**748.** *Solutions in Sulphuric Acid. Part XX.* Cryoscopic Measurements on Some Aromatic Sulphides, Sulphoxides, and Sulphones.*

By R. J. GILLESPIE and R. C. PASSERINI.

Cryoscopic measurements have been made on solutions of a number of aromatic sulphides, sulphoxides, and sulphones in sulphuric acid. The results show that all the compounds studied behave as bases in sulphuric acid. The sulphides and sulphoxides are strong bases, but the sulphones are rather weak bases and are only partially ionised. Diphenyl sulphone and various substituted diphenyl sulphones are stable in sulphuric acid, but diphenyl sulphide and diphenyl sulphoxide undergo sulphonation and oxidation. Both the sulphides and sulphoxides are deactivated towards sulphonation and oxidation by the introduction of NO_2 and NH_3^+ substituents. The effect of nitro-substituents on the basicities of the sulphide and sulphone group is discussed. Some of our results and conclusions differ from those obtained by Szmant and Brost.[1]

IT was first shown by Gillespie[2] that diphenyl sulphone behaves as a weak base in sulphuric acid. A wider investigation of the behaviour of a variety of aromatic sulphides, sulphoxides, and sulphones when dissolved in 100% sulphuric acid has since been carried out by Szmant and Brost, and Szmant and Lapinski,[1] who came to some unexpected conclusions; *e.g.*, they claimed that their results showed that diphenyl sulphoxide ionises according to the equation

$$Ph_2SO + 3H_2SO_4 = Ph_2S^{++} + H_3O^+ + 3HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
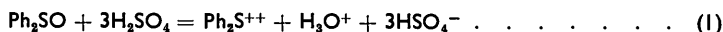
forming the diphenylsulphidonium ion Ph_2S^{++}. They also reached the surprising conclusion that the introduction of p-nitro-groups into diphenyl sulphone increases the basicity of the sulphone group.

It seemed desirable, therefore, to obtain some more information on the behaviour of this group of compounds. We have accordingly made a careful cryoscopic investigation of a number of aromatic sulphides, sulphoxides, and sulphones, some of which had been previously studied by Szmant and Brost. As some of the van't Hoff i-factors on which their conclusions were based appeared to be considerably in error, it was necessary to repeat their work. They did not, as is necessary for basic solutes, use as a solvent sulphuric acid in which the self-ionisation had been adequately repressed by the addition, for example, of a sufficient quantity of water; nor did they alternatively make any allowance in their calculations for the incompleteness in the repression of the self-ionisation equilibria. That is why their i-factors must be in error, and since, in general, the total freezing-point depressions from which they were calculated were rather small (0·2—0·5°) the errors may be considerable, probably as much as 100% in some cases.

EXPERIMENTAL

Apparatus and Procedure.—The apparatus and general procedure for making the cryoscopic measurements have already been described.[3] When the change in the freezing point over a period of time was measured, the cryoscope was maintained at 20° ± 1° between measurements.

Materials.—The method of preparation of the sulphuric acid solvent has been described.[4] The organic solutes were prepared as described below. They were all purified by crystallisation to constant m. p., followed by at least five further crystallisations.

4 : 4'-Dinitrodiphenyl sulphide was prepared by refluxing an ethanol solution of 1-chloro-4-nitrobenzene with a freshly prepared concentrated aqueous solution of sodium sulphide;[5] recrystallised from acetic acid, it had m. p. 158°.

4-Aminodiphenyl sulphide was prepared by reducing 4-nitrodiphenyl sulphide with tin and hydrochloric acid.[6] It was recrystallised from methanol and had m. p. 96—97°.

* Part XIX, *J.*, 1956, 1925.

[1] Szmant and Brost, *J. Amer. Chem. Soc.*, 1951, **73**, 4175; Szmant and Lapinski, *ibid.*, 1952, **74**, 4395.
[2] Gillespie, *J.*, 1950, 2542.
[3] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473; Gillespie and Leisten, *J.*, 1954, 1.
[4] Gillespie and Oubridge, *J.*, 1956, 80.
[5] Nietzki and Bothof, *Ber.*, 1894, **27**, 3261.
[6] Bourgeois and Huber, *Rec. Trav. chim.*, 1912, **31**, 30.

