

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXX.—COMMUNICATIONS FROM THE LABORATORY OF
THE LONDON INSTITUTION.

No. V.—*On the Nitration-products of the Dibromophenolsulphonic Acids.*
(*First Notice.*)

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THE nitration-products of the dichlorophenolsulphonic acid obtained by chlorination of Kekulé's phenolparasulphonic acid have already been described by one of us (this *Journal*, ix, 1112); in the present communication the results of the examination of the corresponding brominated compound are stated.

The products we have obtained are, as was anticipated, the precise analogues of those yielded by the chlorinated acid, but several not uninteresting observations have been made, showing that, although identical in kind, the reactions in the two instances are in several respects different in degree.

It had previously been found (*ibid.* x, 13) that the chlorodinitrophenol prepared from ordinary α -dinitrophenol was identical with the main product of the action of nitric acid on dichlorophenolparasulphonic acid, the corresponding bromo-derivative of α -dinitrophenol has therefore been examined and compared with the bromodinitrophenol obtained by nitration of the dibromosulpho-acid, with the result that they also are identical.

The phenolsulphonic acid employed was prepared by heating a mixture of equal weights of phenol and ordinary concentrated sulphuric acid for 15 hours at 100°, the heating being continued thus long in order to ensure the conversion of the phenol \textit{meta} - into the phenol \textit{para} -sulphonic acid, with what success will afterwards be apparent. The product was dissolved in water, and, after the small quantity of sulphuric acid present had been removed by lead carbonate, &c., the free acid was neutralised by potassium carbonate, and the solution evaporated to the crystallising point. The first crystallisation of the potassium salt thus prepared was separated from the mother-liquor by draining on a vacuum-filter, and afterwards twice recrystallised. Only this purified salt was made use of in the following experiments.

Even when bromine is made to act on an aqueous solution of potas-

sium phenolparasulphonate in the proportion necessary to form the monobrominated derivative, the main product consists, as shown by Senhofer (*Ann. Chem. Pharm.*, clvi, 102), of potassium dibromophenolsulphonate, a very small proportion only of the monobrominated salt being produced; we find that by employing the proportions— $2\text{Br}_2 : \text{C}_6\text{H}_4(\text{OH})\text{SO}_3\text{K}$ —an almost theoretical yield of dibromophenolsulphonate is obtained.

Preparation.—The potassium phenolsulphonate is dissolved in water, and the bromine is added by small quantities to the *cold* solution, the liquid being constantly agitated. The flask containing the solution should be immersed in cold water, in order to prevent the accumulation of the heat evolved in the reaction. The bromine disappears rapidly on agitation, the solution becoming colourless, and it is not until almost the whole of the necessary quantity has been added that it assumes a permanent yellow colour. The dibromo-salt separates out partially, either during the addition of the bromine, or some time afterwards, according to the state of concentration of the solution employed. It is usually in so finely divided a state, however, that it is a matter of extreme difficulty to separate it from the mother-liquor, so that it is advisable to heat and to add water until the whole is dissolved; on cooling, the potassium salt then crystallises out in needles, and a further large quantity is obtained on evaporating the filtrate.

If care be taken to avoid all rise of temperature on the addition of the bromine, the product which separates is entirely soluble in water. but if the bromine act on a warm solution, a certain quantity of an insoluble substance is produced. This melts to an oil under water below 100° ; it is readily soluble in aqueous alcohol, from which it crystallises in long fine needles melting at about 93° . Analysis shows it to be *tribromophenol*, the melting-point of which is stated to be 95° .

·393 grm. of the substance once recrystallised from alcohol gave ·661 grm. AgBr.

·3204 grm. of substance from a second preparation twice recrystallised gave ·542 grm. AgBr.

| | Theory. | I. | II. |
|-----------------------|---------|-------|-------|
| Br_3 | 72·50 | 71·57 | 71·98 |

Senhofer also noticed the formation of a small quantity of a substance melting below 100° by the action of bromine on potassium phenolmetasulphonate, but states that it was not obtained of constant composition in different experiments. He regards it as a mixture of higher brominated benzenes, formed by a secondary reaction—this we are much inclined to doubt; evidently the tribromophenol is simply the product of the further action of bromine on the dibromophenolsul-

phonic acid first formed. We also believe that in our case it was formed from a small quantity of meta-salt present in the para-salt we employed, since we noticed that a relatively greater amount was obtained when a salt was acted upon which was known to contain some quantity of potassium phenol*meta*sulphonate. The dibromophenol*para*-sulphonate does not appear to yield tribromophenol when acted upon by bromine at ordinary temperatures.

