Primary Processes in the Photolysis of Sodium 9,10-Anthraquinone-2-sulphonate in Aqueous Solution

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THE primary processes in the photosensitized oxidation of alcohols by 9,10-anthraquinones and their sulphonates have been characterised.[1,2] The photoexcited quinone in either its singlet[1] or triplet[3] state abstracts a hydrogen atom from the alcohol (A = anthraquinone; RCH_2OH = alcohol).

$$A + h\nu \rightarrow A^* \quad (1)$$

$$A^* \rightarrow A \quad (2)$$

$$A^* + RCH_2OH \rightarrow AH\cdot + R\dot{C}HOH \quad (3)$$

and this subsequently produces oxidation of the alcohol by the well-known Bolland–Cooper mechanism.[4]

In aqueous solutions, sodium 9,10-anthraquinone-2-sulphonate itself undergoes photochemical reaction to give coloured products,[5] and here we summarise the findings of our recent study of this reaction using flash,[6] continuous photolysis,[7] and e.s.r.[8] techniques. Our results clearly differentiate between the reaction path of the photo-excited A* in this reaction and that shown above for the photosensitized oxidation.

When sodium 9,10-anthraquinone-2-sulphonate is flash photolysed in approximately neutral aqueous–alcoholic solution two transients are observed; one has two broad bands at about 275 and 385 mμ and the other a narrow band at 505 mμ. These transients are AH· and $A\cdot^-$ respectively.[1,2] When the quinone is flash photolysed in approximately neutral aqueous solution, again, two transients are detected; one has a very broad band in the region 420 to 530 mμ and the other a narrow band at 505 mμ.

From a comparison of the behaviour of these transients under different pH and deoxygenated conditions, we conclude that the transients observed in aqueous solution are $A\cdot^+$ and $A\cdot^-$ formed by

$$A^* + A \rightarrow A\cdot^+ + A\cdot^- \quad (4)$$

Although process (4) is well established in the case of the xanthene dyes[9] this is the first time that it has been suggested for the anthraquinones. Depending on the pH, process (4) can then be followed by either

$$A\cdot^- + H^+ \rightleftharpoons AH\cdot \quad (5)$$

$$\text{or} \quad A\cdot^+ + OH^- \rightarrow A + OH\cdot \quad (6)$$

The OH radicals formed by process (6) can then give rise to coloured hydroxylated products of the quinone by [10]

$$A + OH\cdot \rightarrow A'OH + H\cdot \quad (7)$$

From these observations we have been able to deduce a mechanism for the photochemical reaction in aqueous solution which includes the processes (1), (2), (4), (5), (6), and (7).[11] The mechanism satisfactorily accounts for the kinetics of the reaction as observed by oxygen absorption measurements under continuous photolysis conditions.

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[1] N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, 1958, *A*, **244**, 259, 277.
[2] N. K. Bridge and M. Reed, *Trans. Faraday Soc.*, 1960, **56**, 1796.
[3] F. Wilkinson, *J. Phys. Chem.*, 1962, **66**, 2569.
[4] J. L. Bolland and H. R. Cooper, *Proc. Roy. Soc.*, 1954, *A*, **225**, 405; C. F. Wells, *Trans. Faraday Soc.*, 1961, **57**, 1703, 1719; *J. Chem. Soc.*, 1962, 3100; *Discuss. Faraday Soc.*, 1960, **29**, 219.
[5] K. Pfeilsticker, *Biochem. Z.*, 1928, **199**, 8; B. Mooney and H. I. Stonehill, *Chem. and Ind.*, 1961, 1309; A. D. Broadbent, *Chem. Comm.*, 1967, 382.
[6] J. F. McKellar, *Proc. Roy. Soc.*, 1965, *A*, **287**, 363.
[7] T. Rickards, Ph.D. Thesis (Wales,) 1965.
[8] P. J. Baugh, G. O. Phillips, and J. C. Arthur, jun., *J. Phys. Chem.*, 1966, **70**, 3061.
[9] L. Lindquist, *Arkiv Kemi.*, 1960, **16**, 79; V. Kasche and L. Lindquist, *Photochem. and Photobiol.*, 1965, **4**, 923; T. Ohno, S. Kato, and M. Koizumi, *Bull. Chem. Soc. Japan*, 1966, **39**, 232.
[10] M. Anbar, D. Meyerstein, and P. Neta, *J. Phys. Chem.*, 1966, **70**, 2660.
[11] G. O. Phillips, N. W. Worthington, J. F. McKellar, and R. R. Sharpe, in preparation.