Photosensitized Reductions of Anthraquinone Sulphonates in Coupled Electron Transfer Reactions

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Photosensitized reductions of anthraquinone sulphonates in SiO_2 colloids are mediated by propyl viologen sulphonate (PVS⁰) (1) as a primary electron acceptor; reduction yields are affected by electrostatic repulsions of the reduced acceptors from the negatively charged colloid.

Electron transfer reactions of quinones are important in photosynthesis where a 'plastoquinone pool' is thought to link photosystems I and II.[1] Recently, it has been demonstrated that colloidal particles such as those in SiO_2 colloids can control photosensitized electron transfer reactions by electrostatic interactions of the charged particle interface with the photoproducts.[2,3] It has been shown that the positively charged photosensitizer, tris(2,2'-bipyridine)ruthenium(II), $Ru(bpy)_3{}^{2+}$, is bound to the negatively charged SiO_2 particle.[4] Similarly, we have demonstrated that the photosensitized reduction of propyl viologen sulphonate (PVS⁰) (1), by $Ru(bpy)_3{}^{2+}$, results in the ejection of the reduced photo-product, PVS·⁻, from the charged interface. Consequently, the back electron transfer of the photoproducts was retarded, and high quantum yields in the electron transfer reaction have been achieved in the SiO_2 colloid, compared with a similar reaction in the homogeneous aqueous phase.

Here we report vectorially photoinduced reductions of anthraquinone sulphonates in SiO_2 colloids. In these reactions the electrons are tunnelled by a primary electron acceptor and a charged colloidal interface to the quinones that function as an electron trap. In such systems $Ru(bpy)_3{}^{2+}$ bound to negatively charged particles acts as the photocentre. PVS⁰ acts as a primary electron acceptor and mediates the reduction of sodium anthraquinone-2-sulphonate (AQS⁻) (2) and disodium anthraquinone-2,6-disulphonate ($AQS_2{}^{2-}$) (3). In all systems triethanolamine (TEOA) acts as an electron donor.

The reaction mixture consisting of 2% SiO_2 colloid, pH 9.8, PVS⁰ (2.0×10^{-4}M), TEOA (2×10^{-4}M), $Ru(bpy)_3{}^{2+}$ (3.5×10^{-5}M), and AQS⁻ or $AQS_2{}^{2-}$ (3.6×10^{-4}M) was illuminated with a 450 W xenon lamp (λ400—500 nm). The reduction of the anthraquinone sulphonates (2) or (3) to their respective semiquinone radicals was observed and their rate of production followed spectroscopically (Figure 1). No formation of PVS·⁻ was observed during the reduction of the quinones. In turn, when PVS⁰ was excluded from the mixture, no reduction of AQS⁻ or $AQS_2{}^{2-}$ was observed upon illumination. Thus, PVS⁰ mediates the reduction of anthraquinone sulphonates in the SiO_2 colloid. Furthermore, it can be seen (Figure 1) that the reduction of $AQS_2{}^{2-}$ in the SiO_2 colloid is substantially enhanced ($\phi_{max} = 3.2 \times 10^{-2}$) compared with that of AQS⁻ ($\phi_{max} = 1.1 \times 10^{-2}$).
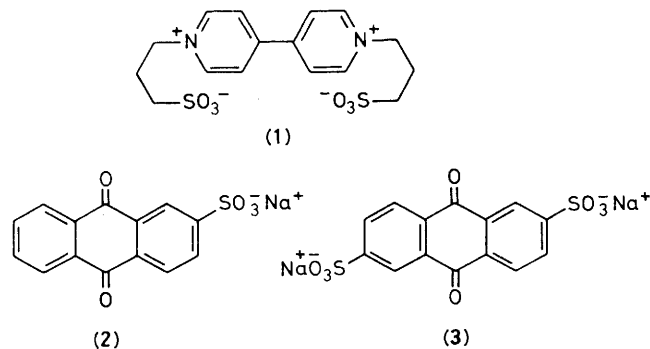
A similar mixture of components was illuminated in a homogeneous aqueous solution (pH 9.8). Under these conditions the rate of reduction of AQS⁻ and $AQS_2{}^{2-}$ was very similar ($\phi_{max} = 5 \times 10^{-3}$), but significantly lower than the reaction rate in the SiO_2 colloid. Exclusion of PVS⁰ from the homogeneous aqueous mixture resulted in an extremely inefficient direct reduction of AQS⁻ and $AQS_2{}^{2-}$.

The difference in the course of the photosensitized reductions of the anthraquinone sulphonates, in the different media, is attributed to electrostatic interactions of the SiO_2 interface (surface potential ca. -170 mV)[4] with the reactants and photoproducts. Fluorescence quenching measurements of $[Ru(bpy)_3{}^{2+}]^*$ by AQS⁻ and $AQS_2{}^{2-}$ indicate that the direct electron transfer from the sensitizer to the quinones in the SiO_2 colloid is retarded by two orders of magnitude compared with the quenching rate in the homogeneous phase.† This reduction in quenching rate constants is attributed to the repulsion of the negatively charged acceptors from the SiO_2
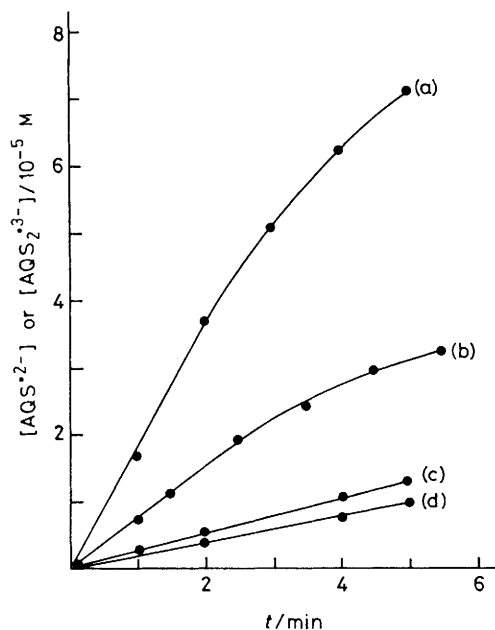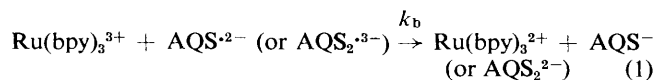

