One-electron Photo-oxidation of Inorganic Anions by 9,10-Anthraquinone-2,6-disulphonic Acid in the Triplet State

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Summary Electron transfer from inorganic anions (CO_3^{2-}, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, SO_3^{2-}, SeO_3^{2-}, SCN^-, OH^-, Ac^-, and $CCl_3CO_2^-$) to 9,10-anthraquinone-2,6-disulphonic acid in the triplet state gives one-electron oxidized inorganic anions and anthrasemiquinone radicals.

THE PHOTOREDUCTION of anthraquinone and its derivatives was studied in alcohol and alcohol–water mixtures.[1–4] It was found that the production of semiquinone radicals occurs by hydrogen abstraction from anthraquinone in the triplet state.[5] The reduction of certain anthraquinones can also occur as a result of electron transfer from a donor molecule (*e.g.* from the hydroxyl ion[6–11]) to the photo-excited anthraquinone. We now report new results related to electron transfer involving the triplet state of anthraquinone

Flash photolysis of aqueous solutions (pH 6 5) of 9,10-anthraquinone-2,6-disulphonic acid results in short-lived (3×10^{-5} s) transient absorption at 490 nm caused by population of the anthraquinone triplet state [equation (1) and (2)] where $A(S_0)$, $A(S^*)$, and $A(T)$ are ground, singlet

$$A(S_0) + h\nu \rightarrow A(S)^* \rightsquigarrow A(T) \qquad (1)$$

$$A(T) \rightsquigarrow A(S_0) \qquad (2)$$

excited, and triplet states of 9,10-anthraquinone-2,6-disulphonic acid, respectively Addition of certain inorganic anions [CO_3^{2-}, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, SO_3^{2-}, SeO_3^{2-}, and SCN^- (10^{-1} M)] results in disappearance of triplet-triplet absorption followed by formation of new bands (lifetime ~ ms) The other absorption observed is due to production of semiquinone radical $A^{\dot{-}}$ (two strong bands at 400 nm and 520 nm) and to the products of one-electron oxidation of inorganic anions $X^{(n-1)\dot{-}}$ [$CO_3^{\dot{-}}$ at 600, $SO_4^{\dot{-}}$ at 460, $Cl_2^{\dot{-}}$ at < 390 nm, $SeO_3^{\dot{-}}$ at 430 nm, $(SCN)_2^{\dot{-}}$ at 500 nm] The production of radicals occurs as a result of electron transfer from inorganic anions to the 9,10-anthraquinone-2,6-disulphonic acid triplet state ($K_3 = 10^6$—10^7 l mol^{-1} s^{-1}) [equation (3)] where $X^{n-} = CO_3^{2-}$, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, SO_3^{2-}, SeO_3^{2-}, SCN^-, OH^-, Ac^-, or $CCl_3CO_2^-$ The

$$A(T) + X^{n-} \rightarrow A^{\dot{-}} + X^{(n-1)\dot{-}} \qquad (3)$$

efficiency of electron transfer is less for bromine and iodine anions This is due to the competing process (4) of triplet state deactivation (external heavy atom effect) The

$$A(T) + Br^-(J^-) \rightarrow A(S_0) + Br^-(J^-) \qquad (4)$$

anions with a high redox potential (F^-, ClO_4^-, $S_2O_5^{2-}$, and BO_3^{3-}) are not oxidized by 9,10-anthraquinone-2,6-disulphonic acid in the triplet state

The difference in the absorption spectra of semiquinone radicals in neutral and acidic solutions is due to acid–base equilibrium (5) (pK value 2 30) The decay of radicals in

$$A^{\dot{-}} + H^+ \rightleftharpoons AH^{\cdot} \qquad (5)$$

oxygen-free aqueous solutions is due to reaction[6] ($K_6 = 10^9$ l mol^{-1} s^{-1})

$$A^{\dot{-}} + X^{(n-1)} \rightarrow A(S_0) + X^{n-} \qquad (6)$$

The retardation effect of photoreduction of anthraquinone sulpho derivatives by addition of halogen ions to the water–alcohol solutions of the substrate[3] can be readily explained by reactions (3), (4), and (6)

The present study shows that the photoreduction of 9,10-anthraquinone-2,6-disulphonic acid can occur both as a result of hydrogen abstraction[1-3] and of electron transfer involving the anthraquinone triplet state

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