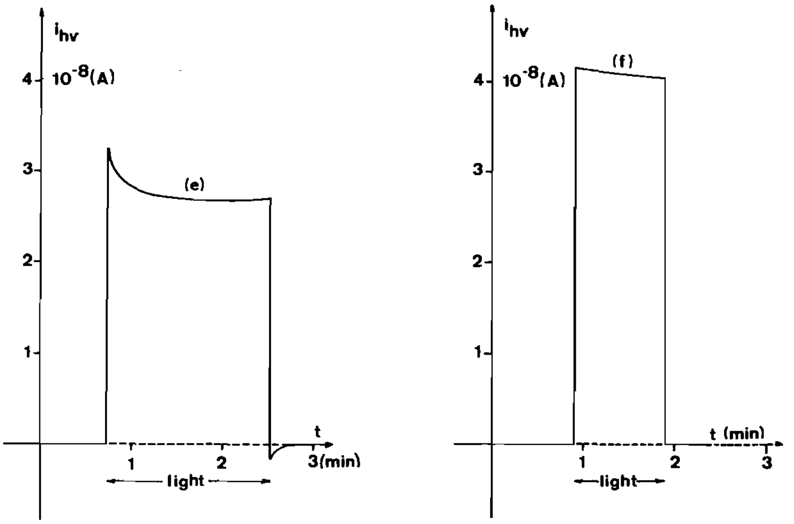

Fig. 2. Photocurrent *vs.* time. e: without hydroquinone, f: with hydroquinone 5×10^{-2} mol X dm^{-3}.

---

*According to the redox potentials of (dmp)$_2$Cu(I)/(dmp)$_2$ Cu(II) (+0.38 V *vs.* SCE) [6] and hydroquinone/quinone (+0.18 V *vs.* SCE) at pH 4.5, reaction 6 is possible and has been tested experimentally.

References

1 C. H. Langford, W. M. Sont and R. Douglas Burch, *Inorg. Chim. Acta, 44,* L73 (1980).

2 Byung-Tae Ahn and D. R. McMillin, *Inorg. Chem., 17,* 2253 (1978).

3 J. Nasielski, A. Kirsch-De Mesmaeker and P. Leempoel, *Electrochim. Acta, 23,* 605-611 (1978).

4 B. Pettinger, H. R. Schöppel and H. Gerischer, *Ber. Bunsenges., 77,* 960 (1973).

5 F. Möllers and R. Memming, *Ber. Bunsenges., 76,* 469 (1972).

6 C. J. Hawkins and D. D. Perrin, *J. Chem. Soc.,* 2996 (1963).

7 A. Kirsch-De Mesmaeker, J. Kanicki, P. Leempoel and J. Nasielski, *Bull. Soc. Chim. Belges, 87,* 849 (1978).

8 B. Pettinger, H. R. Schöppel and H. Gerischer, *Ber. Bunsenges., 78,* 450 (1974).

9 R. Memming, F. Schröppel and U. Bringmann, *J. Electroanal. Chem., 100,* 307 (1979).