CCXXVII.—*The Reaction of* p-*Benzoquinone with Sulphurous Acid and with Alkali. Part I.*

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THE experiments described in this paper were commenced with the intention of elucidating the action of sulphurous acid and sulphites in a solution of quinol when that solution is used as a photographic developer. On the assumption that *p*-benzoquinone is formed during development by the oxidising action of silver bromide in the presence of water, it was considered advisable to start the inquiry with an examination into the action of sulphur dioxide on a solution of *p*-benzoquinone in water at the ordinary temperature.

As is well known, the reduction of *p*-benzoquinone in aqueous solution by sulphur dioxide leads to the formation of quinol, but the yield is always less than the theoretical. The action has been considered to proceed on the lines represented by the equation:

$$C_6H_4O_2 + SO_2 + 2H_2O \longrightarrow C_6H_4(OH)_2 + H_2SO_4.$$

It was also suggested by Mees and Sheppard (*Zeitsch. wiss. Photochem.*, 1902, **2**, 5) that another reaction takes place leading to the formation of dithionic acid:

$$C_6H_4O_2 + 2SO_2 + 2H_2O \longrightarrow C_6H_4(OH)_2 + H_2S_2O_6.$$

EXPERIMENTAL.

A. *Preliminary Experiments on the Decomposition of Dithionate.*

(1) 0·1869 Gram of sodium dithionate ($Na_2S_2O_6,2H_2O$), when dissolved in 400 c.c. of water and boiled for half an hour with 10 c.c.

of concentrated hydrochloric acid, gave on precipitation with barium chloride 0·0233 gram of barium sulphate (0·1869 gram of crystallised sodium dithionate should yield, if completely decomposed, 0·1799 gram of barium sulphate).

(2) 0·2132 Gram of sodium dithionate, dissolved as before and evaporated to dryness with 10 c.c. of fuming nitric acid, gave, on solution of the residue in water and precipitation with barium chloride, 0·4111 gram of barium sulphate (0·2132 gram of the salt when oxidised to sulphate should yield 0·4106 gram of barium sulphate).

Dithionate is therefore only partly decomposed on boiling in dilute acid, but is quantitatively oxidised to sulphate by nitric acid under the conditions of the experiments.

B. *The Reduction of* p-*Benzoquinone.*

(1) In 400 c.c. of water, boiled and cooled in a current of carbon dioxide, 0·25 gram of *p*-benzoquinone was dissolved. Sulphur dioxide was then passed through until reduction was complete. The excess of sulphur dioxide was removed by evaporation, and the sulphuric acid precipitated with barium chloride, when 0·4331 gram of barium sulphate was obtained.

(2) A blank experiment made without *p*-benzoquinone, but otherwise as nearly as possible identical with the foregoing, yielded 0·0120 gram of barium sulphate. The sulphuric acid actually produced during the reduction of 0·25 gram of *p*-benzoquinone was therefore equivalent to 0·4211 gram of barium sulphate.

(3) The filtrate from *B* (1), which contained excess of barium chloride, was oxidised by evaporation to dryness with 10 c.c. of fuming nitric acid, and the residue was boiled with water and filtered, when 0·1134 gram of barium sulphate was obtained, giving a total amount of 0·5345 gram.

If one molecule of *p*-benzoquinone reacted with one molecule of sulphur dioxide, 0·25 gram of *p*-benzoquinone could give rise to the formation of 0·5394 gram of barium sulphate, and with this the total weight obtained fairly closely agrees. Dithionic acid, however, could only be formed by the interaction of one molecule of *p*-benzoquinone and two molecules of sulphur dioxide; and, judging from the experiments on the decomposition of dithionate in the presence of acid, only a small amount of this would be precipitated as sulphate with the first precipitate on boiling, but after oxidation with nitric acid it would be entirely precipitated as barium sulphate. Moreover, as the oxidation converts the whole of the sulphur in dithionic acid to sulphate, the effect would be to cause the total weight of barium sulphate precipitated to exceed 0·5394 gram. The fact that the total barium sulphate was below this amount made it seem extremely probable that dithionic acid is either not formed at all or is produced in such minute quantities as to be within the limits of experimental error.

