Excited State Photoelectrochemical Production of H$_2$O$_2$ and Br$_2$

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An excited state photoelectrochemical cell has been designed in which H$_2$O$_2$ and Br$_2$ are produced in acetonitrile solution in separate cell compartments with a high per photon efficiency.
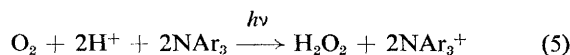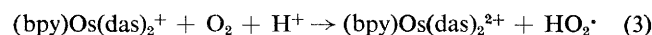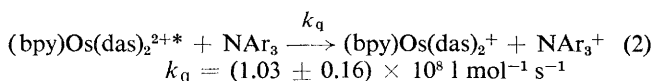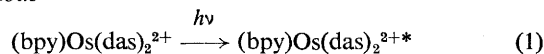
In earlier work a series of excited state photoelectrochemical cells have been described in which a photocurrent is produced, as well as H$_2$, O$_2$, or other chemicals in a separate cell compartment.[1] The cells described so far have been based upon sacrificial reagents or have operated with low quantum efficiencies. We report here a cell where the chemicals H$_2$O$_2$ 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(dimethyl-arsine)] by N(p-C$_6$H$_4$Br)$_3$ (NAr$_3$) in acidic, aerated acetonitrile

solution. For the complex, $\lambda_{max}^{abs} = 380$ cm, $\lambda_{max}^{em} = 575$ nm, τ_0 (MeCN, $23.0 \pm 0\,°C$, 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.
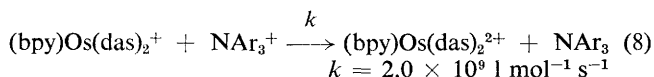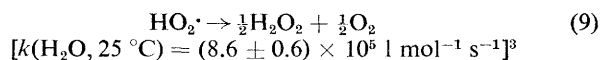
Photocathode

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

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

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

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

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

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

Anode

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

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

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

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 [$I° = 3.0 \times 10^{-9}$ einstein s^{-1}, ϵ_{436} (Os^{II}) $= 1784 \pm 25$ 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'-tetramethyl-benzidine (TMBD), which occurs immediately upon addition of excess of solid TMBD [equation (10)], followed by spectro-photometric determination of TMBD$^+$ ($\epsilon_{790} = 5620$ l mol^{-1} cm^{-1}).‡ (iii) The photocharge produced in the cell was

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

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]

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

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 $(phen)Os(das)_2^{2+}$ ($\lambda_{max}^{em} = 575$ nm, $\tau_0 = 3910$ nsec) as sensitizer gave $\phi_{cell} = 1.20 \pm 0.04$.

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).

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

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: $\phi_{cell} = 1.40 \pm 0.04$ (pp $O_2 = 10^{-3}$), $\phi_{cell} = 1.60 \pm 0.04$ (pp $O_2 = 5 \times 10^{-3}$), $\phi_{cell} = 0.75 \pm 0.03$ (aerated), and $\phi_{cell} = 0.17 \pm 0.03$ (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

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† 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.

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

$$O_2 + 2H^+ + 2Br^- \rightarrow H_2O_2 + Br_2 \qquad (13)$$
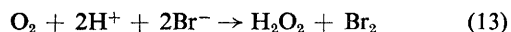
mixing experiments show that the reaction between Br_2 and H_2O_2 remains spontaneous. More importantly, the cell, as operated, becomes an excited state photoelectrochemical synthesis cell for the production of the useful chemicals H_2O_2 and Br_2 with a high per photon efficiency.

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