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PHOTO-ELECTROCHEMICAL BEHAVIOUR OF THE TRIS(2,2'-BIPYRIDYL)-RUTHENIUM(II) ION IN ACIDIC SOLUTION

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A cathodic photocurrent was observed at an SnO_2 electrode immersed in an acidic solution of tris(2,2'-bipyridyl)ruthenium(II) dichloride illuminated with visible light, and the current increased in the presence of methyl viologen. The photo-potential at the electrode was found to be positive enough for water to be oxidized; in fact, chemical species produced in a cell incorporating this photochemical system were identified with oxygen and hydrogen peroxide.

A photogalvanic effect was observed when an acidic solution of tris(2,2'-bipyridyl)ruthenium(II) dichloride ($Ru(bpy)_3Cl_2$) was illuminated in a cell equipped with a window for illumination coated with a thin transparent film of tin dioxide serving as an electrode. Typical current-voltage curves obtained potentiostatically with platinized platinum as an auxiliary electrode are shown in Fig. 1. In the dark, no significant current flowed in the potential region from +0.8 to -0.2 V (vs. SCE) and an anodic and a cathodic current observed at potentials outside this region are obviously attributed, respectively, to oxygen evolution and reduction of tin dioxide or hydrogen evolution.1) Under illumination with visible light ($\lambda > 425$ nm), a cathodic current flowed at any potentials more negative than that corresponding to oxygen evolution, and it increased when oxygen had been bubbled into the solution before the measurement.

The cathodic photocurrent produced by monochromatic light was measured with an ammeter short-circuiting the electrodes and plotted as a function of the wave length of light (Fig. 2). The photocurrent, which attained to a stationary strength in a moment after illumination was begun, increased with the concentration of $Ru(bpy)_3Cl_2$

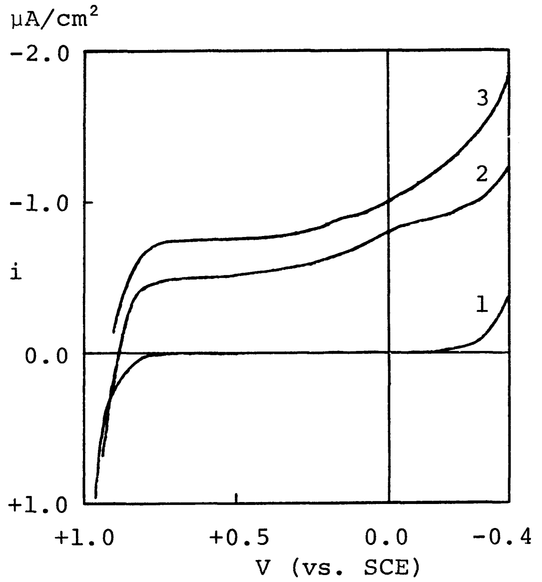


Fig. 1. Current-voltage curves for an SnO_2 electrode in a solution of $Ru(bpy)_3Cl_2$ (8.2×10^{-4} M) in 1.0 N H_2SO_4; curve 1: without illumination; curve 2: under illumination; curve 3: under illumination, after O_2 had been bubbled into the solution.