Barium Dibromophenolparasulphonate $(C_6H_2Br_2OHSO_3)_2Ba + 2 aq.$ —This salt is readily obtained as a crystalline precipitate on the addition of barium chloride to the solution of the above mentioned potassium salt. Recrystallised from water it forms long, brilliant white, silky needles, which contain two molecules of water, as stated by Senhofer.

·7797 grm. of the air-dried salt lost ·07 grm. H_2O at 140° .

| | Theory. | I. |
|--------------------|---------|-----|
| $2H_2O \dots\dots$ | 8·26 | 8·9 |

Sodium Dibromophenolparasulphonate, $C_6H_2Br_2OHSO_3Na + 2 aq.$ —We obtained this salt by the direct action of bromine on a moderately dilute cold solution of sodium phenolparasulphonate. It begins to separate out towards the close of the reaction in long, brilliant white needles, easily soluble in hot, difficultly soluble in cold water.

1·8514 grm. of the air dried salt lost ·180 grm. H_2O at 150° .

1·2338 grm. lost ·1217 grm. H_2O at 170° .

| | |
|---------------------------------------|-------------------------|
| ·383 grm. of the anhydrous salt gave | ·4059 grm. $AgBr$.* |
| ·4488 " " | ·3075 grm. $BaSO_4$. |
| ·3758 " " | ·0752 grm. Na_2SO_4 . |

| | Theory. | I. | II. |
|--------------------|---------|------|------|
| $2H_2O \dots\dots$ | 9·23 | 9·72 | 9·86 |
| $Br_2 \dots\dots$ | 45·19 | 44·7 | — |
| S " | 9·03 | 9·42 | — |
| Na " | 6·49 | 6·48 | — |

Action of Nitric Acid.—One of the objects of the investigation being to ascertain whether the action of bromine on phenolparasulphonic acid gave rise to the formation of more than one dibrominated-derivative, the salt (either potassium or sodium) acted upon by nitric acid in all the following experiments was a portion of the total product obtained by evaporating the solution to dryness, after the addition of the necessary quantity of bromine.

Action at 0° .—The dry salt was added in small portions at a time to nitric acid (sp. gr. 1·36) contained in a flask surrounded by ice, the proportion of acid to salt being about two to one. Under these con-

* A slight loss of bromine was, by accident, incurred in this experiment.

ditions mere traces only of bromine were evolved. After standing for some hours water was added, and the nitro-product removed by filtration. On heating the filtrate, and afterwards leaving it to cool, no separation of nitro-product was observed, thus proving the decomposition of the sulpho-salt to have been complete. The solid nitro-product was suspended in water, treated with potassium carbonate, and the mixture of potassium salts separated by fractional crystallisation. It was thus found to consist in the main of (a) *dibromonitrophenol* melting at 132° (uncorrected), together with small quantities of an isomeric body (c) melting at 117.5° , of *bromodinitrophenol* (b) melting at 117° , and of the potassium salt of a *bromonitrophenolsulphonic acid* (d).

Action at higher Temperatures.—If the salt is added gradually to nitric acid at the ordinary atmospheric temperatures, and the precaution is taken to avoid too great an accumulation of heat by occasionally plunging the flask into cold water, a considerable amount of bromine is set free, but the product still contains a very large quantity of the above dibromonitrophenol (melting point 132°); proportionately more of the dinitrobromophenol is obtained; the same relative proportion of of the isomeric dibromonitrophenol (melting point 117.5°), and little or no bromonitrophenolsulphonic acid.

