Photochemical Reactions of 9,10-Anthraquinones in Water

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THE photochemical oxidation of alcohols, sensitised by 9,10-anthraquinones, has been widely studied. Although permanent, coloured products have been observed on irradiation of aqueous[1,2] and aqueous alcoholic[3] solutions of 9,10-anthraquinonesulphonates, the photochemical reactions of these compounds in aqueous solution have attracted little attention.

On exposing a concentrated aqueous solution of sodium 9,10-anthraquinone-2-sulphonate to daylight, a deep yellow colour rapidly developed, accompanied by a decrease in the pH of the solution. Chromatography of the isolated solid on alumina yielded the starting material, a mixture of 2-hydroxy-9,10-anthraquinone-6- and -7-sulphonates (fraction B), and a mixture of isomeric 1-hydroxy-9,10-anthraquinonesulphonates (fraction A), which were successively eluted with aqueous ethanol. In addition four minor products were observed, three of which behaved as dihydroxyanthraquinonesulphonates. The action of Fenton's reagent on a similar solution, in the dark, gave identical products, with a higher yield of the dihydroxy-compounds. Addition of sodium halide inhibited the reaction, the iodide being particularly effective. These results indicated participation of hydroxyl radicals in the reaction and this was supported by the polymerisation of acrylonitrile and the hydroxylation of benzoic acid,[4] when these compounds were present in the irradiated, anaerobic solution.

Alkaline, oxygen-free sodium 9,10-anthraquinone-2-sulphonate solution became intense olive on exposure to daylight, but this colour immediately faded to a pale orange on introducing air. Such behaviour suggested that photoreduction to a green anthrasemiquinone[5] accompanied the hydroxylation reaction. This was confirmed by using polarographic techniques.

Of the nine water-soluble 9,10-anthraquinones examined,* only the 2-sulphonate and the 2,6- and 2,7-disulphonates gave substantial yields of hydroxy-derivatives on irradiation in water, or of polyacrylonitrile on irradiation in anaerobic aqueous acrylonitrile, although all the compounds reacted readily with Fenton's reagent to give mono- and di-hydroxyanthraquinones. The effect of substituents on the extent of hydroxylation in the presence of acrylonitrile or benzoic acid and on the relative ease of mono- and di-hydroxylation indicated that the reaction between the anthraquinone and hydroxyl radical is very rapid and electrophilic in nature.[6] It appears that only the 2-sulphonates of 9,10-anthraquinone readily produce hydroxyl radicals on irradiation of their aqueous solutions with near-ultraviolet light. This corresponds to the long-wave absorption bands of these compounds. The weak bands observed in their visible absorption spectra[2,7] are caused by impurities, probably hydroxyanthraquinones introduced by the photochemical reaction being described.

It has been suggested that hydrogen transfer occurs from water to the photoexcited 9,10-

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* The 1-sulphonate, 1,5-disulphonate, 1-carboxylate, 1-nitro-6-sulphonate, and the 2-hydroxy-6- and -7-sulphonates were also examined.

anthraquinone-2-sulphonate molecule.[2,8] The primary products of this reaction would be an anthrasemiquinone and a hydroxyl radical, the latter being responsible for hydroxylation of the anthraquinone or one of its reduction products. This seems an oversimplification as the pH of the irradiated aqueous solution affects not only the rate of formation of hydroxyanthraquinones but also the orientation of the hydroxyl groups. Irradiation of sodium 9,10-anthraquinone-2-sulphonate in dilute aqueous sodium hydroxide produced only fraction B. The initial rate of this reaction increased on increasing the hydroxide ion concentration. No fraction A was detected even after considerable exposure. In dilute aqueous sulphuric acid both fractions B and A were formed, the latter predominating. These reactions proceeded readily on irradiation with light of wavelength 4060 Å (mercury lines), provided that the absorbance the incident light was high.

The production of fraction B alone occurs only in strongly alkaline solution, and it appears that the preferential formation of these 2-hydroxy-compounds is related to the high stability of 2-hydroxy-9,10-anthrasemiquinones under these conditions. Further studies of the reaction mechanism are in progress.

(*Received, February 23rd*, 1967; *Com.* 171.)

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