

CLIII.—*The Catalytic Action of Iodine in Sulphonation.*
Part I.

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THE present investigation was undertaken with the view of ascertaining whether the addition of a trace of iodine to sulphuric acid (D 1·84) facilitates the sulphonation of aromatic compounds (compare Heinemann, Brit. Pat. 12260 of 1915). It has been found that ordinary sulphuric acid and a trace of iodine can advantageously be used in place of fuming sulphuric acid with or without the addition of phosphoric oxide, etc. The nature of the product is changed in certain cases, thus making easy the preparation of some of the acids difficult to obtain. The catalytic sulphonation is facilitated by the presence of an amino-, hydroxy-, or halogen group in the molecule, but proceeds with less ease in the case of carboxylic acids, and is inhibited in the case of nitro-compounds. This fact probably explains the non-formation of disulphonic acids in the product. It is significant that there is an optimum temperature for each reaction in which maximum transformation takes place. It has also been noticed that there is some liberation of iodine vapour, but no trace of sulphur dioxide or hydrogen iodide could be detected in the space above the reaction mixture.

The discrepancy between the actual yield and that theoretically possible was accounted for in nearly all cases by the unchanged original material.

EXPERIMENTAL.

In the experiments to be described below, the general method of work was to heat a mixture of a few grams of the substance and the calculated quantity, or an excess, of sulphuric acid (D 1·84), together with a trace of iodine, for a few hours at the temperature, determined by trial, at which the transformation was greatest. The product was poured into water, the free sulphuric acid removed with barium carbonate or hydroxide, and the acid liberated from the filtrate by exactly neutralising with sulphuric acid. The solution of the free acid was concentrated, whereupon it was obtained in a crystalline condition. In some cases the product was poured into a saturated solution of potassium chloride, when the potassium salt separated in fine crystals (*o*-nitrophenol, etc.). The acid or the potassium salt was converted by the usual method into the sulphonyl chloride,

from which the amide, mercaptan, etc., were prepared in order to characterise it. Some of the sulphonic acids described gave colour reactions with ferric chloride and characteristic salts with heavy metals. When the acid could not be satisfactorily identified, it was transformed through its amino- or nitro-groups, etc., into the corresponding hydroxy- or amido-compounds, etc., in order to establish its constitution. In some cases it was found convenient to extract the sulphonic acid from the sulphonated mass with alcohol (*o*-toluidine).

The results obtained from the fusion of the products with potassium hydroxide were not taken into account unless substantiated by further evidence.

Sulphonation of Benzoic Acid.

A mixture of 12 grams of benzoic acid, 9 c.c. of sulphuric acid, and a small crystal of iodine was heated at 175—180° for about six hours, at the end of which time no free benzoic acid separated on diluting a sample. The liquid, after cooling, was poured into water, when a clear solution was obtained. The solution was neutralised with barium carbonate, the precipitated barium sulphate filtered off, and the filtrate exactly neutralised with dilute sulphuric acid. After filtering, the liquid was concentrated to a syrup, and, on keeping in a desiccator, crystals were obtained, which were drained, washed with a small quantity of alcohol, and dried over sulphuric acid in a vacuum. The anhydrous crystals melted at 134—135° (uncorr.), and were very hygroscopic.

A test experiment was conducted side by side with the above in which no iodine was used; almost the whole of the benzoic acid was recovered unchanged.

The crystals in aqueous solution gave a reddish-brown coloration with ferric chloride, but no precipitate, and were identified as *o*-sulphobenzoic acid by the formation of salicylic acid when fused with potassium hydroxide at a moderately low temperature (Found: S=15.0. Calc. for acid + 1H₂O: S=14.57 per cent.).

In the above experiment, about a gram of benzoic acid sublimed away, and was thus not sulphonated.

The following table gives a résumé of the results obtained with other substances:

Substance.	Products by known methods.	By the present method.	Yield. Per cent.	Optimum temperature.	Time of reaction Hours.
Toluene	<i>o</i> - and <i>p</i> -acids	<i>p</i> -acid only	90-95	100°	1
Benzoic acid	<i>m</i> - and <i>p</i> -acids	<i>o</i> -acid	Above 95	175-190	6
Phthalic acid	—	no product	—	—	—
Catechol	3-acid	4-acid	75	50-55	1½
Quinol	mono- and di-sulphonic acids	mono-acid	73	70	4
<i>o</i> -Nitrophenol	<i>p</i> -acid	<i>p</i> -acid	70	120	5
<i>p</i> -Nitrophenol	<i>o</i> -acid	<i>o</i> -acid	50	100-105	5
Nitrobenzene	—	no product	—	—	—
<i>m</i> -Dinitrobenzene	—	no product	—	—	—
<i>o</i> -Nitrotoluene	<i>p</i> -acid	<i>p</i> -acid	70	150	5
<i>p</i> -Nitrotoluene	<i>o</i> -acid	<i>o</i> -acid	5	140	4
<i>o</i> -Nitroaniline	<i>p</i> -acid	<i>p</i> -acid	60	125	4½
<i>p</i> -Nitroaniline	<i>o</i> -acid	<i>o</i> -acid	50	140	3
3-Nitroaniline	6-acid	6-acid	10	150	4½
<i>o</i> -Toluidine	5-acid	5-acid	60-65	150	3
<i>p</i> -Toluidine	—	no product	—	—	—
Chlorobenzene	<i>o</i> - and <i>p</i> -acid	<i>p</i> -acid	85	110	1½
Bromobenzene	<i>o</i> - and <i>p</i> -acid	<i>p</i> -acid	85	100	2

Summary and Conclusions.

- (1) Iodine acts as a positive catalyst in sulphonation.
- (2) Catalysis takes place smoothly when hydroxy-, amino-, chloro-, bromo-, or carboxy-groups are contained in the molecule, but with difficulty, or not at all, with nitro- or sulphonic substituents.
- (3) There is an optimum temperature for each substance when the maximum transformation takes place.

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