By the action of a more concentrated acid (sp. gr. 1.42) under the same conditions, a much greater proportion of bromodinitrophenol is produced, but it is not possible in this way to convert the whole of the dibromonitrophenol (melting point 132°) into bromodinitrophenol, without at the same time risking the conversion of more or less of the latter substance into trinitrophenol.

Our observations lead us to conclude that certainly less heat is evolved by the action of nitric acid on potassium dibromophenolparasulphonate than on the corresponding dichlorinated compound. On the other hand, the bromo-salt is entirely decomposed by nitric acid at 0° , whereas a certain proportion of the chlorinated sulpho-salt always escaped decomposition; at that temperature a comparatively small quantity of the dibromonitrophenol undergoes conversion into bromodinitrophenol by the further action of the nitric acid; a much larger proportion of the corresponding dichloronitrophenol was converted into chlorodinitrophenol, which may doubtless be attributed to the greater amount of heat evolved in the reaction. By the further action of nitric acid, bromodinitrophenol may be converted with moderate ease into trinitrophenol; the corresponding chlorodinitrophenol yields little or no trinitrophenol; it is not attacked by moderately concentrated nitric acid in the cold, and is entirely decomposed by the strongest acid on warming.

Analogous products therefore are obtained by the action of nitric acid upon the dichloro- and dibromo-phenolsulphonic acids prepared from the product of the action of sulphuric acid on phenol; the two

differ only in that they are decomposed with unequal degrees of readiness.

(a.) *Dibromonitrophenol*, $C_6H_2Br_2NO_2OH$ (melting point 132°).—There is no doubt that our product is identical with the dibromorthonitrophenol obtained by Brunck (*Zeitschr. f. Chem.* [2], iii, 204) by the action of bromine on orthonitrophenol. He states, however, that it melts at 141° , and is decomposed a few degrees higher; we find the melting point as above, but that decomposition occurs, with evolution of nitric oxide,* *immediately on fusion*; water is also given off and a brown, friable mass remains, from which at a higher temperature small white shining crystals sublime.

Brunck describes two potassium derivatives of this phenol, one of which is anhydrous, and crystallises in tufts of orange yellow needles; the second, containing 2 molecules of water forms pale-yellow plates. We also have obtained two salts, the one anhydrous and deep orange-yellow, the second containing 2 molecules of water, but crystallised in long yellow prismatic needles, or on slow evaporation of a dilute solution in large prismatic crystals.

We have observed the formation of Brunck's second salt from *impure* solutions, but it has always yielded needles on recrystallisation. The second salt gave the following numbers on analysis:—

1·8556 grm. lost 1·848 grm. H_2O
 ·6137 grm. thus dried gave 1·599 grm. K_2SO_4 .

| | Theory. | I. |
|-----------------|---------|-------|
| $2H_2O$ | 9·7 | 9·9 |
| K. | 11·66 | 11·69 |

The phenol obtained from the above potassium salts by decomposition with dilute nitric acid, is of a pure white colour when freshly precipitated; it is very insoluble in water.

·3599 grm. gave 4535 grm. $AgBr$.

| | Theory. | I. |
|----------------|---------|-------|
| Br_2 | 53·87 | 53·62 |

(b.) *Dinitrobromophenol*, $C_6H_2Br(NO_2)_2OH$. (melting point 117°).—This body, the main product of the action of nitric acid (sp. gr. 1·42) on dibromophenolparasulphonic acid at somewhat elevated temperatures (50° — 80°), crystallises from boiling water, in which, however, it is only slightly soluble, on cooling, in short, fine, almost colourless needles.

·3299 grm. gave 2383 grm. $AgBr$.

* Experiments are in progress to determine the amount of gas evolved, and its composition.

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| | Theory | I. |
|---------|--------|-------|
| Br | 30.41 | 30.73 |

Potassium Derivative, $C_6H_2Br(NO_2)_2OK + Aq.$ —Brilliant yellow, flat needles moderately soluble in hot, difficultly soluble in cold water.

