Studies on the Hydroxylation of Sodium 9,10-Dihydro-9,10-dioxoanthracene-α-sulphonates

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The reaction of disodium-9,10-dihydro-9,10-dioxoanthracene-1,8-disulphonate with hydroxide ion at 145° leads to the formation of the sodium salts of 9,10-dihydro-8-hydroxy-9,10-dioxoanthracene-1-sulphonate, 9,10-dihydro-8-hydroxy-9,10-dioxoanthracene-1,7-disulphonate, 9,10-dihydro-4-hydroxy-9,10-dioxoanthracene-1,3,5-trisulphonate, 9,10-dihydro-7,8-dihydroxy-9,10-dioxoanthracene-1-sulphonate, 9,10-dihydro-1,8-dihydroxy-9,10-dioxoanthracene-2-sulphonate, and 9,10-dihydro-1,8-dihydroxy-9,10-dioxoanthracene-2,7-disulphonate, together with 1,8-dihydroxyanthraquinone and 1,2,8-trihydroxyanthraquinone. The general mechanism of this reaction is discussed and evidence is presented to show that 9,10-dihydrohydroxy-9,10-dioxoanthracene-β-sulphonates are formed by attack of the sulphite radical anion on the respective substrate. A good correlation has been found between the experimentally determined position of radical attack and that calculated by MO theory.

THE considerable technological importance of sodium anthraquinone-α-sulphonates (9,10-dihydro-9,10-dioxoanthracene-α-sulphonates) and their hydroxy-derivatives is reflected in their growing use as intermediates for a large number of anthraquinone dyestuffs.[1] While the photochemical and thermal hydroxylation reactions of sodium anthraquinone-β-sulphonates have received considerable attention [2-12] there is little information available on the corresponding reactions of anthraquinone-α-sulphonates. Recently, it has been claimed that the reaction of disodium anthraquinone-1,8-disulphonate with hydroxide ion at 145° gives 1,8-dihydroxyanthraquinone in good yield.[13]

A reinvestigation of this reaction under similar condi-

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tions to those reported, however, has not confirmed the earlier results. It has been found that treatment of disodium anthraquinone-1,8-disulphonate (I) with aqueous sodium hydroxide at 145° during 18 h leads to the formation of eight main products which have been identified by t.l.c., elemental analysis, and i.r. and ^1H n.m.r. spectroscopy as the sodium salts of 8-hydroxyanthraquinone-1-sulphonate (II), 8-hydroxyanthraquinone-1,7-disulphonate (III), 4-hydroxyanthraquinone-1,3,5-trisulphonate (IV), 7,8-dihydroxyanthraquinone-1-sulphonate (V), 1,8-dihydroxyanthraquinone-2-sulphonate (VI), and 1,8-dihydroxyanthraquinone-2,7-disulphonate (VII), together with 1,8-dihydroxyanthraquinone (VIII) and 1,2,8-trihydroxyanthraquinone (IX). Furthermore, the reactions of the hydroxy-sulphonate (II) and the dihydroxy-compound (VIII) with both aqueous sodium sulphite and sodium hydroxide have been investigated in order to determine whether the other products formed in the original reaction are derived from these intermediates. For this study, an authentic sample of the hydroxy-sulphonate was prepared in 33% yield using a modified preparative route to 1,8-dihydroxyanthraquinone [14] by treatment of disodium anthraquinone-1,8-disulphonate with aqueous calcium hydroxide and magnesium chloride at 210° for 2 h.

Formation of Hydroxyanthraquinone-β-sulphonates.—It has been found that the air-catalysed reaction of the hydroxy-sulphonate (II) with aqueous sodium sulphite and sodium hydroxide during 24 h at 100° gives the hydroxy-disulphonate (III) in 90% conversion (33% yield after isolation) and the hydroxy-trisulphonate (IV) in 5% conversion. The latter product is formed also in 55% yield after isolation from the air-catalysed reaction of the hydroxy-disulphonate with an excess of the same reagents at 100° during 72 h.

A similar reaction occurs when 1,8-dihydroxyanthraquinone is treated with aqueous sodium sulphite and sodium hydroxide at 100° during 72 h to give the dihydroxy-sulphonate (VI) and dihydroxy-disulphonate (VII) in 15 and 5% conversion respectively. It is deduced, therefore, that the hydroxyanthraquinone-β-sulphonates are formed in the original reaction by the displacement of the sulphite anion from the respective anthraquinonesulphonate by hydroxide ion, and its subsequent reaction either with a hydroxyanthraquinone or its sulphonate already formed. A similar reaction between 1,4-dihydroxyanthraquinone and aqueous sodium sulphite is known to give sodium 1,4-dihydroxyanthraquinone-2-sulphonate.[14]

