VII.—*On the Formation of Substituted Nitrophenolsulphonic Acids.*

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ALL attempts to convert the chlorinated nitrophenols by double decomposition with ammonia, &c., into compounds of other series having proved unsuccessful, we were induced to commence the examination of corresponding iodo-compounds, on the assumption warranted by general experience, that they would prove more manageable bodies. Moreover, our knowledge of the iodonitrophenols is almost *nil*, so that considerable interest attaches to their examination on this account alone. A third and indeed chief motive which urged us to make the investigation was to compare the action of iodine with that of chlorine and bromine, and the iodophenol-derivatives generally with the better known chlorinated and brominated compounds.

It appears highly probable that, at least in some instances, iodine which has a so much lower reactive energy than either chlorine or bromine, will differ considerably in its action from either of the latter, indeed the experiments of Körner (*Zeitschr. f. Chem.* [2], iv, 322), and those of Hlasiwetz and Weselsky (*Deut. Chem. Ges. Ber.*, ii, 522) already furnish evidence of the anomalous behaviour of iodine; thus by its action on phenol in presence of iodic acid (in aqueous solution) according to the former observer, a mixture of ortho- and meta-iodophenols is formed, whereas Hlasiwetz and Weselsky state that in presence of mercuric oxide (and in alcoholic solution) the chief product is *para*iodophenol.

At the commencement of our experiments in this direction we were so fortunate as to make certain observations which, although they have for the moment somewhat diverted our attention from the main object in view, possess considerable interest as showing the influence of change of condition on the course of chemical action.

It has been shown by Schmidt and Glutz (*Deut. Chem. Ges. Ber.*, ii, 51) that when a current of chlorine is passed into an aqueous solution of sodium nitrophenolsulphonate dichloronitrophenol (melting point 121.5°) is produced.

Substituting bromine for chlorine we have obtained analogous results: a yellow precipitate is at once thrown down on the addition of bromine to an aqueous solution of potassium nitrophenolsulphonate, consisting of the corresponding dibromonitrophenol (melting point 117.5°), identical with the product of the action of nitric acid on ordinary dibromophenol.

·5400 grm. gave ·6849 grm. AgBr.

	Theory.	I.
Br	53.87	53.97

We expected, therefore, that iodine would yield the corresponding di-iodonitrophenol; but thinking that its insolubility in water would militate against the success of the experiment, an alcoholic solution of nitrophenolsulphonic acid* was employed. In order, however, to withdraw the hydriodic acid formed from the sphere of action, Hlasiwetz and Weselsky's method was adopted, and after each addition of iodine a small quantity of dry, finely powdered mercuric oxide was introduced.

The iodine disappeared slowly on agitation, and the solution became perceptibly warm, but after an amount slightly in excess of that required by the proportion, $I_2 : C_6H_3.NO_2.OH.SO_3H$, had been added, the colour communicated to the solution by the iodine ceased to disappear on shaking. On distilling off the alcohol in the water-bath, after removing the mercuric iodide and excess of mercuric oxide by filtration, a small quantity of iodine passed over with it. The addition of water to the residue caused the separation of traces of a brown crystalline substance, which proved to be a mixture of iodine and di-iodonitrophenol. On treating the filtrate with potassium carbonate, pale yellow crystalline scales, much resembling chloranil in appearance, separated out to such an extent that the solution became almost solid. These were collected on a vacuum filter, recrystallised from hot water, dried at 100° , and analysed.

* Prepared by acting upon volatile nitrophenol with SO_3HCl . This *Journal*, ix, 175.

·5427 grm. gave ·3319 grm. AgI, and ·3456 grm. BaSO₄.

·4665 grm. gave ·1047 grm. K₂SO₄.

·3369 grm. gave ·0762 grm. K₂SO₄.

