

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

By G. O. PHILLIPS\* and N. W. WORTHINGTON

(Department of Chemistry, University College, Cathays Park, Cardiff)

and J. F. MCKELLAR and R. R. SHARPE

(Imperial Chemical Industries Limited, Dyestuffs Division, Hexagon House, Blackley, Manchester, 9)

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



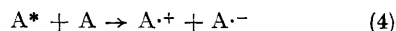
and this subsequently produces oxidation of the alcohol by the well-known Bolland-Cooper mechanism.<sup>4</sup>

In aqueous solutions, sodium 9,10-anthraquinone-2-sulphonate itself undergoes photochemical reaction to give coloured products,<sup>5</sup> and here we summarise the findings of our recent study of this reaction using flash,<sup>6</sup> continuous photolysis,<sup>7</sup> and e.s.r.<sup>8</sup> 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.

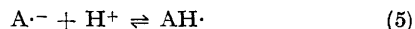
When sodium 9,10-anthraquinone-2-sulphonate is flash photolysed in approximately neutral aqueous-alcoholic solution two transients are observed; one has two broad bands at about 275 and 385 m $\mu$  and the other a narrow band at 505 m $\mu$ . These transients are AH $\cdot$  and A $\cdot^-$  respectively.<sup>1,2</sup> 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 m $\mu$  and the other a narrow band at 505 m $\mu$ .

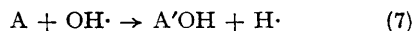
From a comparison of the behaviour of these transients under different pH and deoxygenated conditions, we conclude that the transients observed in aqueous solution are A $\cdot^+$  and A $\cdot^-$  formed by



Although process (4) is well established in the case of the xanthene dyes<sup>9</sup> 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



The OH radicals formed by process (6) can then give rise to coloured hydroxylated products of the quinone by<sup>10</sup>



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).<sup>11</sup> The mechanism satisfactorily accounts for the kinetics of the reaction as observed by oxygen absorption measurements under continuous photolysis conditions.

(Received, July 6th, 1967; Com. 701.)

<sup>1</sup> N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, 1958, **A**, **244**, 259, 277.

<sup>2</sup> N. K. Bridge and M. Reed, *Trans. Faraday Soc.*, 1960, **56**, 1796.

<sup>3</sup> F. Wilkinson, *J. Phys. Chem.*, 1962, **66**, 2569.

<sup>4</sup> 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.

<sup>5</sup> 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.

<sup>6</sup> J. F. McKellar, *Proc. Roy. Soc.*, 1965, **A**, **287**, 363.

<sup>7</sup> T. Rickards, Ph.D. Thesis (Wales,) 1965.

<sup>8</sup> P. J. Baugh, G. O. Phillips, and J. C. Arthur, jun., *J. Phys. Chem.*, 1966, **70**, 3061.

<sup>9</sup> 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.

<sup>10</sup> M. Anbar, D. Meyerstein, and P. Neta, *J. Phys. Chem.*, 1966, **70**, 2660.

<sup>11</sup> G. O. Phillips, N. W. Worthington, J. F. McKellar, and R. R. Sharpe, in preparation.