Furthermore, it has been found that irradiation for 18 h of an aqueous solution of the hydroxy-sulphonate (0·008M) and sodium sulphite (0·08M) at pH 12 with visible light at 18° results in an 85 and 7% conversion into the hydroxy-disulphonate and hydroxy-trisulphonate respectively. In the control dark experiment little reaction occurs. Moreover, treatment of an aqueous solution of the hydroxy-sulphonate (0·008M) and sodium sulphite (0·2M) with aqueous iron(II) sulphate (0·1M) and hydrogen peroxide (0·2M) at pH 9 in the dark results in a 10 and 5% conversion into the hydroxy-disulphonate and hydroxy-trisulphonate respectively. The same products are obtained in conversions of 6 and 4% respectively when titanium(III) chloride is used in place of the iron salt. No reaction occurs in the absence of hydrogen peroxide or the metal ion.

Formation of Hydroxyanthraquinones.—Treatment of 1,8-dihydroxyanthraquinone with aqueous sodium and potassium hydroxides at 180° during 12 h in the presence of sodium nitrate results in the formation of 1,2,8-trihydroxyanthraquinone.[15] A similar reaction with aqueous sodium hydroxide at 140° during 2 h in the absence of the inorganic oxidant has been found also to give the same product in 15% conversion. It is concluded that β-hydroxyanthraquinones may be formed in the original reaction by direct hydroxylation of the respective substrate. The main reaction between anthraquinonesulphonates and the hydroxide ion, however, is the replacement of the sodium sulphonate group in the respective substrate by the hydroxy-group to give either α- or β-hydroxyanthraquinones.

The formation of the main products in the original reaction probably occurs as in Scheme 1 by either (1) the replacement of the sodium sulphonate group by the hydroxy-group, or (2) the replacement of a hydrogen atom by the sodium sulphonate group, or (3) the replacement of a hydrogen atom by the hydroxy-group.

Product Orientation.—The hydroxy-sulphonate (II) [16] and the dihydroxy-sulphonate (V) [17] have been described; details of the i.r. or ^1H n.m.r. spectra have not been reported, however, and their identification has been based previously on elemental analysis or by conversion into a known derivative. In the present studies, the orientation of all the anthraquinone products obtained has been deduced from an analysis of n.m.r. chemical shift and coupling constant data recorded in [$^2H_6$]dimethyl sulphoxide–carbon tetrachloride solution.

The replacement of a hydrogen atom in anthraquinone by another substituent causes changes in the chemical shifts of the remaining protons in the substituted ring, the magnitudes of which are well established for the substituents involved here. For example, while disodium anthraquinone-1,8-disulphonate shows resonances at +0·54 (*o*-H), −0·15 (*m*-H), and −0·07 (*p*-H) p.p.m., 1,8-dihydroxyanthraquinone shows resonances at −0·57 (*o*-H), −0·16 (*m*-H), and −0·50 (*p*-H) p.p.m., all relative to α- and β-H of anthraquinone itself which show resonances at δ 8·12 and 7·78 respectively. Similar shifts are observed also for β,β′-disubstituted anthraquinones. The predicted spectrum for the protons in the disubstituted ring of sodium 7,8-dihydroxyanthraquinone-1-sulphonate, therefore, should consist of two doublets at δ 7·05 and 7·46 whilst that for alternative

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[14] I.G. Farbenindustrie, BIOS 1484.

