

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

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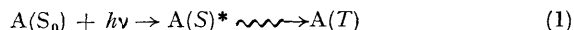
Summary Electron transfer from inorganic anions (CO_3^{2-} , Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , SO_3^{2-} , SeO_3^{2-} , SCN^- , OH^- , Ac^- , and $\text{CCl}_3\text{CO}_2^-$) to 9,10-anthraquinone-2,6-disulphonic acid in the triplet state gives one-electron oxidized inorganic anions and anthrasemiquinone radicals.

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 ion⁶⁻¹¹) to the photo-excited anthraquinone. We now report new results

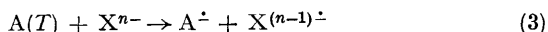
THE PHOTOREDUCTION of anthraquinone and its derivatives

related to electron transfer involving the triplet state of anthraquinone

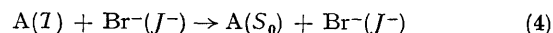
Flash photolysis of aqueous solutions (pH 6.5) of 9,10-anthraquinone-2,6-disulphonic acid results in short-lived (3×10^{-5} s) transient absorption at 490 nm caused by population of the anthraquinone triplet state [equation (1) and (2)] where $A(S_0)$, $A(S^*)$, and $A(T)$ are ground, singlet



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 \sim ms). The other absorption observed is due to production of semiquinone radical $A^{\cdot-}$ (two strong bands at 400 nm and 520 nm) and to the products of one-electron oxidation of inorganic anions $X^{(n-1)\cdot}$ [$\text{CO}_3^{\cdot-}$ at 600, $\text{SO}_4^{\cdot-}$ at 460, $\text{Cl}_2^{\cdot-}$ at < 390 nm, $\text{SeO}_3^{\cdot-}$ at 430 nm, $(\text{SCN})_2^{\cdot-}$ 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 $X^{n-} = \text{CO}_3^{2-}$, Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , SO_3^{2-} , SeO_3^{2-} , SCN^- , OH^- , Ac^- , or $\text{CCl}_3\text{CO}_2^-$. The



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

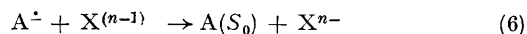


anions with a high redox potential (F^- , ClO_4^- , $\text{S}_2\text{O}_8^{2-}$, and BO_3^{3-}) are not oxidized by 9,10-anthraquinone-2,6-disulphonic acid in the triplet state.

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



oxygen-free aqueous solutions is due to reaction⁶ ($K_6 = 10^9$ l mol $^{-1}$ s $^{-1}$)



The retardation effect of photoreduction of anthraquinone sulpho derivatives by addition of halogen ions to the water–alcohol solutions of the substrate³ 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.

(Received, July 22nd, 1971, Com 1269.)

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