(4) As, however, dithionic acid on boiling might undergo decomposition more readily than an acidified solution of sodium dithionate, the following experiments were carried out. 0·2954 Gram of *p*-benzoquinone (1 mol.) was dissolved in 400 c.c. of air-free water, and 25 c.c. of 0·2188N-sulphurous acid (1 mol.) were added. The *p*-benzoquinone solution was completely decolorised, showing that reduction was complete; the solution had no perceptible odour of sulphur dioxide. The solution was precipitated with barium chloride, and yielded, after correction for the sulphuric acid present in the sulphurous acid, 0·4843 gram of barium sulphate. The filtrate containing excess of barium chloride was boiled for half-an-hour. The decomposition of dithionic acid, if it were present, would lead to the formation of a precipitate of barium sulphate. An almost imperceptible precipitate was produced. The solution was oxidised with nitric acid and evaporated to dryness. The residue yielded 0·1538 gram of barium sulphate.

(5) The experiment was repeated, using 0·4 gram of *p*-benzoquinone instead of 0·2954 gram. Precipitation in the cold with barium chloride gave 0·4884 gram of barium sulphate; the filtrate on boiling for half-an-hour gave no perceptible precipitate, and oxidation with nitric acid yielded 0·1497 gram of barium sulphate.

The results of these experiments, particularly the complete reduction of *p*-benzoquinone with a molecular quantity of sulphur dioxide, and the absence of a weighable amount of precipitate on boiling, confirm the conclusion already arrived at, namely, that *p*-benzoquinone and sulphur dioxide react almost entirely in molecular proportions, and that dithionic acid can only be produced in very minute quantity, if at all.

Referring again to experiment *B* (3), the amount of barium sulphate precipitated before oxidation (0·4211 gram) requires for its formation 0·1952 gram of *p*-benzoquinone, that is, 78·08 per cent. of the weight taken.

(6) *The Formation of Quinol.*

On dissolving 5 grams of *p*-benzoquinone in 400 c.c. of water, reducing with a current of sulphur dioxide, and extracting several times with ether, 4·1 grams of quinol were obtained. This could be formed from 4·025 grams of *p*-benzoquinone, that is, 80·5 per cent. of the weight taken, a result which is fairly in agreement with that of the previous experiment, *B* (3).

It would seem, therefore, that two reactions take place when *p*-benzoquinone is reduced with sulphur dioxide (omitting the possible formation of minute quantities of dithionic acid). About 80 per cent. of the quinone is reduced to quinol with the accompanying oxidation of the sulphur dioxide to sulphuric acid, and the remainder forms a soluble sulphur compound not precipitable with barium chloride until after oxidation.

C. *The Nature of the Second Compound: Preparation of the Sodium Salt.*

Five grams of *p*-benzoquinone were reduced in aqueous solution by sulphur dioxide, and the product was extracted with ether. The liquid left was boiled until free from ether and sulphur dioxide, neutralised with barium carbonate and filtered, and the solution of the barium salt so obtained was carefully precipitated with sodium sulphate and again filtered. The solution of the sodium salt was evaporated to dryness under diminished pressure, and the residue washed with ether. There were thus obtained 1·77 grams of a brown, crystalline substance, which was decolorised with charcoal and recrystallised from methyl alcohol. It crystallised in almost white leaflets; in solution it gave a blue coloration with ferric chloride and other reactions characteristic of a quinolsulphonate (Seyda, *Ber.*, 1883, **16**, 688). One gram of *p*-benzoquinone, that is, 20 per cent. of the amount taken, should yield 1·96 grams of sodium quinolsulphonate (Found, $SO_3=37·10$; $Na=10·94$. $C_6H_5O_5SNa$ requires $SO_3=37·75$. $Na=10·85$ per cent.).