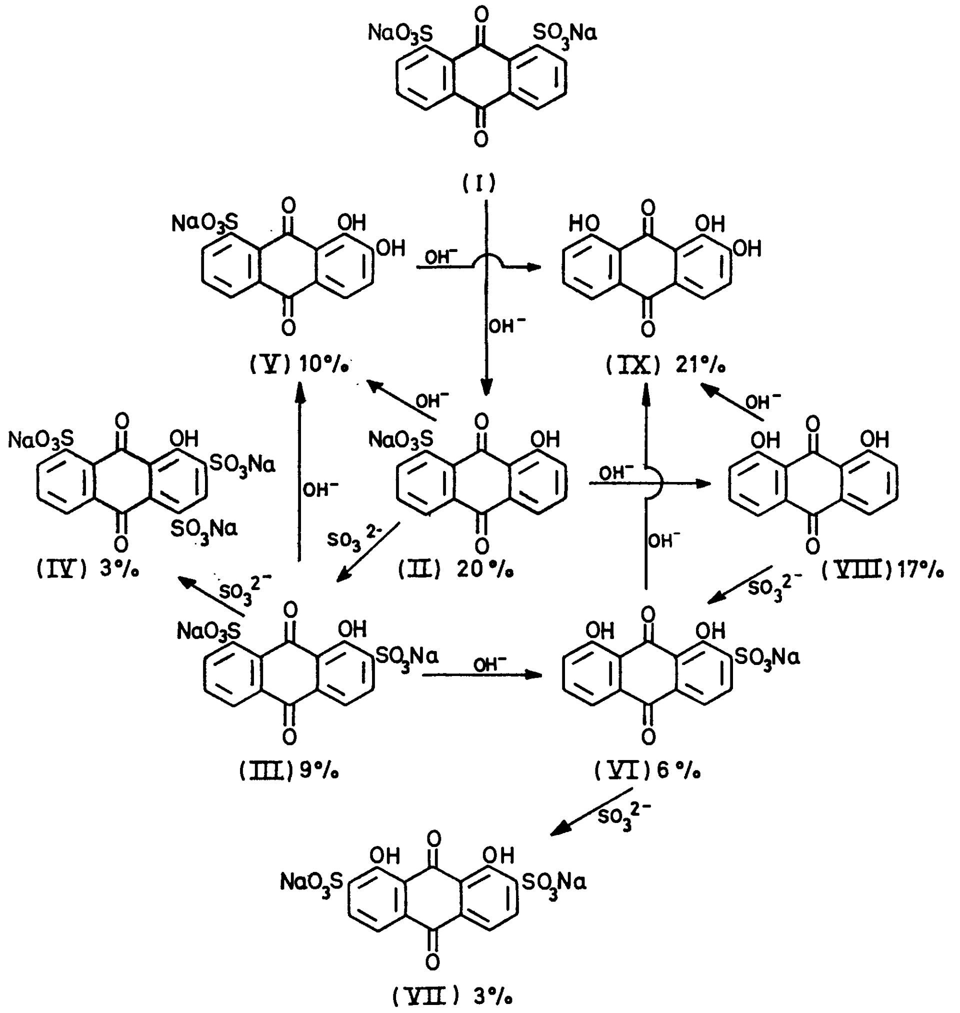
[15] Ger.P. 196,980/1906.

[16] Ger.P. 197,607/1906; V. V. Kozlov, *Zhur. obshchei Khim.*, 1955, **25**, 1206.

[17] Ger.P. 210,863/1907.

structures such as sodium 5,8-dihydroxyanthraquinone-1-sulphonate should consist of two superimposed doublets at δ 7·05. However, the observed spectrum (Table) shows two doublets at δ 7·10 and 7·52 respectively associated with *meta*-coupling in these systems. The observed spectrum, therefore, provides powerful evidence in favour of the 1,2,8-trisubstituted structure.

The n.m.r. spectra of the other compounds described



Scheme 1 Products and yields obtained from the reaction of disodium anthraquinone-1,8-disulphonate with hydroxide ion

N.m.r. spectra of substituted anthraquinones

Compd.	Substituents	8-H	7-H	Chemical shifts (δ (p.p.m.)) * 6-H	5-H	4-H	3-H	2-H	Coupling constants (Hz) $J_{6,7}$	$J_{5,6}$	$J_{5,7}$	$J_{3,4}$	$J_{2,3}$	$J_{2,4}$
(I)	1,8-Disulphonate		8·32(dd)	7·63(t)	8·05(dd)	8·05(dd)	7·63(t)	8·32(dd)	7·5	7·5	2·0	7·5	7·5	2·0
(II)	8-Hydroxy-1-sulphonate		7·35(dd)	7·62(t)	7·75(dd)	8·24(dd)	7·84(t)	8·54(dd)	7·5	7·5	2·0	7·5	7·5	1·5
(III)	8-Hydroxy-1,7-disulphonate			8·06(d)	7·65(d)	8·24(dd)	7·82(t)	8·54(dd)		8·0		7·5	7·5	1·5
(IV)	4-Hydroxy-1,3,5-trisulphonate ‡	8·28(dd)	7·80(t)	8·38(dd)				8·70(s)						
(V)	7,8-Dihydroxy-1-sulphonate			7·10(d)	7·52(d)	8·16(dd)	7·73(t)	8·48(dd)		8·0		7·5	7·5	1·5
(VI)	1,8-Dihydroxy-2-sulphonate		7·21(dd)	[7·61] †		7·56(d)	8·00(d)		7·5		2·0	7·8		
(VII)	1,8-Dihydroxy-2,7-disulphonate			7·63(d)	8·10(d)	7·63(d)	8·10(d)			7·5		7·5		
(VIII)	1,8-Dihydroxy		7·21(dd)	[7·62] †		[7·62] †		7·21(dd)	7·5		2·0		7·5	2·0
(IX)	1,2,8-Trihydroxy		7·20(dd)	[7·61] †		7·52(d)	7·12(d)		7·5		1·5	8·0		

* Relative to sodium 3-(trimethylsilyl)propanesulphonate. † Superimposed resonances. ‡ $J_{6,7}$ 7·5, $J_{6,8}$ 1·5, $J_{7,8}$ 7·5 Hz. s = Singlet; d = doublet; dd = double doublet; t = triplet.

consistent with structure (V). A further alternative containing hydroxy-groups in the 1,3-positions of the disubstituted ring of the molecule can be ruled out as the observed coupling constant of the two remaining protons at 8·0 Hz is considerably greater than that normally (Table) are consistent with the spectra predicted in a similar way, and there seems little doubt that all the structures contain substituents in the positions indicated.

