A Singlet State-driven Photogalvanic Cell Based on the Photoreduction of 3,7-Diaminophenoxazinylium Chloride ('Oxonine') by Iron(II)

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The electrical characteristics and monochromatic power efficiency are given for the first singlet state-driven photogalvanic cell which is based on the photoreduction of the title dye by iron(II) with spontaneous regeneration of the dye and iron(II) from the charge carriers leuco-oxonine and iron(III) at the anode and cathode respectively.

One approach to the development of more quantum efficient photogalvanic cells for solar energy conversion is to make use of the excited singlet states, S_1, rather than the triplet state, T_1, of the chromophore. This avoids the frequently substantial loss of energy† during intersystem crossing and thus, in principle, a higher cell voltage can be achieved. We earlier reported[1] that oxonine (1) (S_1) is directly reduced by iron(II) in the singlet state analogue of the well studied[2] triplet state reduction of thiazine dyes such as thionine (2). The probability of an encounter between (1) (S_1) and Fe^{II} resulting in semireduced dye (3) and Fe^{III} was found to be‡ about 0.12. Both direct[3] and Fe^{II}-induced[1] intersystem crossing of (1) (S_1) to the triplet state (T_1) were shown to be insignificant by flash photolysis. Two semi-reduced radicals (3) disproportionate under diffusion control to give (1) and the doubly reduced leuco-dye (4). We now report the use of (1) and Fe^{II} in the first example of a photogalvanic cell driven by an excited singlet rather than a triplet state.

Our cell was totally illuminated and optically thin. The cathode was gold sputtered over SnO_2 on glass, and the anode, which was nearest the light source, was glass coated with SnO_2 modified by electrodeposition of (2) according to the procedure of Albery et al.[4] Cell pathlengths, b, ranged between 100 and 130 µm with an illuminated area of 2 cm². Illumination was through a 578 nm interference filter by a 500 W tungsten halogen lamp or a 200 W high pressure Hg lamp. Incident power was adjusted with neutral density filters and measured with a photodiode calibrated against a National Bureau of Standards standard. The cell and photodiode were mounted

on a precision turntable so that either could be moved to an identical position in the illuminating beam. A weak probing beam was passed through the cell at an angle to the main beam and monochromated into a photomultiplier. By this means the absorbance of (1) was followed.

A cell using 8.1×10^{-4} mol dm⁻³ of (1) (saturated) in 5×10^{-3} mol dm⁻³ H_2SO_4 and $b = 120$ µm showed facile and symmetrical light-on light-off response with 50 s being required both to reach the photostationary state at the power point and for dark recovery. A similar cell with $[(1)] = 1.8 \times 10^{-4}$ mol dm⁻³, and $b = 130$ µm gave an open circuit voltage $V_{oc} = 21.0$ mV and a short-circuit current $I_{sc} = 2.6$ µA with 1.48×10^{-2} J s⁻² cm⁻² incident power. The optically thin cell absorbed only 15.3% of incident power. Taking this into account led to a monochromatic power efficiency at the power point of $2.9 \times 10^{-4}\%$ (578 nm). There are many possible reasons[5,6] for this poor performance including the low quantum yield[1] for production of (3), aggregation of the dye in H_2O, and electrochemical factors common[5] to all photogalvanic cells so far described.

All measurements were made using 0.20 mol dm⁻³ iron(II) ammonium sulphate as quencher. From the Stern–Volmer slope[1] (7.5 mol⁻¹ dm³) for quenching of the fluorescence of

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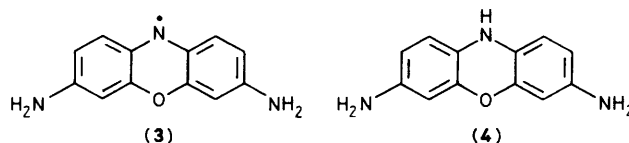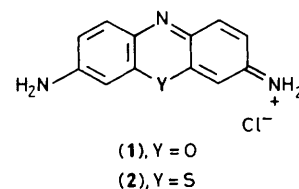
† For thionine, (2), the S_1-T_1 energy gap is ca. 0.9 eV when T_1 is protonated, the usual situation in the (2)–Fe^{II} photogalvanic cell.

