342. *Compounds of* p-*Nitrodiphenyl Sulphide and of* p-*Nitrodiphenyl Ether with Sulphuric Acid. An Example of Thioquinonoid Formation.*

By Herbert H. Hodgson and Reggie Smith.

Cryoscopic investigation has revealed that *p*-nitrodiphenyl sulphide in concentrated sulphuric acid forms two thionium salts of quinonoid character. In comparison therewith *p*-nitrodiphenyl ether affords a single compound. The compounds, however, were not isolated or analysed. In solution in excess of their aromatic constituents some polymerisation of the compounds to double molecules appears to occur. In excess of sulphuric acid, however, association does not take place.

The pronounced red colour produced by nitro-aryl sulphides with concentrated sulphuric acid has long been known, and the present cryoscopic investigation was undertaken to ascertain whether these colours are due to compound formation with consequent rearrangement to quinonoid structures. The compound selected was *p*-nitrodiphenyl sulphide, and for purposes of comparison the work was extended to *p*-nitrodiphenyl ether.

From the freezing-point diagram (Fig. 1) it appears that this sulphide forms two compounds, $(NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_5)_2,H_2SO_4$ (f. p. 51·7° ± 0·1°) and $NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_5,H_2SO_4$ (f. p. 50·3° ± 0·1°), whereas the ether affords only one compound, $NO_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_5,H_2SO_4$ (f. p. 51·8° ± 0·1°), thereby resembling nitrobenzene (Masson, J., 1931, 3200). Unlike the last compound, however, the sulphide and the ether give salts having freezing points lower than those of the aromatic constituents.

FIG. 1.

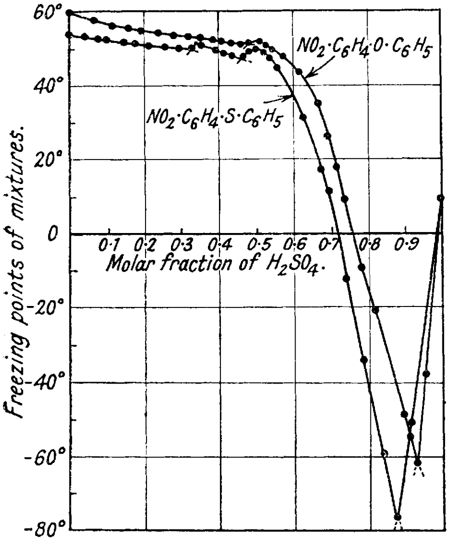
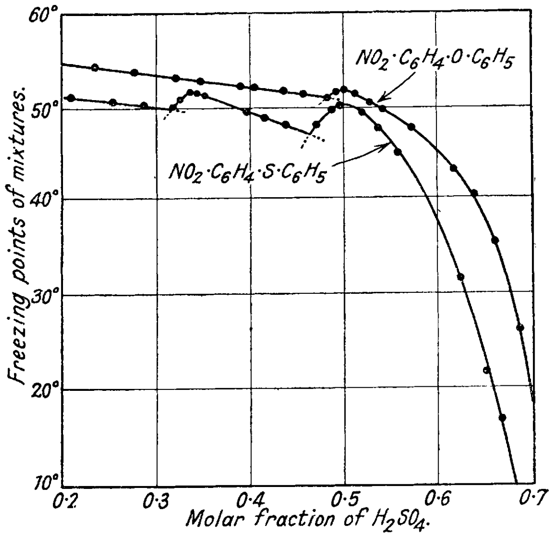
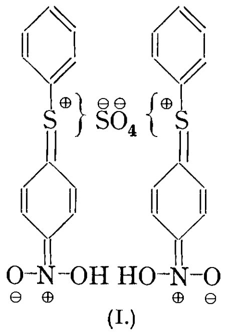


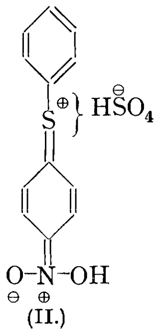
FIG. 2.



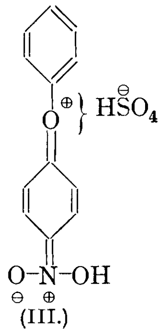
To account for the intense colour changes produced, and also because the compounds are electrolytes, the following structural formulæ are proposed, in which the sulphur and the oxygen function in their basic sulphonium (thionium) and oxonium states, respectively. The fact that *p*-nitrodiphenyl sulphide forms both a normal (I) and an acid (II) salt, would appear to indicate that sulphur in the thioquinonoid–thionium condition is more strongly basic than its quinonoid–oxonium analogue (III).



(I.)



(II.)



(III.)

The compounds themselves were not isolated, but when the various mixtures containing them were diluted with water, the aromatic generators were precipitated with unchanged m. p.

In order to bring about dissolution, it was necessary in some cases, especially where the sulphide and the ether were in excess, to heat the mixture cautiously. The deleterious effect of this heating was investigated for particular mixtures by making a succession of freezing-point determinations at intervals of 5 minutes : generally, after three readings, the freezing point gradually declined and finally became steady at about 5° below the first value ; it then remained constant for several days. When these mixtures were heated on the waterbath during 15 minutes, the colour gradually changed from the original deep red to a very dark green (almost black), which may be due to sulphonation or carbonisation or both. To avoid any such complications, fresh mixtures were made up for each determination, and their freezing points observed as soon as practicable after complete dissolution had been effected. The melting appeared to be accompanied by much reversible dissociation.