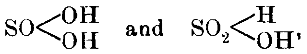
The reactions which take place when *p*-benzoquinone is reduced in aqueous solution by sulphur dioxide may therefore be represented as follows:

$$(1)\ C_6H_4O_2+H_2SO_3+H_2O \longrightarrow C_6H_4(OH)_2+H_2SO_4.$$
$$(2)\ C_6H_4O_2+H_2SO_3 \longrightarrow C_6H_3(OH)_2\cdot SO_3H.$$

The formation of quinolsulphonic acid when quinol is oxidised by silver bromide in the presence of sulphite was suggested by Bogisch (*Photo. Korresp.*, 1900, 93) and by Andresen (*ibid.*, 1900, 185), but was questioned by Lüther and Leubner on the grounds that "ring substitution of the SO_3H group in the benzene nucleus is possible only at fairly high temperature and by the use of strong sulphuric acid" (Leubner, *Diss.*, Dresden, 1912). This view is, of course, correct as regards the direct sulphonation of quinol with sulphuric acid. The reaction in the case now being considered is, however, essentially different, as *p*-benzoquinone and sulphurous acid are the reagents concerned. It is an instance of "indirect addition" similar to that which leads to the formation of chloroquinol when concentrated hydrochloric acid acts on *p*-benzoquinone.

The formation of quinolsulphonic acid in developing solutions during use has been confirmed by Pinnow (*Zeitsch. wiss. Photochem.*, 1913, **13**, 41), who has isolated the sodium salt from a used developer.

The formation of both sulphuric acid and quinolsulphonic acid, in the reduction of *p*-benzoquinone by sulphur dioxide, supports the hypothesis that a sulphurous acid solution contains molecules of each of the forms:



$$SO{<}^{OH}_{OH} \quad \text{and} \quad SO_2{<}^{H}_{OH},$$

and suggests that the former may lead to the formation of quinol and sulphuric acid, and the latter to that of the sulphonic acid, the relative amounts of each product being determined (*a*) by the proportion of each form present in the sulphurous acid, (*b*) the relative velocities of the two reactions, and possibly by other factors. The point, together with the constitution of sulphurous acid, is being further investigated in this laboratory.

D. In the experiments which follow, solutions of sulphur dioxide of known strength were employed instead of the gas, and in estimating the sulphuric acid formed, correction was made in all cases for the small amount of sulphuric acid present in these solutions.

(1) *Effect of Variation of Temperature.*

Four experiments were made at 0°, room temperature (about 20°), 50°, and 80° respectively. The sulphur dioxide solution used was 0·2576*N*. The water was well boiled and cooled in a current of

TABLE I.

Temperature.	*A.* *p*-Benzoquinone solution	*B.* Sulphur dioxide solution. c.c.	Barium sulphate from sulphuric acid formed. Gram.	from sulphonic acid Gram.	Total. Gram.
0°	0·25 gram in 100 c.c. of water (added to *B*)	50 with 250 c.c. of water	0·4167	0·1167	0·5334
20°	0·25 gram in 375 c.c. of water	25 (added to *A*)	0·4166	0·1167	0·5333
50°	0·25 gram solid (added to *B*)	50 with 350 c.c. of water	0·4221	0·1172	0·5393
80°	0·25 gram solid (added to *B*)	50 with 350 c.c. of water	0·4273	0·1153	0·5426

carbon dioxide, which was also allowed to pass through the apparatus throughout each experiment. The sulphur dioxide used was always in excess of that actually required to reduce the amount of *p*-benzoquinone taken.

From the results shown in table I it is obvious that change of temperature within the limits taken is practically without effect on the relative amounts of sulphate and sulphonate produced.

(2) *Reduction in the Presence of Hydrochloric Acid.*

TABLE II.

p-Benzoquinone solution.	Concentrated hydrochloric. acid. c.c.	Sulphur dioxide solution. c.c.	Barium sulphate from sulphate. Gram.	Barium sulphate from sulphonate. Gram.	Barium sulphate Total. Gram.
0·25 gram in 375 c.c. of water	none	25	0·4166	0·1167	0·5333
0·25 gram in 275 c.c. of water	100	25	0·4142	0·1153	0·5295
0·25 gram in 175 c.c. of water	200	25	0·0374	0·0112	0·0486

The *p*-benzoquinone was dissolved in the stated quantity of water, and the acid added; this was followed by the addition of the sulphur dioxide solution, when in each case the yellow colour of the *p*-benzoquinone solution was immediately discharged. It is obvious, however, that much hydrochloric acid greatly affects the course of the reaction. That this is due to the formation of chloroquinol was proved by dissolving 5 grams of *p*-benzoquinone in 200 c.c. of water and adding 400 c.c. of concentrated hydrochloric acid. Chloroquinol was easily extracted from the liquid with ether.

