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Excited State Photoelectrochemical Production of H_2O_2 and Br_2

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An excited state photoelectrochemical cell has been designed in which H_2O_2 and Br_2 are produced in acetonitrile solution in separate cell compartments with a high per photon efficiency.

In earlier work a series of excited state photoelectrochemical cells have been described in which a photocurrent is produced, as well as H_2, O_2, or other chemicals in a separate cell compartment.[1] The cells described so far have been based upon sacrificial reagents or have operated with low quantum efficiencies. We report here a cell where the chemicals H_2O_2 and Br_2 are produced in acetonitrile solution with a high per photon quantum efficiency.

The cell is based on reductive quenching of the metal-to-ligand charge transfer (MLCT) excited state of $(bpy)Os(das)_2^{2+}$ [bpy = 2,2′-bipyridine, das = *o*-phenylene-bis(dimethylarsine)] by $N(p\text{-}C_6H_4Br)_3$ (NAr_3) in acidic, aerated acetonitrile

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solution. For the complex, $\lambda_{max}^{abs} = 380$ cm, $\lambda_{max}^{em} = 575$ nm, τ_0 (MeCN, 23.0 ± 0 °C, Ar deaerated) = 1580 nsec. The estimated reduction potential for the $(bpy)Os(das)_2^{2+*/+}$ excited state couple is $E_{\frac{1}{2}} = 1.14 \pm 0.08$ V *vs.* S.C.E. (standard calomel electrode). For the quencher, $E_{\frac{1}{2}}(NAr_3^{+/0}) = 1.07 \pm 0.02$ V *vs.* S.C.E. The reactions which occur in the cell are shown in Scheme 1 below.

Photocathode

$$(bpy)Os(das)_2^{2+} \xrightarrow{h\nu} (bpy)Os(das)_2^{2+*} \quad (1)$$

$$(bpy)Os(das)_2^{2+*} + NAr_3 \xrightarrow{k_q} (bpy)Os(das)_2^{+} + NAr_3^{+} \quad (2)$$
$$k_q = (1.03 \pm 0.16) \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$$

$$(bpy)Os(das)_2^{+} + O_2 + H^+ \rightarrow (bpy)Os(das)_2^{2+} + HO_2^{\cdot} \quad (3)$$

$$HO_2^{\cdot} + NAr_3 + H^+ \rightarrow H_2O_2 + NAr_3^{+} \quad (4)$$

$$O_2 + 2H^+ + 2NAr_3 \xrightarrow{h\nu} H_2O_2 + 2NAr_3^{+} \quad (5)$$

$$2NAr_3^{+} \xrightarrow{+2e^-} 2NAr_3 \quad (6)$$

Anode

$$2Br^- \xrightarrow{-2e^-} Br_2 \quad (7)$$

Scheme 1

Following excitation and quenching [equations (1) and (2)], the reduced complex $(bpy)Os(das)_2^+$ is captured by O_2 to give $HO_2^{\cdot}$ [equation (3)] before back electron transfer between NAr_3^+ and $(bpy)Os(das)_2^+$ can occur [equation (8)]. A rapid reaction between $Ru(bpy)_3^+$ and O_2 has been shown to occur.[2]

$$(bpy)Os(das)_2^{+} + NAr_3^{+} \xrightarrow{k} (bpy)Os(das)_2^{2+} + NAr_3 \quad (8)$$
$$k = 2.0 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$$

The appearance of H_2O_2 as a product could occur either by oxidation of a second NAr_3 by $HO_2^{\cdot}$ [equation (4)] or by disproportionation [equation (9)], a point which will be considered below. The net effect of the photochemical sequence in

$$HO_2^{\cdot} \rightarrow \tfrac{1}{2}H_2O_2 + \tfrac{1}{2}O_2 \quad (9)$$
$$[k(H_2O, 25\ ^\circ\text{C}) = (8.6 \pm 0.6) \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}][3]$$

the photocathode is the buildup of NAr_3^+, which oxidizes Br^- to Br_2 in a separate cell compartment.

In a typical experiment, a solution containing $(bpy)Os(das)_2^{2+}$ (6×10^{-5} M), NAr_3 (5×10^{-3} M), and $LiClO_4$ (*ca.* 0.1 M) in acidic ([$HClO_4$] *ca.* 0.3 M) acetonitrile was photolysed at 436 nm [$I^\circ = 3.0 \times 10^{-9}$ einstein s^{-1}, ϵ_{436} (Os^{II}) = 1784 ± 25 l mol^{-1} cm^{-1}] for 30 min, using a cell design previously described.[4] The anode consisted of a Pt gauze electrode and a solution containing Bu^n_4NBr and the electron transfer relay $Ru(bpy)_2(PPh_3)Cl^+$† [$E_{\frac{1}{2}}(Ru^{2+/+}) = +0.92 \pm 0.03$ V *vs.* S.C.E.]. The output of the cell was monitored in three ways: (i) H_2O_2 produced in the photocathode was determined by a leuco-crystal violet analysis modified for use in MeCN.[5] (ii) Br_2 produced in the anode was determined by reduction of Br_2 by *N,N,N′,N′*-tetramethylbenzidine (TMBD), which occurs immediately upon addition of excess of solid TMBD [equation (10)], followed by spectrophotometric determination of $TMBD^+$ (ϵ_{790} = 5620 l mol^{-1} cm^{-1}).‡ (iii) The photocharge produced in the cell was

