Photoreduction of 2-Piperidinoanthraquinone by Electron Transfer

By G. O. PHILLIPS,* A. K. DAVIES, and J. F. MCKELLAR†

(Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT)

Summary Photoreduction of 2-piperidinoanthraquinone in alkaline alcohol–water solutions occurs by a process of electron transfer from hydroxide and alkoxide ions to the photoexcited charge-transfer state of the quinone.

IN an earlier communication[1] we showed that the lowest lying excited state of unprotonated 1- and 2-piperidinoanthraquinones is of the intramolecular charge-transfer (C-T) type. In acidic and neutral alcohol–water solutions the photosensitizing behaviour of the quinones depends primarily on their degree of protonation.

Photolysis of neutral anaerobic solutions (4 : 1 propan-2-ol : water) of the 2-piperidino-derivative yields the anthrahydroquinone (AH_2). Photolysis under the same conditions at pH above 11 produces only the radical anion $A\cdot^-$. This product is stable for long periods (> 12 hr.) and is readily characterised by its visible absorption and e.s.r. spectrum.[2–4] Sharp isosbestic points for the reaction to

---

† Visiting Fellow from Imperial Chemical Industries Limited, Dyestuffs Division, Hexagon House, Blackley, Manchester 9.

the radical anion $A\cdot^-$ were observed at 346, 374, 495, and 560 nm, and when irradiation was stopped no further change in the absorption spectrum of reactant and product occurred. From initial rates of formation, we estimate the ratio of quantum yields of $A\cdot^-$ (at pH 12) and AH_2 (at pH 7) to be $(\phi A\cdot^-)/(\phi AH_2) > 100$. Clearly, the magnitude of this ratio indicates that two distinct mechanisms of photoreduction are operative at neutral and high pH.

For the reaction at high pH with 2-piperidinoanthraquinone, we postulate that formation of $A\cdot^-$ proceeds mainly by an electron-transfer process from hydroxide and alkoxide ions to the C-T excited state responsible for photoreduction

$$A^* + OH^- \rightarrow A\cdot^- + OH\cdot \qquad (1)$$

$$A^* + RCH_2O^- \rightarrow A\cdot^- + RCH_2O\cdot \qquad (2).$$

Investigation of the effect of varying $[OH^-]_T$, the total added hydroxide ion concentration, showed that the reciprocal rate of formation of $A\cdot^-$, as predicted by reactions (1) and (2), followed the kinetics

$$1/\mathrm{d}(A\cdot^-)/\mathrm{d}t = 1/2I + k_0/2I[OH^-]_T k'$$

where k_0 is the rate constant for the deactivation process $A^* \rightarrow A$, I = rate of activation, proportional to intensity of light, and k' is a constant which incorporates k_1 and k_2, the rate constants for reactions (1) and (2), and the equilibrium constant[5] for

$$OH^- + RCH_2OH \rightleftarrows RCH_2O^- + H_2O \qquad (3).$$

At high pH we did not observe a similar reaction with the 1-piperidinoanthraquinone. Here, reaction to the dianion A^{2-} occurred and appeared to proceed *via* the well-established hydrogen-abstraction process[6,7]

$$A^* + RCH_2OH \rightarrow AH\cdot + R\dot{C}HOH \qquad (4)$$

followed by

$$AH\cdot \rightarrow A\cdot^- + H^+ \qquad (5)$$

$$2A\cdot^- \rightarrow A^{2-} + A \qquad (6).$$

Recent work[8] has shown that the 2-piperidino-derivative sensitizes the photodegradation of nylon fibre much more readily than the 1-piperidinoanthraquinone. This observation cannot be accounted for by a difference in the rate of the hydrogen abstraction reaction (4) for the derivatives.[8] We believe, however, that it can be explained by an electron transfer from the polymer to the photoexcited quinone, which like the electron transfer process studied above, proceeds much more rapidly with the 2-piperidino-derivative. In 1949 Bamford and Dewar[9] postulated that reaction (1) is responsible for the accelerating effect of water vapour on the phototendering of the anthraquinone dyes on cellulosic materials. The observation of reaction (1) with the 2-piperidino-derivative is, to our knowledge, the first detailed kinetic evidence in support of their hypothesis.

(*Received, March 9th,* 1970; *Com.* 318.)

---

[1] G. O. Phillips, A. K. Davies, J. F. McKellar, and D. Price, *Chem. Comm.*, 1969, 1097.

[2] V. G. Eigenmann, *Chimia (Switz.)*, 1965, **19**, 333.

[3] J. H. Sharp, T. Kuwana, A. Osborne, and J. N. Pitts, *Chem. and Ind.*, 1962, 508.

[4] P. J. Baugh, G. O. Phillips, and J. C. Arthur, *J. Phys. Chem.*, 1966, **70**, 3061.

[5] J. Hine and M. Hine, *J. Amer. Chem. Soc.*, 1952, **74**, 5266.

[6] J. L. Bolland and H. R. Cooper, *Proc. Roy. Soc.*, 1954, *A*, 225, 405; C. F. Wells, *Trans. Faraday Soc.*, 1961, **57**, 1703, 1719.

[7] N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, 1958, *A*, **244**, 259, 276.

[8] G. S. Egerton, N. E. N. Assaad, and N. D. Uffindell, *J. Soc. Dyers and Colourists*, 1967, **83**, 409.

[9] C. H. Bamford and M. J. S. Dewar, *J. Soc. Dyers and Colourists*, 1949, **65**, 674.