E. *Reduction of* p-*Benzoquinone in the Presence of Alkali Hydroxide.*

(1) A series of experiments was carried out with varying amounts of alkali, and the results obtained are shown in the tables below.

In each experiment the volume of alkali (0·3080*N*-sodium hydroxide) stated in the table was placed in a flask with water, making together 275 c.c.; 25 c.c. of sulphur dioxide solution (0·2734*N*) were then added, followed by the *p*-benzoquinone in 100 c.c. of water. The mixed solutions were acidified after remaining about five minutes with 10 c.c. of concentrated hydrochloric acid, and the excess of sulphur dioxide was boiled off. As the sulphur dioxide was always in excess of the amount required to reduce the quinone, slight variations in the strength of the solution used had no effect on the results obtained. The solution was, however, standardised from time to time, and estimations of the amounts of sulphuric acid present in it were made. The figures given in the tables have been corrected accordingly.

TABLE III.

Mols. alkali to 1 mol. SO_2.	Colour on adding *p*-benzoquinone.	Colour on acidifying.	Barium sulphate		
			from sulphate. Gram.	from sulphonate. Gram.	Total. Gram.
0·0	colourless	no acid added	0·4166	0·1167	0·5333
0·5	,,	colourless	0·4162	0·1084	0·5246
1·0	,,	,,	0·4150	0·1070	0·5220
1·5	very pale yellow	nearly colourless	0·0172	0·4291	0·4463
2·0	bright green changing to yellow	very pale yellow	0·0166	0·3085	0·3251
2·5	red-brown	yellow	0·0191	0·2162	0·2353
3·0	dark red-brown	brownish-yellow	0·0182	0·1992	0·2174
4·0	dark brown	yellow-brown	0·0207	0·1897	0·2104
6·0	very dark brown	yellow-brown	0·0183	0·1884	0·2067

The above results show that as long as the alkali present is not larger in quantity than is required to form sodium hydrogen sulphite with the sulphur dioxide used, the reactions proceed on practically the same lines as in the total absence of alkali, but that when this amount is exceeded there is more than a reversal of the amounts of barium sulphate obtained, nearly the whole of the precipitate being formed after oxidising with nitric acid, whilst the barium sulphate precipitated before oxidation sinks to a small and almost constant quantity. Independent experiments showed that the solutions obtained with excess of alkali, after acidifying with sulphuric acid, neutralising with barium carbonate, and filtering gave the blue colour with dilute ferric chloride solution indicative of the presence of the sulphonate.

It is noticeable from the above that the gradual addition of alkali leads to a continual decrease in the amount of sulphate precipitated after oxidation, suggesting a progressive destruction of the quinone, and the following experiments were carried out with the intention of measuring the extent of this destruction by estimating its residual activity, as regards oxidising and sulphonation, after treatment with alkali.

(2) To 0·25 gram of *p*-benzoquinone in water, 0·3080*N*-sodium hydroxide solution was added; the action of the alkali was then checked as quickly as possible by the addition of 10 c.c. of concentrated hydrochloric acid, and 25 c.c. of 0·2726*N*-sulphur dioxide solution were added. The total volume of the mixture was then 400 c.c., as in the previous series of experiments. The excess of

sulphur dioxide was boiled off, and the sulphate estimated before and after oxidation. A current of hydrogen was kept passing through the apparatus until the excess of sulphur dioxide had been removed.

The results were as follows:

TABLE IV.