$$\tfrac{1}{2}Br_2 + TMBD \rightarrow Br^- + TMBD^+ \quad (10)$$

measured by connecting the cathode and anode through a 1000 Ω resistor, and integrating photocurrent *vs.* time curves. The per photon quantum efficiency of the cell was calculated from equation (11):[4]

$$\phi_{cell} = \frac{q}{nFI^\circ 10^{-A_s}(1 - 10^{-A_{Os}})t} \quad (11)$$

where q = integrated photocurrent, I° = incident light intensity, $n = 1$ (the number of electrons transferred), A_S = absorbance of Pt screen, collector electrode which was attached to the front face of the cell, A_{Os} = absorbance of sensitizer, t = photolysis time, and F = the Faraday, 96 500 C mol^{-1}. The results of all three methods of analysis were internally consistent with the predictions of Scheme 1 in terms of the amounts of H_2O_2 and Br_2 produced and the magnitude of the integrated photocurrent. For example, the per photon efficiency of the cell, ϕ_{cell}, measured electrochemically was 0.75 ± 0.03, ϕ_{Br_2} was approximately half that (0.35 ± 0.12), as expected from Scheme 1. Using the analogous 1,10-phenanthroline complex $(phen)Os(das)_2^{2+}$ (λ_{max}^{em} = 575 nm, τ_0 = 3910 nsec) as sensitizer gave ϕ_{cell} = 1.20 ± 0.04.

A point of concern with the proposed mechanistic scheme was the role of O_2 quenching, which occurs with $k(q,O_2)[O_2] = 1.20 \times 10^6$ s^{-1}. In related systems, O_2 quenching is known to give singlet oxygen ($^1\Sigma_g$).[6] A possible origin for $HO_2^{\cdot}$ could lie in energy transfer between $(bpy)Os(das)_2^{2+*}$ and O_2 to give $^1O_2$ followed by electron transfer quenching of $^1O_2$, as shown in equation (12).

$$^1O_2 + NAr_3 + H^+ \rightarrow HO_2^{\cdot} + NAr_3 \quad (12)$$

The value of ϕ_{cell} was measured as a function of the partial pressure of O_2 (*pp* O_2) in Ar–O_2 mixtures, and the following results were obtained: ϕ_{cell} = 1.40 ± 0.04 (*pp* $O_2 = 10^{-3}$), ϕ_{cell} = 1.60 ± 0.04 (*pp* $O_2 = 5 \times 10^{-3}$), ϕ_{cell} = 0.75 ± 0.03 (aerated), and ϕ_{cell} = 0.17 ± 0.03 (O_2 saturated). The trend of the data is consistent with O_2 quenching as the dominant process at high [O_2], but without the production of a significant photocurrent or of redox products. The maximum cell efficiency of *ca.* 1.6 is reached at low [O_2], where reductive quenching by NAr_3 is the only important quenching process, but sufficient O_2 is still present to capture $(bpy)Os(das)_2^+$ before back electron transfer with NAr_3^+ [equation (8)] can occur. Maximum cell efficiencies exceeding 1 show that, at least in part, the fate of $HO_2^{\cdot}$ is further reduction by NAr_3 [equation (4)] rather than disproportionation [equation (9)].

Over a sustained photolysis period (>1 h), the observed photocurrent gradually begins to fall, apparently because of

† The role of the electron transfer relay is to overcome overvoltage problems associated with the oxidation of Br^- to Br_2. In the cell, NAr_3^+ oxidizes $Ru(bpy)_2(PPh_3)Cl^+$ to $Ru(bpy)_2(PPh_3)Cl^{2+}$, which, in turn, rapidly oxidizes Br^- to Br_2.

‡ The spectrophotometric analysis was carried out using only a slight excess of Bu^n_4NBr in the anode compartment. Excess of Br^- interferes with the spectrophotometric analysis.

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oxidation of H_2O_2 by NAr_3^+ as the concentration of H_2O_2 rises. The net reaction in the cell involves the production of H_2O_2 and Br_2 as in equation (13), a reaction that is energy storing. In water, $\Delta G^\circ = +0.4$ V; in acetonitrile, simple

$$O_2 + 2H^+ + 2Br^- \rightarrow H_2O_2 + Br_2 \qquad (13)$$

mixing experiments show that the reaction between Br_2 and H_2O_2 remains spontaneous. More importantly, the cell, as operated, becomes an excited state photoelectrochemical synthesis cell for the production of the useful chemicals H_2O_2 and Br_2 with a high per photon efficiency.

Acknowledgements are made to the Department of Energy for support of this research, the National Science Foundation for a fellowship for W.J.D., and GTE Laboratories of Waltham, Mass., for financial support during the summer of 1980 for J.L.M.

Received, 28th April 1982; Com. 484

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