Photochemical Hydroxylation of Anthracene-9,10-dione in Sulphuric Acid Solution

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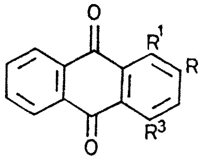
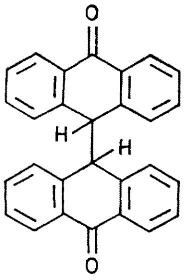
Summary. Near u.v. irradiation of anthracene-9,10-dione in deoxygenated 96% H_2SO_4 generates the sulphate ester of 2-hydroxyanthracene-9,10-dione in high yield along with the 1-hydroxy isomer and the novel reduction products anthracen-9(10*H*)-one and 9,9′-bianthracene-10,10′(9*H*,9′*H*)-dione; contrary to previous results, the product distribution and the rate of reaction are dependent upon the concentration of O_2 in the solution.

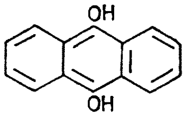
Two recent publications[1,2] dealing with the photochemical reaction of anthracene-9,10-dione (**1**) in H_2SO_4 solution have reported conflicting results. One paper[1] concludes that the sulphate ester of 2-hydroxyanthracene-9,10-dione (**2**) is the sole product of an efficient, regioselective, substitution reaction, while the other[2] reports that a small amount of the 1-hydroxy isomer (**3**) is also formed and undergoes a secondary photochemical reaction yielding 1,4-dihydroxyanthracene-9,10-dione (**4**). Both publications, however, agree that the presence or absence of O_2 has no profound effect upon the reaction. We now report that the product distribution is more complex than previously described, that O_2 has some novel effects on both the product distribution and the rate of reaction, and, when O_2 is absent, (**1**) undergoes an unusual photoreduction yielding anthracen-9(10*H*)-one (**8**) and 9,9′-bianthracene-10,10′(9*H*,9′*H*)-dione (**6**).



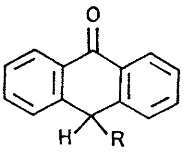
(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^3 = H, R^2 = OH$
(3) $R^1 = OH, R^2 = R^3 = H$
(4) $R^1 = R^3 = OH, R^2 = H$
(5) $R^1 = R^2 = OH, R^3 = H$



(6)



(7)



(8) R = H
(9) R = OH

Irradiation of (**1**) in 96% H_2SO_4 at 15 °C, stirring with N_2, with a medium-pressure Hg lamp through Pyrex, gave (**2**) as the major isolated product [80% yield based on (**1**) consumed] but accompanied by (**3**) and the reduction products (**8**) and (**6**). An identical reaction, but stirred by O_2, was very similar except that only traces of (**8**) and (**6**) were detected, but, in this case, isolable quantities of the minor products (**4**) and 1,2-dihydroxyanthracene-9,10-dione (**5**) were found. The initial rate of conversion of (**1**) was lower in the presence of O_2, but the final yield of (**2**) was somewhat larger than in the N_2-stirred reaction. In the more oxidising environment of 100% H_2SO_4, where the HSO_4^- concentration is considerably lower,[3] the reaction was much less efficient, particularly under O_2, and gave only traces of the reduction products even under N_2.

Analysis of the reaction products by t.l.c. showed rapid accumulation of (**8**) only in the N_2-stirred reaction and its later conversion into (**6**). Studies of the interaction of anthracene-9,10-diol (**7**) and its tautomer 10-hydroxyanthracen-9(10*H*)-one with deoxygenated H_2SO_4 in the dark indicated rapid back-oxidation to (**1**) and also the formation of (**8**). In the photochemical reaction, we propose that reduction of (**1**) occurs, *via* reaction of the excited state of the protonated quinone with HSO_4^- (nucleophilic substitution[1] or electron transfer and subsequent addition of $HSO_4\cdot$), yielding (**7**), which then undergoes disproportionation *via* (**9**) to (**1**) and 9,10-dihydroxy-9,10-dihydroanthracene,[4] if not oxidised to (**1**) by the solvent or O_2. The latter product readily dehydrates to give (**8**), which undergoes efficient photo-oxidation to (**6**) in H_2SO_4.[5] Such extensive reduction of (**1**) in photochemical reactions is quite rare.[6]

The dihydroxylated products (**4**) and (**5**) were generated in small but isolable quantities only from the photochemical reaction in the presence of O_2. This was quite evident from comparative spectrophotometric examination of the irradiated H_2SO_4 solutions. The monohydroxy products (**2**) and (**3**) were shown to be quite stable under the irradiation conditions, so that neither (**4**) nor (**5**) is generated by a secondary photochemical reaction of (**3**) as previously suggested[2] but presumably by secondary thermal reactions which are greatly enhanced by O_2.[7]

The kinetics of the photochemical reaction have been studied on an optical bench using incident light at 366 nm and monitoring the loss of (**1**) at 270 nm or the appearance of hydroxy products at 520 nm, where (**1**) has negligible absorbance. The quantum yield of (**2**) is *ca.* 0·5 in 96% H_2SO_4 under N_2, and may be even higher with optimum mixing to ensure homogeneity during irradiation, a situation not easily achieved in the viscous solvent. In direct contrast to the previous studies, the rate data show that O_2 is an effective quencher of the reaction, particularly at the low light intensities used on the optical bench. As the incident light intensity is increased, the very low rate of product formation in the O_2-stirred solution increases until it approaches that for an N_2-stirred reaction, indicating that the reaction may be quenched by and also consume O_2 so that depletion occurs.

Our results show that O_2 has a pronounced influence on both the product distribution and the rate of reaction.

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