

CCCXXX.—*The Reduction of Substituted p-Benzoquinones by Sulphur Dioxide alone and in the Presence of Alkali.*

By JOHN WALLIS DODGSON.

THE investigation (J., 1914, **105**, 2435) on the reduction of *p*-benzoquinone by sulphur dioxide in the presence of water and of alkali has been extended to include certain substituted *p*-quinones.

The method of experiment was the same throughout. In a flask through which nitrogen was continuously passed, water (400 c.c.) and the calculated quantity of standard sodium hydroxide solution were boiled and cooled and 25 c.c. of a standardised solution of sulphur dioxide were added, followed by the quinone (0.25 g.) dissolved in alcohol. After 15 minutes, excess of hydrochloric

acid was added, the liquid was boiled to expel the excess of sulphur dioxide, and the sulphuric acid which had been formed was estimated by means of barium chloride. The filtrate and washings were evaporated to dryness with concentrated nitric acid and again with concentrated hydrochloric acid, the residue was treated with water, and the residual barium sulphate was washed and ignited. Before being finally weighed, the sulphate was warmed with dilute hydrochloric acid to remove barium oxide left by ignition of any slight residue of barium nitrate and more particularly of barium oxalate, which was always formed in considerable quantity by the oxidation of the quinolsulphonic acid or quinol with nitric acid and often separated in crystals, $\text{BaC}_2\text{O}_4, \frac{1}{2}\text{H}_2\text{O}$.

The quinones examined were: (a) toluquinone, (b) *o*- and *p*-xyloquinones (Clark, *J. Amer. Chem. Soc.*, 1892, **14**, 565), (c) monochlorobenzoquinone, (d) 2:5- and 2:6-dichlorobenzoquinones, and (e) tetrachlorobenzoquinone.

The action was in all cases somewhat similar to that which takes place with *p*-benzoquinone: quinol was formed by direct reduction (measured by the amount of barium sulphate first precipitated) together with sulphonic acid (measured by the barium sulphate obtained after oxidation).

The results given by the first four quinones are in Table I. In each case there is the reversal of the percentages of the quinone reduced and sulphonated when more alkali than is necessary to form acid sulphite is added (compare *p*-benzoquinone). The reversal is by no means so sudden with the two xyloquinones as with the others. The results for *p*-benzoquinone are included for comparison.

Experiments with monochloroquinone were made to ascertain if chlorine was liberated during the reaction. None was detected until the molecular ratio of alkali to sulphur dioxide was 1:1; thereafter the quantity increased with the proportion of alkali, but it was never large. It is probable therefore that the higher percentages of sulphonation are due to the displacement of chlorine and consequent formation of a disulphonic acid.

The displacement of chlorine from the dichloroquinones was more marked, and was accompanied by a considerable excess of sulphonation, which was for the first three experiments of each series sensibly equivalent to the chlorine liberated (Table II).

The Barium Salts of the Sulphonic Acids.—10 G. of each quinone were mixed with water and reduced with sulphur dioxide and the filtered solution was boiled to expel the excess of sulphur dioxide, cooled, extracted several times with ether, and treated with barium carbonate. The salts were very soluble in water and not easily

TABLE I.

Mols. NaOH to 1 mol. SO ₂	0.0	0.5	1.0	1.5	2.0	2.5	3.0	4.0	6.0
<i>p</i> -Benzoquinone	77.24 21.63	77.16 21.00	76.94 19.92	3.19 79.55	3.07 57.20	3.54 40.09	3.38 36.93	3.83 35.18	3.38 34.93
Toluquinone	75.34 24.21	75.19 24.23	75.51 24.30	6.30 57.63	4.62 51.89	3.00 43.92	1.74 38.42	1.96 35.04	— —
<i>p</i> -Xyloquinone	82.90 16.88	83.06 16.89	81.02 17.13	50.67 44.13	25.29 52.89	2.97 51.83	2.34 45.21	2.35 38.66	2.63 33.95
<i>o</i> -Xyloquinone	77.30 22.68	77.09 22.56	77.12 22.67	48.16 48.13	30.48 55.56	6.51 50.90	4.67 46.74	4.69 45.88	3.30 42.75
Monochloro- benzoquinone	86.27 13.34	86.37 13.38	86.33 13.26	9.35 80.72	5.82 74.70	3.82 59.45	2.91 54.20	2.76 51.78	1.82 49.53

TABLE II.