1.0865 grm. lost .0597 grm. H_2O at 140° .
 .4729 grm. thus dried gave .1357 grm. K_2SO_4 .

| | Theory. | I. |
|-------------|---------|-------|
| H_2O | 5.6 | 5.49 |
| K..... | 12.95 | 12.88 |

Barium Derivative $(C_6H_2Br(NO_2)_2O)_2Ba + 4-5aq.$ —This salt is very difficultly soluble in cold water. It crystallises in short needles of a more or less deep yellow colour, according to the state of concentration and temperature of the solution from which it separates; this difference in colour corresponds to a difference in the amount of water of crystallisation, thus one sample was found to lose 11.3 per cent. of water on drying at 180° , whilst a second, darker coloured sample lost only 10.18 per cent. By calculation, a loss of 9.8 per cent. corresponds to 4 molecules, a loss of 11.9 per cent. to 5 molecules.

Calcium Derivative $(C_6H_2Br(NO_2)_2O)_2Ca + 7-8aq.$ —The salt containing 7 molecules of water separates from a hot concentrated solution on cooling in brilliant, deep orange-coloured, rhombic plates; the filtrate from these crystals deposits the second salt in the form of short, yellow needles, difficultly soluble in cold water. If the first salt be allowed to remain in the solution, it is gradually converted into the second; indeed the tendency to undergo this change is so great, that it is extremely difficult to obtain the former in a state of purity. A sample rapidly dried between folds of bibulous paper lost 18.2 per cent. H_2O on drying at 180° ; a second similarly prepared, lost 18.4 per cent. The calculated loss corresponding to 7 molecules is 18.2 per cent.; to 8 molecules 20.3 per cent. A quantity of the yellow salt lost 20.3 per cent. of H_2O at 180° . The above-described behaviour is peculiarly characteristic, and may be employed with great advantage as a means of recognising the presence of the dinitrobromophenol in question.

The action of bromine on ordinary dinitrophenol has already been studied by Laurent (*Kekulé's Lehrbuch.*, iii, 56): he obtained a bromo-dinitrophenol melting at 110° . We have repeated his experiments, and can confirm his observations, with the one exception that we find the melting point to be 117° . The bromodinitrophenol thus prepared is identical in all particulars with the above described; the calcium salts of the two products behave in exactly the same manner.

Dinitrophenol was digested with an excess of bromine in a retort on

the water-bath so long as hydrobromic acid was evolved; the excess of bromine was then distilled off, and the product purified by recrystallisation of its potassium salt.

The purified salt gave the following numbers on analysis:—

·9552 grm. lost ·0532 grm. OH_2 at 140°
 ·3078 grm. thus dried gave ·0887 grm. K_2SO_4 .

| | Theory. | I. |
|---------------------------|---------|-------|
| H_2O | 5·6 | 5·5 |
| K..... | 12·95 | 12·93 |

The phenol obtained by decomposition of this salt with dilute nitric acid exhibited the constant melting point of 117° — $117\cdot5^\circ$.

·570 grm. gave ·4055 grm. AgBr .

| | Theory. | I. |
|---------|---------|-------|
| Br | 30·41 | 30·27 |

A barium salt prepared from it lost 10·18 per cent. of water at 180° . Of the two calcium salts obtained, a quantity of the yellow (second) salt lost 20·1 per cent. of water on drying; the orange salt on one occasion was very rapidly dried by pressing between folds of paper, and lost only 16·05 per cent. of water on heating; other specimens lost from 18 to 19 per cent. This would seem to render it probable that the orange salt, when it first separates from the solution, contains less than 7 molecules of water.

(c.) *D bromonitrophenol*, $\text{C}_6\text{H}_2\text{Br}_2\text{NO}_2\text{OH}$ (melting point $117\cdot5^\circ$).—This body was always obtained in relatively the same, though small proportion, whatever the conditions of temperature, and the strength of acid employed. It is identical with the product of the direct action of nitric acid on ordinary dibromophenol. We are therefore led to conclude, as in the case (this *Journal*, ix, 1120) of the corresponding dichloronitrophenol (melting point 125°) obtained by nitration of dichlorophenol-sulphonic acid, that it is formed from a small quantity of dibromophenolmetasulphonate. If this be so, it is evident that the phenol-sulphonic acid employed contained a certain quantity of phenolmeta-sulphonic acid, the which, notwithstanding the long continued heating, had escaped conversion into the isomeric para-acid.