Diphenyl sulphoxide, prepared by oxidation of the sulphide with an equimolecular amount of a 30% solution of hydrogen peroxide in glacial acetic acid [7] and recrystallised from ligroin, had m. p. 70·7°.

4-Nitro- and 4 : 4'-dinitro-diphenyl sulphoxide were prepared in the same manner as diphenyl sulphoxide from the corresponding sulphide, and after recrystallisation from ethanol had m. p.s [8] 108—109° and 178°, respectively. The corresponding sulphones were prepared by oxidation with an excess of 30% hydrogen peroxide in glacial acetic acid at 100°.[9] They were recrystallised from acetic acid and had m. p.s [8] 141° and 251°, respectively.

TABLE 1.

m_2	F. p. (obs.)	F. p. (corr.)	θ	ν'	m_2	F. p. (obs.)	F. p. (corr.)	θ	ν'
4-Nitrodiphenyl sulphoxide					4 : 4'-Dinitrodiphenyl sulphoxide				
0·00000	10·359°	10·515°	—	—	0·00000	10·365°	10·515°	—	—
0·01185	10·262	10·365	0·150°	2·07	0·02245	10·155	10·224	0·291°	2·12
0·02146	10·165	10·242	0·273	2·08	0·05061	9·837	9·874	0·641	2·07
0·03413	10·026	10·082	0·433	2·07	0·08523	9·418	9·441	1·074	2·06
0·04823	9·865	9·909	0·606	2·05	0·1256	8·904	8·919	1·596	2·08
4-Nitrodiphenyl sulphone					4 : 4'-Dinitrodiphenyl sulphone				
0·0000	10·365	10·515	—	—	0·00000	10·365	10·515	—	—
0·0430	10·089	10·163	0·352	1·34	0·01896	10·238	10·370	0·145	1·25
0·0792	9·817	9·863	0·652	1·34	0·03143	10·155	10·275	0·240	1·25
0·1100	9·569	9·604	0·911	1·36	0·04125	10·074	10·184	0·331	1·31
0·1280	9·419	9·450	1·065	1·36	0·04838	10·031	10·136	0·379	1·28
0·1453	9·296	9·324	1·191	1·34	0·05051	9·957	10·054	0·461	1·29
					0·06537	9·908	10·001	0·514	1·28

TABLE 2.

Time (hr.)	m_2	F. p. (obs.)	F. p. (corr.)	θ	ν'	Time (hr.)	m_2	F. p. (obs.)	F. p. (corr.)	θ	ν'
Diphenyl sulphoxide (Expt. A)						Diphenyl sulphoxide (Expt. B)					
—	0·00000	10·365°	10·580°	—	—	—	0·0000	10·365°	10·580°	—	—
0·25	0·02935	9·992	10·035	0·545°	3·03	0·22	0·1007	9·110	9·123	1·457°	2·35
0·48	0·02935	9·961	10·004	0·576	3·17	0·52	0·1007	8·990	9·003	1·577	2·54
1·42	0·02935	9·939	9·982	0·598	3·32	1·13	0·1007	8·940	8·953	1·627	2·62
3·00	0·02935	9·935	9·978	0·602	3·35	2·18	0·1007	8·855	8·868	1·712	2·76
4·34	0·02935	9·931	9·974	0·606	3·37	3·32	0·1007	8·798	8·811	1·769	2·85
23·2	0·02935	9·925	9·968	0·612	3·40	19·1	0·1007	8·665	8·678	1·902	3·07
47·2	0·02935	9·921	9·964	0·616	3·42	23·3	0·1007	8·655	8·668	1·912	3·08
4 : 4'-Dinitrodiphenyl sulphide											
—	0·0000	10·359	10·515	—	—	2	0·1011	9·256	9·281	1·234	1·99
0	0·0486	9·902	9·946	0·569	1·91	3	0·1251	8·997	9·017	1·498	2·00
1	0·0772	9·593	9·627	0·888	1·88	24	0·1251	8·837	8·858	1·657	2·21
4-Aminodiphenyl sulphide (Expt. A)						4-Aminodiphenyl sulphide (Expt. B)					
—	0·00000	10·362	10·515	—	—	—	0·00000	10·365	10·515	—	—
0·26	0·02496	9·845	9·885	0·630	4·12	0·28	0·03436	9·573	9·601	0·914	4·34
0·52	0·02496	9·844	9·884	0·631	4·13	2·27	0·03436	9·562	9·590	0·925	4·40
1·05	0·02496	9·840	9·880	0·635	4·16	20·1	0·03436	9·524	9·552	0·963	4·58
3·8	0·02496	9·812	9·852	0·663	4·34	48·7	0·03436	9·422	9·450	1·065	5·06
23·5	0·02496	9·786	9·826	0·689	4·51	120	0·03436	9·294	9·322	1·193	5·67
54·5	0·02496	9·699	9·739	0·776	5·08	288	0·03436	9·259	9·287	1·228	5·84
200	0·02496	9·652	9·692	0·823	5·39						