The water-insoluble products obtained during the present studies, *i.e.* 1,8-dihydroxyanthraquinone and

1,2,8-trihydroxyanthraquinone, were identified by a comparison with authentic samples using both i.r. and n.m.r. spectroscopy.

DISCUSSION

While the replacement of the sodium sulphonate group in a number of the structures considered here and during the course of the original reaction with hydroxide ion at 145° resembles the corresponding nucleophilic substitution reactions of benzene- and naphthalene-sulphonates with the same reagent, a considerable amount of evidence has been accumulated to show that this type of reaction is radical in character.[2,4,6] Thus, the conversion of sodium anthraquinone-2-sulphonate into 2-hydroxyanthraquinone with hydroxide ion at 150° is believed to proceed *via* the intermediacy and subsequent combination of the corresponding anthrasemiquinone radical anion and the hydroxyl radical, both generated initially by electron transfer from the reagent to the substrate.[2,4] However, as little attention has been focused on the related hydroxylations of anthraquinone-α-sulphonates it is not possible to differentiate between a radical process or an alternative nucleophilic mechanism for the formation of products such as the hydroxy-sulphonate or 1,8-dihydroxyanthraquinone in the reaction described here.

The appreciable concentration of anthrasemiquinone radical anion formed at 150—200° from the reaction of sodium 4-aminoanthraquinone-1-sulphonate with aqueous sodium sulphite suggests that this type of reaction is also radical in character.[18-20] Furthermore, the presence of 2-hydroxynaphthalene in the reactants gives a partial conversion into sodium 2-hydroxynaphthalene-1-sulphonate which has led to the suggestion that the sulphite radical anion is the effective attacking reagent.[19] As the thermal reactions described here are similar to those of the aminoanthraquinone systems, and since the hydroxy-disulphonate and hydroxy-trisulphonate are formed from both the photochemical and thermal reactions between the hydroxysulphonate and aqueous sodium sulphite it is probable that radical species are involved here also.

It is suggested, therefore that the first step of the photochemical reaction is analogous to the corresponding photochemical reaction of sodium anthraquinone-2-sulphonate with hydroxide ion which is known to lead to the formation of anthrasemiquinone radical anion either (1) by direct electron transfer from the reagent to a triplet excimer,[2] or (2) by interaction of the excimer with a ground state molecule to give a radical anion and cation and subsequent reduction of the latter by the reagent,[9] or (3) by electron transfer from the adduct formed by interaction of excimer with the reagent to a ground state molecule,[11] *i.e.* reactions (1)—(3) where A represents sodium anthraquinone-2-sulphonate or the hydroxysulphonate and X^- represents the hydroxide or sulphite anion respectively. The original evidence for the quenching mechanism, ${}^3A^*/A$, shown in reaction (2), however, has been questioned,[11] and furthermore, reaction (3) does not explain the observation that when alkaline solutions of anthraquinonesulphonates containing benzene are illuminated phenol is formed.[2]

$$A \xrightarrow{h\nu} {}^3A^* \xrightarrow{X^-} \dot{A}^- + \dot{X} \qquad (1)$$

$$A + {}^3A^* \longrightarrow \dot{A}^- + \dot{A}^+ \xrightarrow{X^-} \dot{A}^- + A + \dot{X} \qquad (2)$$

$${}^3A^* \xrightarrow{X^-} AX^- \xrightarrow{A} \dot{A}^- + A\dot{X} \qquad (3)$$

It is well established, however, that the photochemical hydroxylation of sodium anthraquinone-2-sulphonate results in the eventual formation of products which are mono- and di-hydroxylated mainly in the α- and β-positions of the unsubstituted ring of the molecule.[11,12] Similar products have been obtained in small yield from the corresponding thermal reaction [2] and also from the reaction of the same substrate with Fenton's reagent.[12] These and related studies [2,6] have provided strong evidence to show that the hydroxylated products arise by direct attack of the hydroxyl radical on the substrate itself. In contrast, the formation of 2-hydroxyanthraquinone from the thermal reaction is evidently accomplished by combination of the hydroxyl radical with the anthrasemiquinone radical anion in a solvent cage.[2,6]