With excess of *p*-nitrodiphenyl sulphide and also of the ether, eutectics were formed at 50·2° and 48·2° for the former and 51·0° for the latter, *i.e.*, only 1·5°, 2·1°, and 0·8° below the freezing points of the compounds, but with excess sulphuric acid they were very pronounced at — 78° and — 62° respectively.

The molecular-depression constants were found to be *ca.* 107° for *p*-nitrodiphenyl sulphide, and *ca.* 130° for *p*-nitrodiphenyl ether, *p*-dichlorobenzene being used as solute. Application of these data to the earlier depression readings, where the curves are linear, shows that the complexes $[(NO_2\cdot C_6H_4\cdot S\cdot C_6H_5)_2,H_2SO_4]_n$ and $[NO_2\cdot C_6H_4\cdot O\cdot C_6H_5,H_2SO_4]_n$ have $n = ca.$ 2·0 in each case, indicating some polymerisation to double molecules. In excess of sulphuric acid, however, the compounds are not polymerised.

EXPERIMENTAL.

Materials.—*p*-Nitrodiphenyl sulphide was prepared by acting on sodium thiophenoxide with excess of *p*-chloronitrobenzene, steam-distilling the product to remove excess of the latter, and finally crystallising it thrice from glacial acetic acid. The pale yellow crystals obtained had m. p. 54·5° (Kehrmann and Bauer, *Ber.*, 1896, **29**, 2364, give m. p. 55·0°; Bourgeois and Huber, *Rec. trav. chim.*, 1912, **31**, 141, give m. p. 54·4°) (Found: N, 6·1; S, 13·9. Calc.: N, 6·0; S, 13·8%).

p-Nitrodiphenyl ether was prepared by heating a mixture of *p*-chloronitrobenzene (1 part), potassium phenoxide (2 parts), and phenol (2 parts) at 150° for 5 hours under reflux. The product was purified as for the sulphide and obtained in very pale yellow crystals, m. p. 60·0° (Haeussermann and Teichmann, *Ber.*, 1896, **29**, 1446, give m. p. 61·0°) (Found: N, 6·6. Calc.: N, 6·5%).

Both products were kept over sulphuric acid in a vacuum desiccator for the stock used for the mixtures.

The sulphuric acid was made by adding the calculated amount of 26% oleum to the ordinary pure concentrated acid, stirring the externally ice-cooled mixture, removing the crystals by filtration through an externally cooled Buchner funnel, remelting the crystals, and repeating the whole process; f. p. 9·6°, *d* 1·8435; the concentration (estimated gravimetrically) was 99·56% of H_2SO_4.

Freezing Points.—The mixtures were made up by weight, with air access only at the beginning of each experiment, and the stirring was performed by a spiral of platinum wire, worked by an electromagnetic device. This method proved to be much superior to that of agitation by a current of air, dried by passage through acid from the stock used for the mixtures, for the efficiency declined with increase of viscosity. Temperatures over the range 10·0—60·0° were measured by an ordinary standardised thermometer to an accuracy of ± 0·05°, and from 10·0° to — 80·0° by a standardised pentane thermometer to an accuracy of ± 0·1°; and were checked by means of measurements with a copper–constantan thermocouple made immediately after the thermometer reading. Solid carbon dioxide (" drikold ") was used to obtain low temperatures. Every pre-

Cryoscopic Data.

(i) $NO_2\cdot C_6H_4\cdot S\cdot C_6H_5$.

N.	F. p.	*N.*	F. p.	*N.*	F. p.
0·000	54·5°	0·335	51·7°	0·555	45·2°
0·034	53·8	0·339	51·6	0·561	43·0
0·074	53·0	0·349	51·3	0·621	31·7
0·091	52·5	0·394	49·6	0·667	17·0
0·144	51·7	0·410	49·0	0·696	11·9
0·175	51·3	0·432	48·7	0·741	−12·6
0·208	51·1	0·469	48·3	0·784	−34·0
0·253	50·7	0·489	49·8	0·846	−59·0
0·287	50·2	0·495	50·2	0·870	−76·4
0·316	50·3	0·518	49·6	0·919	−50·8
0·323	50·7	0·532	47·9	1·000	9·6

(ii) $NO_2\cdot C_6H_4\cdot O\cdot C_6H_5$.

N.	F. p.	*N.*	F. p.	*N.*	F. p.
0·000	60·0°	0·433	51·8°	0·659	35·5°
0·061	58·0	0·454	51·3	0·689	26·5
0·110	56·2	0·478	51·0	0·710	18·5
0·151	55·6	0·490	51·6	0·731	9·2
0·188	55·0	0·499	51·8	0·775	− 9·5
0·233	54·5	0·510	51·5	0·812	−20·6
0·278	53·8	0·512	51·2	0·890	−48·6
0·319	53·1	0·524	50·5	0·905	−54·0
0·344	52·8	0·538	49·9	0·925	−61·8
0·386	52·3	0·570	48·0	0·949	−38·0
0·401	52·2	0·615	43·6	0·982	− 4·6
0·431	51·8	0·635	40·6	1·000	9·6

caution was taken to prevent access of moisture to the apparatus, which was also shielded from irregular air currents.

The " freezing point " adopted in these experiments was the highest temperature which the mixture attained after slight supercooling. Several determinations were made, from which it was established that the freezing point could be reproduced with an accuracy of ± 0·1°.

The data are shown in the foregoing table, in which N represents the molar fraction of sulphuric acid, and the freezing points are corrected values. The diagram (Fig. 2) illustrates the nature of the curves in the region of the compound formation, the actual points being denoted by dots.

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