Results.—Table 1 gives the results for those substances that gave stable solutions, as indicated by their time-independent values of ν', and that could be recovered on dilution of their solutions with water. Table 2 gives the results for those substances that reacted with the solvent. Their ν' values were time-dependent and they could not be recovered on dilution of their solutions with water. Both Tables give the observed freezing points of the solutions and the freezing points corrected for incomplete repression of the self-ionisation equilibria.[3, 4, 10]

The freezing-point depression θ is related to the molality of the solute m_2 by the equation

$$\theta/m_2 = 6{\cdot}12\,\nu'(1 - 0{\cdot}00195\theta)[1 + (2s_2 - \nu_2)m_2/2m_1]$$

[7] Hinsberg, *Ber.*, 1910, **43**, 289.
[8] Szmant and McIntosh, *J. Amer. Chem. Soc.*, 1951, **73**, 4356.
[9] Gilman and Broadbent, *ibid.*, 1947, **69**, 2056.
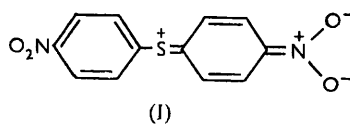[10] Flowers, Gillespie, and Oubridge, *J.*, 1956, 1925.

which is equation (2) of Part XIX,[10] where s_2 is the number of moles of the solvent reacting with one mole of the solute, and $v' = v_2 g$ where v_2 is the number of moles of solute particles formed from one mole of the solute and g is the osmotic coefficient of the solvent. As g is approximately unity,[4, 10] v' is an approximation to v_2. The last column in both Tables gives the values of v' calculated by means of the above equation. Szmant and Brost[1] present their results in terms of the van't Hoff i factor which is also an approximation to v_2.

DISCUSSION

Sulphides.—Szmant and Brost[1] found that diphenyl sulphide, dibenzyl sulphide, and 4 : 4'-dinitrodibenzyl sulphide all gave unstable solutions and high time-dependent i-values. They also found that the solutions evolved sulphur dioxide and that the original substance could not be recovered on dilution of the solution with water. On the other hand, they found that 4 : 4'-dinitrodiphenyl sulphide apparently gave a stable solution, could be recovered on dilution, and had an i-factor of 2·3 (after 11—15 hr.). They took these results to indicate a simple basic ionisation :

$$(NO_2 \cdot C_6H_4)_2S + H_2SO_4 = (NO_2 \cdot C_6H_4)_2SH^+ + HSO_4^- \quad \ldots \ldots (2)$$
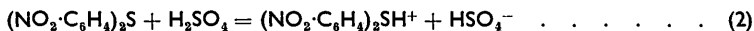
We have re-investigated the behaviour of 4 : 4'-dinitrodiphenyl sulphide and as may be seen from Table 2 we obtained an initial v' value of approximately 1·9 which increased in 24 hr. to approximately 2·2. Thus it seems likely that a simple 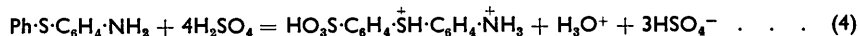basic ionisation does occur although, as one might expect the nitro-groups to be ionised to a small extent[2] also, the protonation of the sulphur atom may be incomplete. The basicity of the sulphur may be appreciably reduced by the contribution of resonance structures such as (I). The slow increase of v' with time indicates the occurrence of some additional slow reactions such as sulphonation and oxidation. The rates of these reactions are, however, much less than for the unsubstituted sulphide.