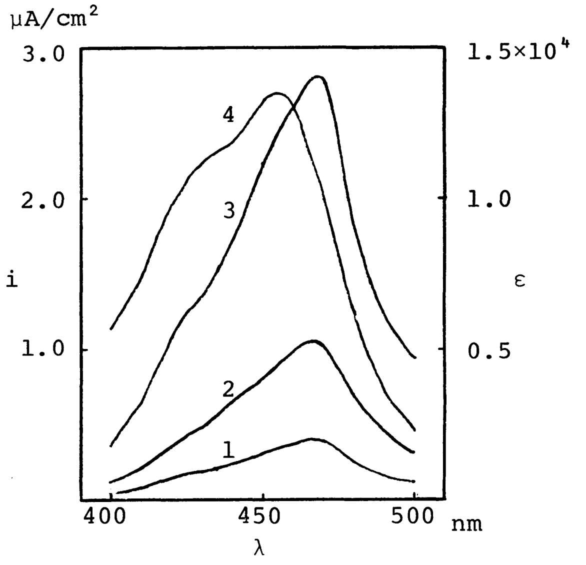


Fig. 2. Spectral distribution of photocurrents caused by $Ru(bpy)_3Cl_2$ in various concentrations in 1.0 N H_2SO_4; curve 1: 7.86×10^{-4} M; curve 2: 3.19×10^{-3} M; curve 3: 3.19×10^{-3} M with methyl viologen (7.8×10^{-3} M); curve 4: absorption spectrum of $Ru(bpy)_3Cl_2$.

and also by a factor of 3 on addition of methyl viologen, which is known to quench oxidatively the photo-excited $Ru(bpy)_3{}^{2+}$ (2). The quantum yield of the current at 470 nm under conditions corresponding to curve 3 in Fig. 2 was found to be 0.005 by means of ferrioxalate actinometry. The action spectra obtained are essentially similar in shape to the absorption spectrum of $Ru(bpy)_3{}^{2+}$, although the spectral peaks are 15 nm apart from each other, probably owing to the uneven spectral distribution of light intensity of a xenon lamp used as a light source with rather higher intensity at about 470 nm.(3) It is therefore concluded that the photocurrent arises as a consequence of light absorption by the $Ru(bpy)_3{}^{2+}$ ion.

A plausible mechanism, which involves electron transfer from the photo-excited $Ru(bpy)_3{}^{2+}$ to an acceptor such as oxygen and methyl viologen (X) to give $Ru(bpy)_3{}^{3+}$ ions, this in turn receiving an electron from the tin dioxide electrode, is as follows:

$$Ru(bpy)_3{}^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3{}^{2+} \tag{1}$$

$$^*Ru(bpy)_3{}^{2+} \longrightarrow Ru(bpy)_3{}^{2+} \tag{2}$$

$$^*Ru(bpy)_3{}^{2+} + X \longrightarrow Ru(bpy)_3{}^{3+} + X^{\overline{\cdot}} \tag{3}$$

$$Ru(bpy)_3{}^{3+} + X^{\overline{\cdot}} \longrightarrow Ru(bpy)_3{}^{2+} + X \tag{4}$$

$$Ru(bpy)_3{}^{3+} \xrightarrow{\text{electrode}} Ru(bpy)_3{}^{2+} \tag{5}$$

If a photocurrent is not withdrawn, a photo-stationary state will be established, for which, on the basis of the above scheme, the usual stationary state approximation predicts

$$\frac{[\mathrm{Ru(bpy)_3}^{3+}]}{[\mathrm{Ru(bpy)_3}^{2+}]} \propto [\text{Quanta of light absorbed per unit time}]^{1/2}$$

provided that the light intensity is weak enough. The electric potential E at an electrode immersed in the solution, therefore, is correlated with the relative intensity of light I by the expression:

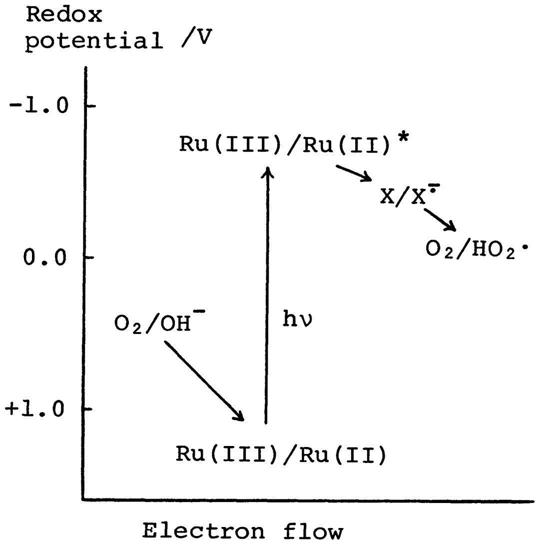
$$E = \frac{RT}{F}\ln\frac{[\mathrm{Ru(bpy)_3}^{3+}]}{[\mathrm{Ru(bpy)_3}^{2+}]} + \text{const.} = \frac{2.303}{2}\cdot\frac{RT}{F}\log I + \text{const.}$$