‡ In more recent laser flash photolysis work using a much shorter excitation pulse we find that the quantum yield of (3) formation extrapolated to 100% quenching of (1) (S_1) by iron(II) sulphate is ca. 0.2.
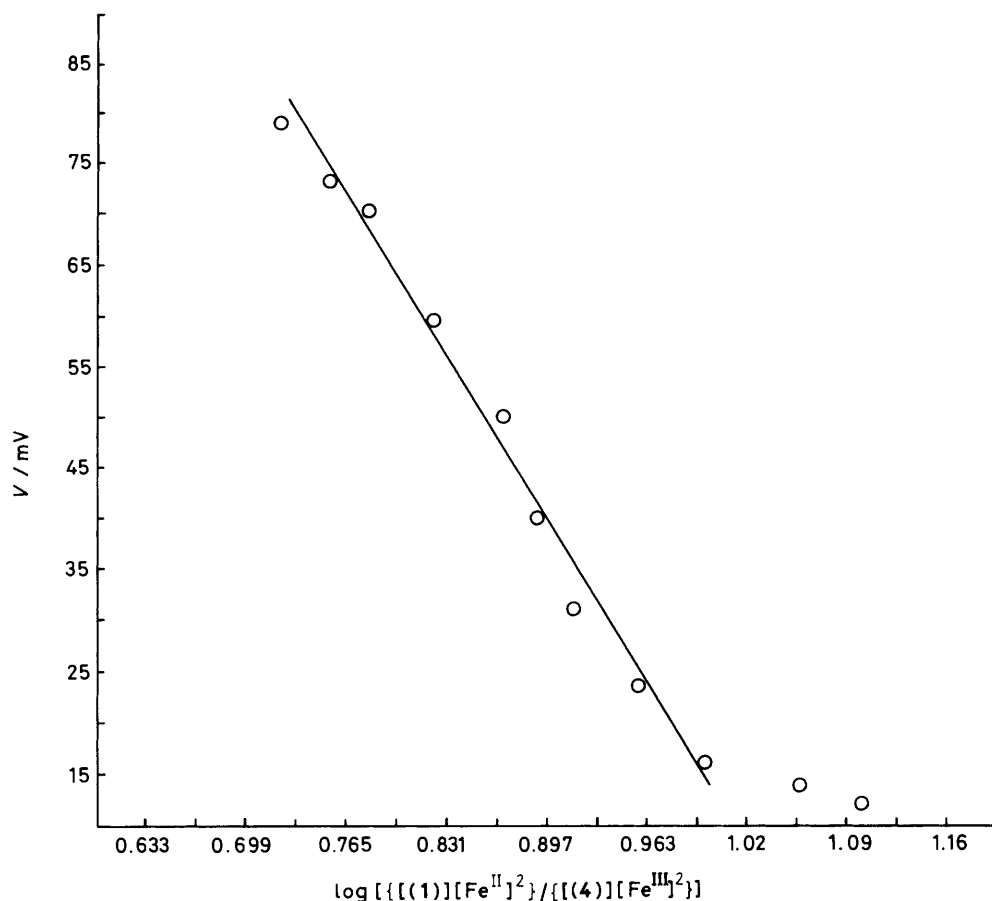

(1), Y = O
(2), Y = S

(3)   (4)

Figure 1. Logarithmic Nernstian concentration term *vs.* open circuit voltage of the oxonine cell.

(1) in 5×10^{-3} mol dm^{-3} H$_2$SO$_4$, we calculate that oxonine (S_1) is 60% quenched. Higher concentrations of iron(II) salts could be used and thus the kinetic problem of intercepting a large fraction of short-lived S_1 is not insuperable.

Albery and Archer[6] have defined characteristic parameters β, γ, and κ for photogalvanic cells. Calculation of these parameters for our cell gives: $\beta = 5 \times 10^{-3}$, a small β value indicates that the intensity of illumination throughout the cell is nearly constant; $\gamma = 3 \times 10^{-4}$ ($\Phi = 0.12$, $I_0 = 4.8 \times 10^{-10}$ mol cm^{-2} s^{-1}), a small γ value implies that the diffusion length of (1) is much greater than the cell pathlength so that (1) is uniformly distributed throughout the cell; $\kappa = 4 \times 10^{-3}$, a small κ value means that (4) may on average diffuse throughout the cell without being oxidized to (1) by reaction with Fe^{III} so that (4) is uniformly distributed throughout the cell.

In a separate series of experiments with [(1)] $= 8.1 \times 10^{-4}$ mol dm^{-3} and [H$_2$SO$_4$] $= 5 \times 10^{-3}$ mol dm^{-3}, V_{oc} was measured as a function of photostationary state concentrations of (1), (4), Fe^{II}, and Fe^{III} at pH = 2.3. Concentrations were calculated from cell absorbance for different incident light levels at 578 nm. It was assumed that $[(4)]_{ps} = [(1)]_0 - [(1)]_{ps}$, that $[Fe^{III}]_{ps} = 2[(4)]_{ps}$, and that $[Fe^{II}]_{ps} = [Fe^{II}]_0 - [Fe^{III}]_{ps}$, where 0 and ps refer to initial and photostationary concentrations.

Although the photostationary state is not a true equilibrium state, and one normally expects the electrode potentials to be mixed owing to non-specific dye-to-quencher response, nevertheless, and since concentrations in our cell were essentially uniform throughout, we used the data from the absorption measurement described above to calculate, for different

incident intensities, values of the term: $\log[\{[(1)][Fe^{II}]^2\}/\{[(4)][Fe^{III}]^2\}]$, which is the concentration term, with [H$^+$] removed, from the Nernst expression of open circuit cell potential for a cell with both redox couples at equilibrium. By plotting values of the above term against V_{oc} we obtained the result shown in Figure 1. The slope of the upper, linear portion of the curve is -23 mV per decade. This is surprisingly close to the theoretical slope of -29 mV per decade. We consider this to be evidence for leuco-oxonine being the electroactive species at the anode where it apparently undergoes a 2-electron oxidation back to oxonine. Not surprisingly, the intercept of Figure 1 is much too low to be accounted for by the algebraic sum of the theoretical formal cell potential and pH term.

References

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