

CCCCXLIV.—*A Compound of Nitrobenzene and Sulphuric Acid.*

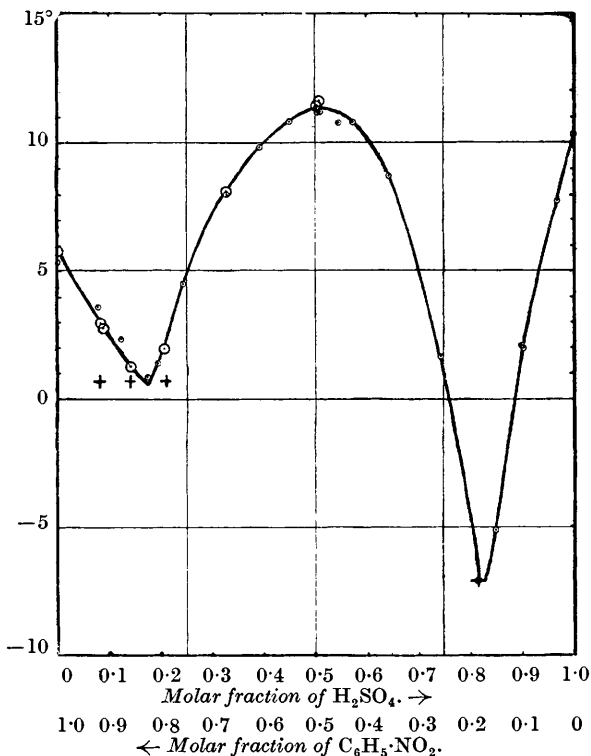
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DURING some work upon nitration by Mr. J. A. Hetherington and the writer, it was found that, when nitrobenzene is shaken with aqueous sulphuric acid of the composition  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , it extracts practically anhydrous sulphuric acid from the acid layer, leaving this relatively more aqueous than before. In view of the considerable stability of sulphuric acid monohydrate and its recognition by several kinds of test even above its melting point ( $8.6^\circ$ ), the inference was drawn that nitrobenzene must form a compound with

sulphuric acid. The experiments now recorded were therefore carried out, and they establish the fact that there is a crystalline compound between these substances; it has the composition, ascertained by synthesis, by analysis, and by the melting-point method,  $C_6H_5 \cdot NO_2, H_2SO_4$ . The same compound was obtained in 1923 by Cherbuliez (*Helv. Chim. Acta*, 6, 281), by cooling an

FIG. 1.

*Freezing Points of Mixtures of Nitrobenzene and Sulphuric Acid.*



- = Series I.; nitrobenzene of m. p. 5.35°, sulphuric acid 99.65%.  
 ⊙ = Series II.; purest nitrobenzene, m. p. 5.8°, sulphuric acid 99.65%.  
 + = Series I., II., eutectic arrest-temperatures.

equimolecular mixture of the components. The melting point is 11.6° (Cherbuliez found 11°), and this is higher than that of either of its components (5.8° and 10.5°). The diagram shows the freezing-point relationships in the system; it will be noted that no more than one compound between sulphuric acid and nitrobenzene appears to exist.

The compound is formed as colourless needles when suitable

mixtures of nearly absolute sulphuric acid and nitrobenzene are cooled and then locally chilled by applying a small pad of carbon dioxide snow to the outside of the vessel at the level of the meniscus. At 18° it is an oily liquid of  $d$  1.42; its density when solid is near 1.5. On standing for a day or two at room temperature, no more than traces of sulphonation take place, as the analyses prove; but the freezing point falls by 0.1—0.2°, and the liquor darkens. The melted compound is surprisingly sluggish towards water, and does not liberate much heat on being decomposed by it—a sign of the stability of the compound.

With excess of nitrobenzene, a eutectic is formed at 0.65°; this, like all the solid phases of the system, is very liable to undercooling. From the initial slope of the curve for the freezing point of nitrobenzene, it would appear that the complex has undergone polymerisation to double molecules. In excess of sulphuric acid, however, it is not appreciably polymerised; and in this solvent the compound forms solutions which conduct electricity better than sulphuric acid itself.

Since the compound is an electrolyte, its structure may most probably be described by  $[\text{C}_6\text{H}_5\cdot\text{NO}_2\cdot\text{H}]^+[\text{HSO}_4]^-$ . Cherbuliez also noted that the conductance of sulphuric acid is increased by dissolving in it nitrobenzene (but not dinitrobenzene), or some other mononitro-compounds; and he formulated the complex as an acid sulphate of nitrobenzene. In this salt-like compound, the hydrogen ion or proton can be regarded as being co-ordinated with one of the oxygen atoms of the nitro-group; and if Sugden is correct in inferring from the parachor of nitrobenzene that one of these oxygen atoms is attached to the nitrogen by a semipolar or co-ordinate link, this would be the atom to be coupled with the hydrogen ion. In any case, the attachment of a positive hydrogen ion to the nitro-group must modify the potential gradients along the atoms of the phenyl nucleus; more precisely, it should promote meta-substitution, in the same way as happens with an arylammonium ion. The stability of the compound suggests, indeed, that in the dinitration of nitrobenzene it may well be the positive nitrobenzene-hydrogen ion, rather than the neutral nitrobenzene molecule, which is the main organic reagent and thus the source of the preponderating meta-derivative.