Figure 1. Progress of photosensitized reductions of anthraquinone sulphonates as function of illumination time. In all experiments $[Ru(bpy)_3{}^{2+}] = 3.5 \times 10^{-5}$ M, $[TEOA] = 2 \times 10^{-4}$ M, and $[PVS^0] = 2.0 \times 10^{-4}$ M, solutions at pH 9.8. (a) 2% SiO_2 colloid, $[AQS_2{}^{2-}] = 3.6 \times 10^{-4}$ M. (b) 2% SiO_2 colloid, $[AQS^-] = 3.6 \times 10^{-4}$ M. (c) Homogeneous $[AQS_2{}^{2-}] = 3.6 \times 10^{-4}$ M. (d) Homogeneous $[AQS^-] = 3.6 \times 10^{-4}$ M.

(1)

(2)   (3)

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† The quenching rate constants of $[Ru(bpy)_3{}^{2+}]^*$ by AQS⁻ are $k_q = 2.5 \times 10^9$ 1 mol⁻¹ s⁻¹ (in homogeneous aqueous phase, pH 9.8) and $k_q = 1.1 \times 10^8$ 1 mol⁻¹ s⁻¹ (in 2% SiO_2 colloid). Quenching rate constants of $[Ru(bpy)_3{}^{2+}]^*$ by $AQS_2{}^{2-}$ are $k_q = 1.6 \times 10^{10}$ 1 mol⁻¹ s⁻¹ (in homogeneous aqueous solution, pH 9.8) and $k_q = 1.2 \times 10^8$ 1 mol⁻¹ s⁻¹ (in 2% SiO_2 colloid).
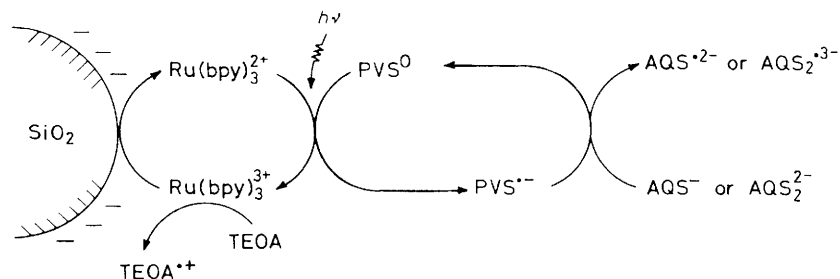
Scheme 1. Schematic photoinduced reduction of anthraquinone sulphonates in SiO_2 colloids.

interface to which the sensitizer is bound. Consequently, the direct reduction of AQS^- and $AQS_2{}^{2-}$ in the SiO_2 colloid is prevented. Introduction of PVS^0 as a neutral primary electron acceptor results in efficient quenching of the excited species $(k_q = 1.5 \times 10^9 \, l \, mol^{-1} \, s^{-1})$.[3] The negatively charged reduced acceptor formed, $PVS^{\cdot-}$, is ejected from the interface, and mediates the reduction of the anthraquinones‡ (Scheme 1). The enhanced rate of reduction of $AQS_2{}^{2-}$ compared with that of AQS^- is attributed to the extent of stabilization of the intermediate photoproducts by the charged interface (equation 1). The two photoproducts $AQS^{\cdot 2-}$ and $AQS_2{}^{\cdot 3-}$ are repelled by the SiO_2 interface and thus their recombination with the oxidized sensitizer is retarded. However, owing to the additional negative charge at $AQS_2{}^{\cdot 3-}$, this photoproduct is further stabilized over $AQS^{\cdot 2-}$ and enhanced quantum yield in its formation is achieved.

$$Ru(bpy)_3{}^{3+} + AQS^{\cdot 2-} \text{ (or } AQS_2{}^{\cdot 3-}) \xrightarrow{k_b} Ru(bpy)_3{}^{2+} + AQS^- \text{ (or } AQS_2{}^{2-}) \quad (1)$$

‡ The reduction of anthraquinone sulphonates by $PVS^{\cdot-}$ is thermodynamically favoured, $E^0 \, (PVS^0/PVS^{\cdot-}) = -0.41 \, V.$

In conclusion, we have demonstrated that the inefficient reduction of anthraquinone sulphonates in a homogeneous aqueous phase can be improved by using a mediating primary electron acceptor in SiO_2 colloids. In such coupled systems efficient quenching of the excited species as well as stabilization of the intermediate photoproducts is achieved. The function of the anthraquinone sulphonates in trapping the electrons from the photocentre present on the SiO_2 particles resembles that of the 'plastoquinone pool' in photosynthesis.

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