This relation was borne out by experiments in which the potential at a tin dioxide electrode was measured against a saturated calomel electrode in a solution of $Ru(bpy)_3Cl_2$ (1.2×10^{-2} M) and methyl viologen (7.8×10^{-3} M) in 0.1 N hydrochloric acid; plots of E vs. log I represent a straight line, the slope being 0.027 V in good agreement with the theoretical value 2.303RT/2F = 0.029 V.

The observed photogalvanic effect does not probably involve any electronic process peculiar to tin dioxide as semiconductor; separate experiments showed that a transparent film of platinum deposited on a glass plate functions in a similar manner in producing a cathodic current, although it was not as efficient as tin dioxide because of its low transmittance.

Reaction products were examined with an apparatus consisting of two half-cells connected with each other by means of a salt bridge supported by agar-agar. The cathode cell was equipped with a tin dioxide electrode about 12 cm^2 in area and contained a solution of $Ru(bpy)_3Cl_2$ (3.12×10^{-3} M) and methyl viologen (7.8×10^{-3} M) in 1.0 N sulphuric acid. The anode cell contained a solution of sodium hydroxide and sodium sulphate both in the concentration of 1.0 M and a platinized platinum electrode was used. On illumination with visible light ($\lambda > 425$ nm) a short-circuit photocurrent of about 160 μA flowed. The gas evolved at the anode was shown to be oxygen by means of mass spectrometry and oxygen collected in six hours amounted to 4.9×10^{-3} mmole. That the source of oxygen is none other than water was demonstrated by an experiment with $H_2{}^{18}O$ (isotopic abundance 11.4 %) and sodium dissolved in it, the isotopic distribution found in the evolved gas being ${}^{18}O_2$:${}^{18}O{}^{16}O$:${}^{16}O_2$ = 1.7:19.7:78.6 (%) in good agreement with the statistical value. The catholyte was passed through a column of a cation exchange resin to remove $Ru(bpy)_3{}^{2+}$ ions and methyl viologen and analyzed for hydrogen peroxide, which could have been formed from dissolved oxygen by reduction with monocationic reduced methyl viologen produced in reaction 3.[4)] Polarography ($E_{1/2}$ for H_2O_2 = -0.98 V vs. SCE) and permanganometry both gave 1.6×10^{-2} mmole of hydrogen peroxide, and in the latter analysis the gas evolved was identified with oxygen by mass spectrometry. Thus it is evident that in the present photochemical system oxygen is reduced to hydrogen peroxide by monocationic reduced methyl viologen. Fig. 3 represents the reaction sequence in terms of the redox couples involved shown in the positions corresponding to their respective standard redox potentials; the net effect of the light, as regards the chemical reaction, amounts to $O_2 + 2H_2O \longrightarrow 2H_2O_2$.

Fig. 3



The present results suggest possible ways in which visible light is utilized to make water function as reducing agent through the intermediacy of suitable chemical species in a manner mimicking the primary photochemical process in the photosynthetic system in green plants.

References

(1) F. Möllers and R. Memming, Ber. Bunsenges. Phys. Chem., 76, 496 (1972).
(2) C. R. Bock, T. J. Meyer, and D. G. Whitten, J. Amer. Chem. Soc., 96, 4710 (1974).
(3) Cf., e.g., A. Schönberg, G. O. Schenck, and O.-A. Neumüller, "Preparative Organic Photochemistry," Springer-Verlag, Berlin, 1968, p. 473.
(4) Cf. W. R. Boon, Chem. Ind., 782 (1965).

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