#### EXPERIMENTAL.

*Materials.*—For the main series of freezing points, nitrobenzene of no more than ordinary purity was used, prepared from commercial nitrobenzene by crude freezing and draining several times; it melted at 5.35°, and was not free from traces of dissolved water.

(The addition of a few drops of sulphuric acid is a very delicate test for water in nitrobenzene, a local turbidity being observed.)

For measuring the depression of freezing point of nitrobenzene by small proportions of sulphuric acid, pure and dry nitrobenzene was required; this preparation was made the subject of a separate study, the results of which are described elsewhere with reference to the m. p.'s of nitrobenzene and benzene (*Nature*, 1931, **128**, 726), and need only be indicated here. As commercial nitrobenzene derives impurities from crude benzene as well as from the treatment which it receives in the technical nitration, it was not used as the source; instead, very pure benzene was first isolated, by a special method of freezing, from the only one of several tested varieties of "pure" benzene which proved really satisfactory. The fraction so prepared melted at  $5.58^{\circ}$ . This was then converted into mononitrobenzene by the use of an acid which in other work had been shown to produce no dinitrobenzene, having the molecular composition  $\text{H}_2\text{SO}_4$ , 0.33;  $\text{HNO}_3$ , 0.18;  $\text{H}_2\text{O}$ , 0.49; the product, quantitative in yield, after being distilled from phosphoric oxide at  $60^{\circ}/1.2$  mm., was put through the same process of freezing as the original benzene, and some was again distilled. The purest fractions froze at  $5.83^{\circ}$ ,  $5.84^{\circ}$ ; those used in most of the present experiments froze at  $5.77^{\circ}$ . These temperatures are true to the nearest  $0.05^{\circ}$ ; their value as the true m. p.'s of the pure substances concerned is discussed in the note already referred to.

Sulphuric acid was made by thrice freezing and partially melting a fresh supply of the purest commercial "100 per cent." acid. The latter contained quite negligible traces of sulphur dioxide, was colourless, and was almost free from turbidity. The stock prepared from it had f. p.  $10.35^{\circ}$ ,  $d_4^{19.7^{\circ}}$  1.832, and contained, according to volumetric determinations of acidity, 99.65% of  $\text{H}_2\text{SO}_4$ .

*Freezing Points.*—For the first series, the mixtures were made up by weight or by volume from protected burettes, and their f. p.'s were observed in boiling tubes to which the air had only intermittent access. The second series, using pure nitrobenzene, was made with mixtures synthesised by weight, with rigorous exclusion of moisture. The apparatus made for this purpose enclosed the whole thermometer, no corks or bungs being used. Side tubes with ground glass connexions and taps, and a sealed-in tube dipping to the foot of the vessel, allowed the whole to be filled with dry nitrogen, and enabled the components to be admitted from their containers with no exposure to air; it was also possible to stir the contents with dry nitrogen and, when desired, to expel liquid samples for analysis. The whole apparatus was weighable

to a few milligrams. Nitrogen was preferred to other gases for the sake of inertness, and also because it did not alter significantly the weight of the apparatus when filled with it instead of with air. The thermometer was graduated in  $0.1^\circ$  and was read to  $0.01^\circ$  with a lens; it was very carefully checked between  $0^\circ$  and  $15^\circ$  with a similar thermometer which was certified to the nearest  $0.05^\circ$  by the National Physical Laboratory as soon as the work was over. Series II had to be curtailed owing to the loss of some of the nitrobenzene.

So slow are the rates of crystallisation and melting in this system, and so poor is the thermal conductance of the mixtures, that very careful control of the bath temperatures is needed in order to avoid fictitious results due to overheating and to undercooling. In the first series, the temperatures usually taken were the highest at which crystals appeared to remain in equilibrium with liquid, but this was not in all cases possible to secure definitely. In the second series, therefore, the temperatures taken were the highest to which the mixtures rose spontaneously after being undercooled, the temperature of the bath being kept about  $0.1^\circ$  below that of the mixture, and the proportion of crystallised substance being kept to a minimum. The last-named condition depends upon the correct use of the method of external inoculation mentioned on p. 3202. With these precautions, the "arrest maxima" are believed to be close enough to the true liquidus points to allow the solute molecular weights at the two ends of the curve to be calculated within about 10% of the truth. The data for the few points concerned with this may be tabulated. The molecular depression constants adopted were 69 for nitrobenzene and 70 for sulphuric acid, and in the last line, which gives the value of  $x$  in  $(C_6H_5 \cdot NO_2, H_2SO_4)_x$ , allowance has been made for the amount of solvent used in forming the complex with the other component.