Mols. NaOH to 1 mol. SO ₂	0.0	0.5	1.0	1.5	2.0	2.5	3.0	4.0	6.0
2 : 5-Dichloro- <i>p</i> -benzo- quinone	75.80 34.35 10.15	75.67 34.27 9.94	45.01 98.03 43.04	23.88 164.1 87.98	19.57 188.9 108.47	16.44 184.9 105.34	9.57 162.9 72.47	2.72 145.3 48.02	2.79 102.2 4.99
2 : 6-Dichloro- <i>p</i> -benzo- quinone	82.75 17.66 0.41	79.20 26.71 5.91	59.90 57.65 17.55	14.95 171.7 86.65	11.43 171.9 83.33	6.56 162.8 69.36	2.22 129.3 31.52	0.61 112.0 12.61	0.18 97.23 —
Chlorine liberated	0.406	5.58	17.96	93.0	121.9	129.1	168.2	154.9	—
Chlorine liberated	—	—	—	—	—	—	not estimated	—	—

purified. Sufficient *p*-2 : 3-xyloquinone was not available for the preparation of a workable quantity of the barium salt, but a dilute solution was obtained which gave a faint blue colour with ferric chloride solution and reduced an ammoniacal silver oxide solution—this property is common to all these sulphonic acids. It was necessary to free the barium salts prepared from the dichloro-compounds from barium chloride: the analyses suggest a mixture of a monosulphonate and a disulphonate, $C_6HCl(OH)_2(SO_3)_2Ba$.

Barium toluquinolsulphonate. Found: Ba, 25.4; SO_3 , 29.3. $[C_6H_2Me(OH)_2 \cdot SO_3]_2Ba$ requires Ba, 25.2; SO_3 , 29.5%. Ferric chloride reaction, blue. *Barium p-xyloquinolsulphonate*. Found: Ba, 23.3; SO_3 , 27.3. $[C_6HMe_2(OH)_2 \cdot SO_3]_2Ba$ requires Ba, 24.0; SO_3 , 28.0%. Reaction, greenish-blue. *Barium chloroquinolsulphonate*. Found: Ba, 21.6; SO_3 , 24.5. $[C_6H_2Cl(OH)_2 \cdot SO_3]_2Ba$ requires Ba, 23.4; SO_3 , 27.4%. Reaction, blue. *Barium 2 : 5-dichloroquinolsulphonate*. Found: Ba, 23.35; SO_3 , 26.5. $[C_6HCl_2(OH)_2 \cdot SO_3]_2Ba$ requires Ba, 21.0; SO_3 , 24.5%. Reaction, bluish-violet. *Barium 2 : 3-dichloroquinolsulphonate*. Found: Ba, 19.9; SO_3 , 23.2%. Reaction, bluish-violet.

Tetrachloroquinone.—The insolubility of this compound in water and hot alcohol made impossible any series of reductions by the process described. As it is known also that the action of sulphite upon it is to give the corresponding salt of 2 : 5-dichloroquinolsulphonic acid (Greiff, *Z. Chem.*, 1863, 341) and that it is converted into chloroanilic acid by alkali, experiment was confined to the action of sulphur dioxide alone. The results obtained were: quinol reduced, 39.67; sulphonic acid formed, 70.65; chlorine displaced, 70.53 equivs. %.

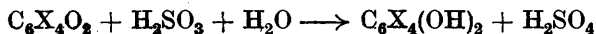
The sulphonation is directly proportional to the chlorine displaced. The above figures also suggest the formation of a mixture of mono- and di-sulphonic acids containing about 21% of the latter. A mixture of the barium salts, assumed to be $[C_6Cl_3(OH)_2 \cdot SO_3]_2Ba$ and $C_6Cl_2(OH)_2(SO_3)_2Ba$, in this proportion would require Ba, 21.1; SO_3 , 24.7%. The barium salt prepared in the usual way gave Ba, 20.4; SO_3 , 23.95%.

These salts in water (they were not separated) gave a deep bluish-purple colour with ferric chloride solution.

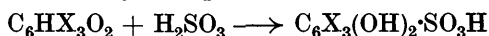
Summary.

(a) Sulphonic acids are regularly formed by the action of sulphurous acid on quinones (compare Pinnow, *J. pr. Chem.*, 1914, 89, 536).

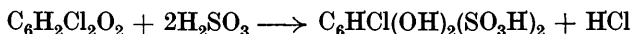
(b) Direct reduction also takes place according to the equation :



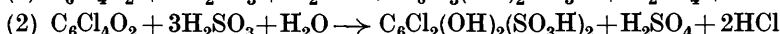
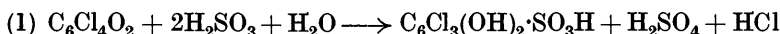
(c) While the quinone molecule contains one or more hydrogen atoms, the reaction may be expressed :



(d) In chloroquinones there is a marked tendency to form disulphonic acids : *e.g.*,



(e) With tetrachloroquinone, which no longer contains a labile hydrogen, the sulphonation must be expressed by the equations :



(f) The formation of sulphonic acids by neutral sulphites is largely in excess of reduction of the quinone. It must be the result of the presence of sulphonic ion. This demands previous hydrolysis of the sulphite. Additional alkali inhibits this hydrolysis, and this is probably a contributing cause of the falling off of sulphonate as the proportion of alkali is increased.

(g) The action of excess of alkali apparently leads to destruction of the quinone through the formation of highly coloured unstable compounds.

I wish to thank Professor H. Bassett for his interest in this work and for his many valuable suggestions.

THE UNIVERSITY, READING.

[Received, August 2nd, 1930.]