Molecular proportions of NaOH to SO_2.		Barium sulphate		
NaOH.	SO_2.	from sulphate. Gram.	from sulphonate. Gram.	Total. Gram.
None	—	0·4166	0·1167	0·5333
1 Mol.	1 Mol.	0·1806	0·0373	0·2179
1½ ,,	1 ,,	0·1727	0·0353	0·2080
2½ ,,	1 ,,	0·1484	0·0256	0·1740
5 ,,	1 ,,	0·1437	0·0211	0·1648

(3) *Effect of Time.*

To 0·25 gram of *p*-benzoquinone in 350 c.c. of water, 33 c.c. of 0·3080*N*-sodium hydroxide were added, and the solution was allowed to remain in an atmosphere of hydrogen for forty-eight hours; it was then acidified, and 25 c.c. of 0·2721*N*-sulphur dioxide solution were added (molecular proportion NaOH to SO_2 3 : 1 approx.). The weight of barium sulphate obtained before oxidation was 0·0014 gram, and after oxidation 0·0085 gram, giving a total of 0·0099 gram.

From the above series of experiments it appears that:

(i) The addition of alkali hydroxide diminishes very materially both the oxidising power of a solution of *p*-benzoquinone and also the formation of sulphonic acid.

(ii) The action of the alkali, although rapid in its earlier stages, is not instantaneous, and on prolonged action further changes take place which almost totally prevent both oxidation and sulphonation.

Here it may be noted that Mees and Sheppard (*loc. cit.*) state that alkali hydroxide acts on *p*-benzoquinone with the formation of quinol and hydrogen peroxide. They were able to obtain the usual blue colour reaction with acidified dichromate, and they represent the reaction by the equation:

$$C_6H_4O_2 + 2KOH \rightleftharpoons C_6H_4(OK)_2 + H_2O_2.$$

The reaction has been questioned by M. A. Gordon (*J. physical Chem.*, 1913, **17**, 1) and by Lüther and Leubner (*loc. cit.*), who suggest a totally different action. Up to the present the author has not been able to repeat Mees and Sheppard's observation. Moreover, it is difficult, by means of their hypothesis, to account for the great reduction in the oxidising power of *p*-benzoquinone resulting from the action of alkali. The equation given by Mees and Sheppard would suggest that this oxidising power should be increased, owing to the substitution of some of the *p*-benzoquinone by its equivalent of hydrogen peroxide, and at the same time the amount of sulphonate produced should be diminished owing to the conversion of the quinone into quinol. It is possible that some dithionate might be formed, but this if produced at all would only be in very minute quantities (Nabl, *Monatsh.*, 1901, **22**, 737). The results given in table IV, however, show a considerable decrease in the production of sulphate, although the ratio of sulphate to sulphonate actually increases from slightly less than 4 : 1 when no alkali is used to somewhat more than 7 : 1 with five molecules of alkali to one of sulphur dioxide. In view, therefore, of the complex nature of the conditions under which the reactions take place, the results obtained (tables III and IV) do not appear to render possible at present the formation of any satisfactory hypothesis as to the nature of the action of alkaline sulphite or of alkali on *p*-benzoquinone. Further experiments are in progress, the results of which will be communicated later.

Summary.

(1) When *p*-benzoquinone is reduced by sulphurous acid, quinol, sulphuric acid, and quinolsulphonic acid are formed; the sulphonic acid to an extent equivalent to about 20 per cent. of the *p*-benzoquinone employed.

(2) The reaction is not affected by reasonable amounts of hydrochloric acid, but is strongly inhibited by large quantities, owing to the formation of chloroquinol. It is also not materially affected by temperature.

(3) When *p*-benzoquinone is reduced with alkaline sulphite the production of the sulphonate is greatly increased, whilst the sulphate formed sinks to a very small and almost constant quantity.

(4) Further addition of alkali leads to a diminution in the amount of sulphonate formed, without any increase in the amount of sulphate produced.

Prolonged action of the alkali almost completely prevents both reactions.

(5) Dithionic acid, if formed at all, is produced in very minute quantity.

I wish to thank Prof. H. Bassett for suggesting this work and for his interest in it.

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