The thermal reactions of 1,8-dihydroxyanthraquinone and the hydroxy-sulphonate with the hydroxide ion or the sulphite anion, which result in the formation of 1,2,8-trihydroxyanthraquinone or hydroxyanthraquinonesulphonates (III), (IV), (VI), and (VII), are probably analogous to the reactions discussed above and related to the reactions of sodium 4-aminoanthraquinone-1-sulphonate with the sulphite anion and probably proceed by the generation of the hydroxyl radical or sulphite radical anion respectively by direct electron transfer from the reagent (X^-) to the substrate (A), *i.e.* reaction (4), and are followed by the attack of the respective radical on the substrate to yield substituted products.

$$A \xrightarrow[\Delta]{X^-} \dot{A}^- + \dot{X} \qquad (4)$$

The analogy drawn between the hydroxylations and the reactions with the sulphite anion is further supported by the results of radical experiments since treatment of the hydroxy-sulphonate with the sulphite radical anion, generated by a similar procedure to that adopted by Norman and Storey [21] from the reaction of titanium(III) or iron(II) ion with sodium sulphite and hydrogen peroxide, *i.e.* reactions (5) and (6), results in the formation

$$Ti^{3+} + H_2O_2 \longrightarrow Ti^{4+} + OH^- + \dot{O}H \qquad (5)$$

$$\dot{O}H + SO_3^{2-} \longrightarrow OH^- + \dot{S}O_3^- \qquad (6)$$

of the hydroxy-disulphonate and hydroxy-trisulphonate. All the available evidence suggests, therefore, that the

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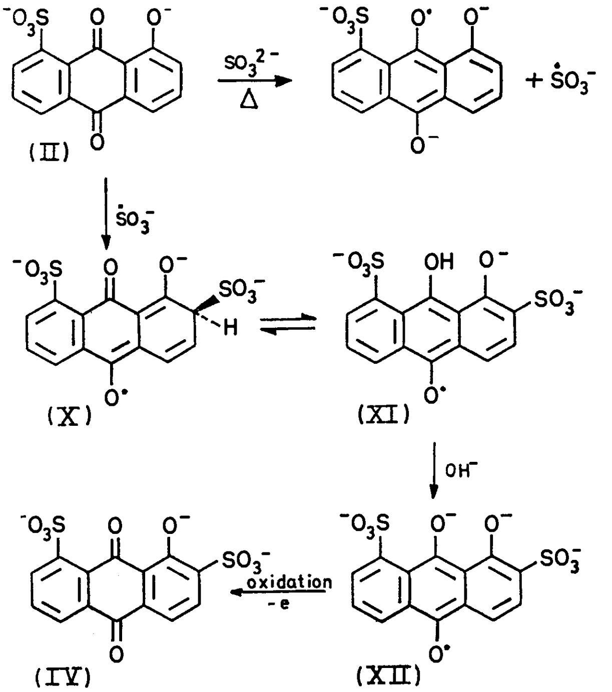
[19] G. V. Fomin, N. S. Dokunikhin, and A. N. Strube, *Russ. J. Phys. Chem.*, 1970, **44**, 745.

[20] G. V. Fomin, N. S. Dokunikhin, and A. N. Strube, *Russ. J. Phys. Chem.*, 1971, **45**, 1502.

[21] R. O. C. Norman and P. M. Storey, *J. Chem. Soc. (B)*, 1971, 1009.

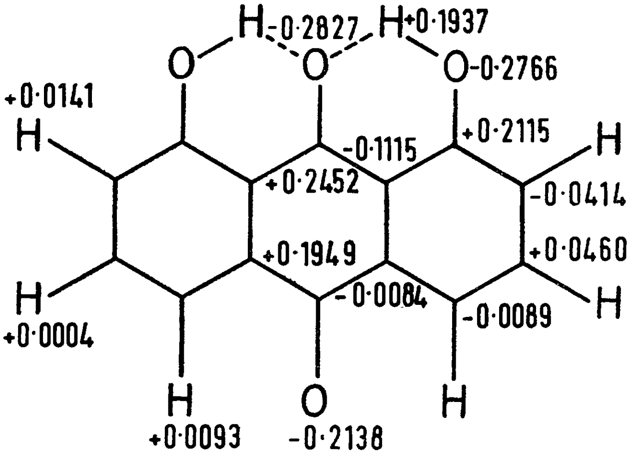
reactions described here proceed by the initial generation of the sulphite radical anion and its subsequent reaction with the substrate to form an adduct, *e.g.* (X). A similar adduct has been detected by e.s.r. studies during the reaction of the hydroxyl radical with substituted benzenes[22] and by pulse radiolysis during the photochemical hydroxylation of sodium anthraquinone-2-sulphonate.[7,23] At high pH, proton abstraction from the adduct or its tautomer (XI) would be expected to yield the anthrasemiquinone radical anion (XII) which would be oxidised in the presence of air to yield the hydroxy-disulphonate (Scheme 2).