	C ₆ H ₅ INO ₂ OHSO ₃ K.	I.	II.
I.	33·15	33·05	—
S	8·35	8·77	—
K	10·20	10·07	10·15

The action of iodine, therefore, on an alcoholic solution of nitrophenolsulphonic acid in presence of mercuric oxide gives rise to the formation of an iodonitrophenolsulphonic acid, according to the equation:—

The above potassium salt is readily soluble in boiling water, but slightly soluble in cold water; it crystallises in short fine needles, united in groups; the air-dried salt is anhydrous. It dissolves in a solution of potassium carbonate with effervescence, forming a deep red-yellow liquid, from which the dipotassium salt may be obtained on evaporation. This salt when finely divided has a bright red colour, but the larger crystals obtained on allowing a solution to evaporate spontaneously are of a very deep red colour, and consist apparently of rhombic prisms. These crystals are anhydrous.

·7825 grm. gave ·3283 grm. K₂SO₄:—

	Theory.	I.
K.	18·56	18·83

On the addition of barium chloride to a moderately dilute solution of the mono-potassium salt, barium iodonitrophenolsulphonate is precipitated in the form of pale-yellow, silky needles, containing four molecules of water of crystallisation.

·8428 grm. lost ·0576 grm. H₂O at 180°:—

	Theory.	I.
4H ₂ O.	7·3	6·83

On exposure to the air, this salt loses its lustre, evidently owing to loss of water of crystallisation.

The action of iodine on an aqueous solution of nitrophenolsulphonic acid also gives rise to the formation of mono-iodonitrophenolsulphonic acid, but owing to the insolubility of iodine in water, the reaction takes place with extreme slowness. As in the former experiment mere traces only of di-iodonitrophenol were produced, and there would seem to be little tendency to form this compound, even by the action of an excess of iodine either in alcoholic or in aqueous solution.

Before the action of iodine in aqueous solution had been examined, it was thought that perhaps the employment of alcohol as solvent had influenced the formation of the monoiodo-compound, and preliminary experiments as to the action of chlorine and bromine under like conditions were instituted in order to obtain evidence on this point.

The results show that, although in the case of iodine the solvent simply influences the rate of action by increasing the solubility of the iodine, this solvent does exercise an influence on the course of the action when chlorine or bromine are the agents.

By acting upon carefully cooled alcoholic solutions of nitrophenolsulphonic acid with bromine and chlorine respectively, we have succeeded in obtaining monobromo- and monochloronitrophenolsulphonic acids. The monopotassium salt of the former crystallises in pale-yellow needles; its di-potassium salt in bright-red needles closely resembling the corresponding salt of the γ -bromonitrophenolsulphonic acid, described in the previous communication.

The chloronitrophenolsulphonic acid is isomeric with the similar compound formed by nitration of dichlorophenolparasulphonic acid (this *Journal*, ix, 1118); its dipotassium salt forms small orange-yellow, sharply defined prismatic needles totally different from the corresponding salt of the latter acid.

At present we have not yet examined these bodies in detail, but propose to do so. Their formation shows clearly, however, that the formation of dichloro- or dibromo-nitrophenol from an aqueous solution of nitrophenolsulphonic acid by the action of chlorine or bromine, is preceded by that of monochloro- and monobromo-nitrophenolsulphonic acids.

It is well known that anthracene cannot be nitrated by the action of aqueous nitric acid, whereas by Bolley's method of nitration in alcoholic solution, it readily yields mono- and di-nitroanthracene. Similarly by acting upon an alcoholic solution of β -naphthol by nitric acid, Wallach and Wichelhaus (*Deut. Chem. Ges. Ber.*, iii, 846) were able to obtain dinitro- β -naphthol, all other methods having failed. Again, Griess has shown (*Ann. Chem. Pharm.*, cliv, 202) that an aqueous solution of ammonium trinitrophenol is easily reduced to diamidonitrophenol, whereas in alcoholic solution the reduction stops so soon as amidodinitrophenol is formed. All these are instances parallel with the above, and show clearly the influence which change of condition has on the course of chemical change.