$H_2SO_4$ , mol. fraction .....	0	0.0828	0.0853	1.000	0.969
F. p. ....	$5.77^\circ$	$2.96^\circ$	$2.77^\circ$	$10.35^\circ$	$7.75^\circ$
$x$ .....	—	1.99	1.92	—	1.1

*Analyses.*—In the second series, a mixture, made up by weight to be equimolecular, was frozen in the apparatus described, the f. p. being  $11.42^\circ$ . About a quarter of it was allowed to melt, with gas-stirring, and this liquor was expelled. The f. p. of the crystal residue was measured and was again  $11.42^\circ$ . Both fractions, having been weighed, were analysed; for this purpose the whole of each was diluted and the nitrobenzene was separated; the nitrobenzene which remained emulsified was extracted with acid-free chloroform, and the acidity of the aqueous solution was determined volumetrically with sodium hydroxide and methyl-orange,

the ultimate standard being Iceland spar. The nitrobenzene content followed, by difference. The results show, incidentally, that less than  $\frac{1}{2}\%$  of the total acid initially weighed out had disappeared. This proves that practically no sulphonation had occurred, the compound being thus a purely additive one. This fact was further confirmed by weighing the nitrobenzene which separated on dilution of the crystal fraction; its weight was within  $1\%$  of the ideal content of the additive compound. The titrations and weighings gave :

	By synthesis. Initial mixture.	By analysis.		Crystal + liquor.
		Crystal fraction.	Liquid fraction.	
H <sub>2</sub> SO <sub>4</sub> actual, g. ....	{ 10.358	7.763	2.527	10.290
H <sub>2</sub> O (by diff.), g. ....	{ 0.038			
C <sub>6</sub> H <sub>5</sub> ·NO <sub>2</sub> , g. ....	13.014 }	9.921*	3.194	13.115
Totals .....	23.410	17.684	5.721	23.405

\* Nitrobenzene actually recovered, 9.82. Correspondingly, the weights of the substances which contain 1 g.-mol. of sulphuric acid are :

Stock sulphuric acid, 98.4 (calc. for H<sub>2</sub>SO<sub>4</sub> : 98.1).

Crystal fraction, 223.4.

Liquid fraction, 222.0 (calc. for C<sub>6</sub>H<sub>5</sub>·NO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> : 221.2).

*Conductances.*—These measurements were intended as comparative only. They were made at 18° with the materials used in the first series of melting points, in an air-tight cell with platinised electrodes; the current used was direct, of six different voltages from 4 to 130 volts for each measurement, and the current passed ranged from a fraction of a milliamp. to some 6 milliamps. No polarisation was observed during the 1—2 secs. in which the current passed; and for any one mixture the resistance found for one voltage agreed within 2% with that found at the others. The cell-constant being taken as approximately given by Kohlrausch's value of 0.0148 ohm<sup>-1</sup> for 99.6% H<sub>2</sub>SO<sub>4</sub>, 0.4% H<sub>2</sub>O, the conductances found were :

Nitrobenzene, mols. % ...	0	2.6	5.7	10.15
Conductance, ohm <sup>-1</sup> .....	(0.0148)	0.0218	0.0244	0.0238
Nitrobenzene, mols. % ...	12.0	32.1	50.0	67.6
Conductance, ohm <sup>-1</sup> .....	0.0230	0.0104	0.0045	0.0023

The rise in conductance was not due to the small traces of water introduced with the nitrobenzene, since the conductance of an acid made to have the same water content as the mixture of maximal conductance gave a figure of only 0.0166 ohm<sup>-1</sup>.

#### Summary.

A crystalline compound, C<sub>6</sub>H<sub>5</sub>·NO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, f. p. 11.6°, is formed from sulphuric acid of f. p. 10.35° and nitrobenzene of f. p. 5.8°. In solution in sulphuric acid it is an electrolyte. The same facts

(with f. p. 11°) were found and discussed in 1923 by Cherbuliez. The compound is considered to be  $[\text{C}_6\text{H}_5\cdot\text{NO}_2\cdot\text{H}]^+[\text{HSO}_4]^-$ , in agreement with Cherbuliez. In solution in nitrobenzene it is doubly polymerised; but in its conducting solution in sulphuric acid, not appreciably so. The probable influence of the combination on aromatic substitution is referred to. New values for the freezing points of nitrobenzene and of benzene are given.

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