SCHEME 2

Position of Substitution.—It is well established that the hydroxyl radical shows electrophilic character in its reactions with aromatic substrates,[23-25] but displays only a low substrate and positional selectivity by comparison with electrophilic reagents.[26,27] However, as the mechanism of attack is analogous to an electrophilic substitution,[25] it follows that the transition state occurs early along the reaction co-ordinate and probably bears a structural resemblance to the aromatic substrate. A picture of the charge distribution in the molecule under attack would be expected, therefore, to show a correlation with the observed reactivity. Furthermore, radicals in which the unpaired electron is associated with an electronegative atom frequently possess electrophilic character[28] and it seems likely on this basis that the sulphite radical anion would display similar characteristics to the hydroxyl radical.

The results of MO calculations (CNDO/2 method[29] using Program 141 of QCPE[30]) performed on 1,8-dihydroxyanthraquinone, which was selected because it is attacked by both the hydroxyl radical and sulphite radical anion, are illustrated (Figure). The molecular geometry and assumptions adopted for the anthraquinone nucleus have been described previously;[31] the hydroxyl substituents were assumed to be connected to the aromatic ring by standard[32] carbon–oxygen and hydrogen–oxygen bond lengths of 1·36 and 0·96 Å respectively. It is evident from the results shown that the greatest charge density is found at the 2-position of the molecule. The experimentally determined position of substitution, therefore, is fully consistent with the theoretical model with both radicals showing a very high degree of positional selectivity in their reactions.



Total charge distribution in 1,8-dihydroxyanthraquinone calculated by the CNDO/2 method

EXPERIMENTAL

AnalaR grade reagents were used throughout. Glass plates coated with 0·5 mm Cellulose F (Merck) were used for t.l.c. analysis unless stated otherwise and 2% sodium dihydrogen phosphate–ammonia (*d* 0·88) (9 : 1) used as eluant. I.r. spectra (mulls in Nujol and in hexachlorobutadiene) were recorded on a Perkin-Elmer model 457 spectrophotometer, and n.m.r. spectra were recorded on solutions in [$^2H_6$]dimethyl sulphoxide–carbon tetrachloride with a Varian HA 100 instrument operating at 100 MHz, a temperature of 90°, and using the c.a.t. technique. In some cases water-soluble products were separated by t.l.c. and estimated by u.v. spectroscopy in water on a Unicam SP 700 instrument in the wavelength range 400—600 nm.

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[30] P. A. Dobosh, CNINDO, Program 141, Quantum Chemistry Program Exchange, Indiana University.

[31] J. O. Morley, *J.C.S. Perkin II*, 1972, 1223.

[32] J. A. Pople and D. L. Beveridge, ' Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

Authentic samples of disodium anthraquinone-1,8-disulphonate, 1,8-dihydroxyanthraquinone, and 1,2,8-trihydroxyanthraquinone were provided by I.C.I. Ltd. The disulphonate was purified by repeated recrystallisation from water until t.l.c. analysis showed that it was completely free from other isomers. The hydroxy-compounds were purified by vacuum sublimation at 200° and subsequent recrystallisation from toluene. Product samples were dried carefully at 130—150° *in vacuo* prior to elemental analysis.

Sodium 9,10-*Dihydro*-8-*hydroxy*-9,10-*dioxoanthracene*-1-*sulphonate*.*—Disodium anthraquinone-1,8-disulphonate (20·6 g, 50 mmol), calcium hydroxide (11·1 g, 150 mmol), and magnesium chloride hexahydrate (12·2 g, 60 mmol) were added to water (100 ml) and the mixture stirred vigorously for 30 min. The resulting suspension was heated in a stainless steel autoclave (150 ml) for 2 h at 210°, then cooled, and added to water (500 ml). The dark red mixture was acidified with concentrated hydrochloric acid (100 ml), heated at 100° for 1 h to destroy calcium sulphite, the yellow precipitate was filtered, washed free of acid with 10% aqueous sodium chloride, dried, and extracted with toluene in a Soxhlet apparatus. Evaporation of the solvent gave 1,8-dihydroxyanthraquinone (4·80 g, 40%), identified by i.r. spectroscopy. The residue remaining after extraction was recrystallised from hot water and dried at 150° to yield the 8-hydroxy-1-sulphonate (5·30 g, 32·5%) (Found: C, 51·3; H, 1·0; S, 10·0. Calc. for $C_{14}H_7NaO_6S$: C, 51·5; H, 2·2; S, 9·8%), identified by n.m.r. spectroscopy. T.l.c. analysis gave an orange band at R_F 0·62.