The following analysis of the above nitro-product was made:—

·3935 grm. gave ·4948 grm. Ag Br .

| | Theory. | I. |
|---------|---------|-------|
| Br | 53·87 | 53·50 |

The potassium derivative crystallises in anhydrous crimson needles, which exhibit, more especially when seen floating in the solution, a magnificent metallic green lu tre.

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(d.) *α-Bromonitrophenolsulphonic Acid*, $C_6H_2BrNO_2OH(SO_3H)$.

The mono-potassium salt of this acid crystallises in flat, yellow, silky needles, very soluble in hot water, moderately soluble in cold. It is anhydrous.

·4396 grm. gave ·335 grm. $BaSO_4$ and ·278 grm. $AgBr$.

| | Theory. | I. |
|--------------|---------|-------|
| S | 10·73 | 10·46 |
| Br | 26·84 | 26·91 |

The dipotassium salt, which crystallises in orange plates, is extremely soluble even in cold water.

β-Bromonitrophenolsulphonic Acid, $C_6H_2BrNO_2OH(SO_3H)$.

On one occasion, on converting the total nitro-product obtained by the action of nitric acid at 0° on a quantity of 100 grms. of potassium dibromophenolsulphonate into potassium salts, a small residue (about 2 grms.) remained on the filter through which the solution was passed. This was first exhausted with alcohol, by which, however, but little was extracted, and then with boiling water, in which the greater part dissolved. The solution assumed a deep red colour on the addition of potassium carbonate, and carbonic anhydride was set free; on evaporating to a small bulk, and allowing to stand, a crystallisation of brilliant red needles was obtained. The latter dissolved in water gave, on the addition of acetic acid, a precipitate of short yellow needles, which are the monopotassium salt of an isomeric bromonitrophenolsulphonic acid.

Several suppositions may be made as to the origin of this body: either it is formed from the dibromophenolparasulphonate, from which the isomeric α -compound is undoubtedly derived, or from the isomeric dibromophenolmetasulphonate; or it owes its origin, and we are inclined to consider this the most probable, to the presence of a small quantity of a potassium monobromophenolsulphonate.

In his paper on the nitrochlorophenols, Petersen (*Ann. Chem. Pharm.*, clvii, 182) discusses the relations between the melting points of corresponding chlorinated and brominated nitrophenols, and comes to the conclusion that the melting points of the former are from 3° to 4° higher than those of the latter.

He compares Laurent's bromodinitrophenol (m. p. 110°) with a chlorodinitrophenol melting at 114° . Faust's experiments and our own prove, however, that it corresponds to the chlorodinitrophenol melting at 110° — 111° , and we have also shown in the above that 117° (approximately) is the true melting point.

Petersen also takes the melting point of dibromonitrophenol as at 141° , whereas we believe it to be much lower (132°).

The supposed relation, therefore, does not exist, as will be evident from the following comparison :—

| <i>Derivatives of Orthonitrophenol.</i> | | <i>Derivatives of Nitrophenol.</i> | |
|---|---------------|------------------------------------|---------------|
| Bromorthonitrophenol | 102° | Bromonitrophenol | 88° |
| Chlororthonitrophenol | 109° | Chloronitrophenol | 86·5° |
| | <u>— 7°</u> | | <u>+ 1·5°</u> |
| Dibromorthonitrophenol | 132° | Dibromonitrophenol | 117·5° |
| Dichlororthonitrophenol | 125° | Dichloronitrophenol | 121·5° |
| | <u>+ 7°</u> | | <u>— 4·0°</u> |
| Nitrobromorthonitrophenol | 117° | Nitrobromonitrophenol | 78° |
| Nitrochlororthonitrophenol | 110·5° | Nitrochloronitrophenol | 80·5° |
| | <u>+ 6·5°</u> | | <u>— 2·5°</u> |

There is an evident relation, however, between the melting points of corresponding chloro- and bromo- phenols *derived from the same parent compound*, which indeed appears extremely probable on a *priori* grounds. More than this cannot be said, since the above numbers are but approximate. We hope, by extending our experiments, to obtain further evidence as to the nature of the relation.