Disodium 9,10-*Dihydro*-8-*hydroxy*-9,10-*dioxoanthracene*-1,7-*disulphonate and Trisodium* 9,10-*Dihydro*-4-*hydroxy*-9,10-*dioxoanthracene*-1,3,5-*trisulphonate*.—(a) *From the thermal reaction.* An aqueous suspension (150 ml) of sodium 8-hydroxyanthraquinone-1-sulphonate (3·26 g, 10 mmol), sodium hydroxide (0·4 g, 10 mmol), and sodium sulphite heptahydrate (5·04 g, 20 mmol) was heated under reflux and a stream of air blown through the liquor for 24 h. After reaction, the mixture was cooled, acidified with concentrated hydrochloric acid (6 ml), and the product precipitated by the addition of sodium chloride (30 g). The product was filtered and recrystallised several times from water to give the 8-*hydroxy*-1,7-*disulphonate* (1·43 g, 33%) (Found: C, 38·9; H, 1·7; S, 14·7. $C_{14}H_6Na_2O_9S_2$ requires C, 39·2; H, 1·4; S, 15·0%), identified by n.m.r. spectroscopy. T.l.c. analysis gave a red band at R_F 0·77.

T.l.c. and spectroscopic analysis of the original reaction liquors showed that two products were present, one of which was identical with the isolated product (3·85 g, 90% conversion) and the other (0·26 g, 5% conversion) was identical with the product obtained from the following preparation. An aqueous suspension (100 ml) of disodium 8-hydroxyanthraquinone-1,7-disulphonate (4·28 g, 10 mmol), sodium hydroxide (0·4 g, 10 mmol), and sodium sulphite heptahydrate (25·2 g, 100 mmol) was heated under reflux and a stream of air blown through the liquor for 72 h. After reaction, the mixture was acidified with concentrated hydrochloric acid (6 ml) and evaporated to 40 ml. On cooling, the product was filtered and recrystallised several times from water to give the 4-*hydroxy*-1,3,5-*trisulphonate* (2·90 g, 54·7%) (Found: C, 31·4; H, 1·3; S, 17·8. $C_{14}H_5Na_3O_{12}S_3$ requires C, 31·7; H, 1·0; S, 18·1%), identified by n.m.r. spectroscopy. T.l.c. analysis gave an orange band at R_F 0·92.

(b) *From the photochemical reaction.* An aqueous solution (1 l) of sodium 8-hydroxyanthraquinone-1-sulphonate (0·008M) and sodium sulphite heptahydrate (0·08M) was prepared in the dark at 18° and adjusted to pH 12 with aqueous ammonia. A portion of the resulting solution (50 ml) was placed in a glass vessel (100 ml) fitted with a water-cooled glass surround and stirrer and was irradiated with visible light (Mazda 150 W tungsten filament lamp) at 18°. T.l.c. and spectroscopic analysis after 18 h showed that the substrate had been converted into the 8-hydroxy-1,7-disulphonate (85%; R_F 0·77) and the 4-hydroxy-1,3,5-trisulphonate (7%; R_F 0·92). In the control dark experiment, only a little reaction could be detected after 18 h.

(c) *From the radical reaction.* Aqueous 0·1M-iron(II) sulphate (100 ml) was treated with aqueous ammonia to give pH 9, and mixed in the dark with a solution (100 ml) containing sodium 8-hydroxyanthraquinone-1-sulphonate (0·008M) and sodium sulphite heptahydrate (0·2M) also at pH 9. Aqueous hydrogen peroxide (0·2M, 50 ml) was added slowly to the well agitated solution over 30 min at 18°. T.l.c. and spectroscopic analysis showed that the substrate had been converted into the 8-hydroxy-1,7-disulphonate (10%) and the 4-hydroxy-1,3,5-trisulphonate (5%). A similar experiment using titanium(III) chloride in place of iron(II) sulphate at pH 9 gave the same products in 6 and 4% conversion respectively. In the absence of the metal ion or hydrogen peroxide no reaction occurred and only the substrate could be detected by t.l.c. analysis.

Sodium 9,10-*Dihydro*-1,8-*dihydroxy*-9,10-*dioxoanthracene*-2-*sulphonate and Disodium* 9,10-*Dihydro*-1,8-*dihydroxy*-9,10-*dioxoanthracene*-2,7-*disulphonate*.—An aqueous suspension (400 ml) of 1,8-dihydroxyanthraquinone (24·0 g, 0·1 mol), sodium sulphite heptahydrate (25·2 g, 0·1 mol), and sodium hydroxide (8·0 g, 0·2 mol) was heated under reflux and a stream of air blown through the liquor for 72 h. The mixture was then acidified with concentrated hydrochloric acid (40 ml), boiled, and the resulting precipitate filtered, dried, and identified as 1,8-dihydroxyanthraquinone (18·3 g, 76%) by i.r. spectroscopy. Sodium chloride (40 g) was added to the filtrates and the resulting precipitate was filtered and washed free of acid with 10% aqueous sodium chloride. Two components were isolated from the product mixture by column chromatography using the same stationary phase and eluant as that adopted for t.l.c. to give the 1,8-*dihydroxy*-2-*sulphonate* (0·5 g) (Found: C, 48·9; H, 2·4; S, 9·6. $C_{14}H_7NaO_7S$ requires C, 49·1; H, 2·1; S, 9·3%), identified by n.m.r. spectroscopy, and the 1,8-*dihydroxy*-2,7-*disulphonate* (0·4 g) (Found: C, 37·5; H, 1·5; S, 14·4. $C_{14}H_6Na_2O_{10}S_2$ requires C, 37·8; H, 1·4; S, 14·4%), identified by n.m.r. spectroscopy. The monosulphonate gave a red band at R_F 0·38 and the disulphonate a purple band at R_F 0·59 on t.l.c. analysis. T.l.c. and spectroscopic analysis of the original filtrates showed that they contained the monosulphonate (5·13 g, 15% conversion) and the disulphonate (2·22 g, 5% conversion) respectively.

1,2,8-*Trihydroxyanthraquinone*.— 1,8-Dihydroxyanthraquinone (12·0 g, 50 mmol) and sodium hydroxide (40 g, 1 mol) were added to water (700 ml) and the mixture heated at 145° for 2 h in a stainless steel autoclave (1 l). On cooling, the red solution was acidified with concentrated hydrochloric acid (150 ml) and the resulting precipitate was filtered, washed free of acid with water, and dried at 100°. T.l.c. analysis and separation of the product mixture using a stationary phase of polyamide with ethanol as an eluant

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* Based on a modified preparative method for 1,8-dihydroxyanthraquinone.[14]

gave 1,8-dihydroxyanthraquinone (9·60 g, 80%), identified by i.r. spectroscopy, and 1,2,8-trihydroxyanthraquinone (1·92 g, 15% conversion), identified by comparison with an authentic sample.

Reaction of Disodium Anthraquinone-1,8-*disulphonate with Aqueous Sodium Hydroxide*.—The reported procedure was adopted.[13] Disodium anthraquinone-1,8-disulphonate (20·6 g, 50 mmol) and sodium hydroxide (36·4 g, 0·91 mol) were added to water (700 ml) and the mixture heated in a stainless steel autoclave (1 l) with agitation at 145° for 18 h. On cooling, the red mixture was divided into two equal parts. One part was acidified with concentrated hydrochloric acid (55 ml) and the resulting yellow precipitate was filtered, washed free of acid with 10% aqueous sodium chloride, dried at 100°, and extracted with toluene in a Soxhlet apparatus. Evaporation of the solvent gave a mixture of 1,8-dihydroxyanthraquinone (1·02 g, 17%) and 1,2,8-trihydroxyanthraquinone (1·34 g, 21%) which were separated by t.l.c. using a stationary phase of polyamide and an eluant of ethanol and identified by i.r. spectroscopy. The residue remaining after extraction was recrystallised several times from water and dried at 150° to yield sodium 9,10-dihydro-7,8-dihydroxy-9,10-dioxoanthracene-1-sulphonate (0·45 g) (Found: C, 49·0; H, 2·4; S, 9·4. Calc. for $C_{14}H_7NaO_7S$: C, 49·1; H, 2·1; S, 9·3%), identified by n.m.r. spectroscopy. T.l.c. analysis gave a purple band at R_F 0·20.

The other part of the reaction mixture was acidified with hydrochloric acid, as before, and the yellow precipitate was filtered and extracted with boiling water. The extracts and filtrates were combined, evaporated to 100 ml, and made alkaline with aqueous ammonia. T.l.c. and spectroscopic analysis of the red solution gave the following products: the 7,8-dihydroxy-1-sulphonate (0·85 g, 10%), the 1,8-dihydroxy-2-sulphonate (0·51 g, 6%), the 1,8-dihydroxy-2,7-disulphonate (0·33 g, 3%), the 8-hydroxy-1-sulphonate (1·63 g, 20%), the 8-hydroxy-1,7-disulphonate (0·96 g, 9%), the 4-hydroxy-1,3,5-trisulphonate (0·40 g, 3%), and small amounts of two unidentified compounds.

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