The rate of sulphonation is considerably reduced by the introduction of nitro-groups into the *para*-positions of the aromatic rings as a consequence of their electron-withdrawing properties. The rate of oxidation at the sulphur atom is also considerably decreased and this is consistent with a mechanism for the oxidation such as that involving nucleophilic attack of the sulphur atom on an oxygen atom of the sulphuric acid molecule (reaction 3).

$$Ph_2\ddot{S} \colon \quad \longrightarrow \quad Ph_2\ddot{S}{=}O \;+\; SO_2 \;+\; H_2O \quad \ldots \ldots \ldots \ldots (3)$$
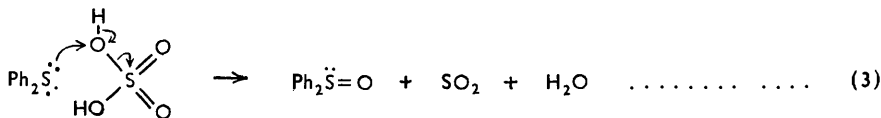
We also investigated the behaviour of 4-aminodiphenyl sulphide, which was found to give initial v' values of 4·1 and 4·3 in different experiments which increased to 4·5—4·6 in approximately 24 hr., and to values greater than 5·0 after several days. It seems likely that both the amino-groups and the sulphur atom are protonated and that the unsubstituted ring initially undergoes rather rapid sulphonation, although the reaction becomes slow in its later stages because of the water liberated by the reaction (cf. the following discussion of the sulphonation of sulphoxides). Oxidation probably also occurs. Complete sulphonation and protonation of the sulphur and amino-groups would give a v value of 5·0.

$$Ph \cdot S \cdot C_6H_4 \cdot NH_2 + 4H_2SO_4 = HO_3S \cdot C_6H_4 \cdot \overset{+}{S}H \cdot C_6H_4 \cdot \overset{+}{N}H_3 + H_3O^+ + 3HSO_4^- \quad \ldots \ldots (4)$$

Sulphoxides.—Szmant and Brost reported that diphenyl sulphoxide gave a constant value of i of 4·8 over a period of 2—20 hr. after addition to sulphuric acid. As may be seen from Table 2 and the Figure, we found that v' increases with time, reaching a reasonably constant value of 3·4 after about 2 hr. in expt. A and 3·1 after about 10 hr. in expt. B. The colour of the solution faded from a deep green to a pale blue-green as the freezing point decreased. Contrary to the observations of Szmant and Brost, who claimed that diphenyl sulphoxide could be recovered unchanged on dilution of its sulphuric acid solution, we found

that only a very small precipitate, insufficient to identify with certainty, was obtained on diluting a solution after its freezing point had become approximately constant.

Our results do not therefore support Szmant and Brost's conclusion that the diphenyl-sulphidonium ion Ph_2S^{++} is formed according to equation (1), since this requires a constant ν value of 5 and complete recovery on dilution according to the equation :

$$Ph_2S^{++} + 3H_2O = Ph_2S{:}O + 2H_3O^+ \quad \dots \dots \dots \dots \quad (5)$$
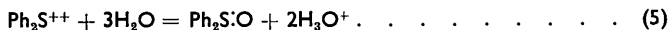
Our observations may be reasonably explained by assuming that there is an initial protonation of the sulphoxide group

$$Ph_2SO + H_2SO_4 = Ph_2S{:}OH^+ + HSO_4^- \quad \dots \dots \dots \dots \quad (6)$$

giving an initial ν value of 2·0 which is followed by a rather rapid sulphonation in one of the aromatic rings,

$$Ph_2S{=}OH^+ + 2H_2SO_4 = HO_3S{\cdot}C_6H_4{\cdot}SPh{=}OH^+ + H_3O^+ + HSO_4^- \quad \dots \dots \quad (7)$$

which on completion would give a ν value of 4. The initial increase in ν' is very rapid and our ν'–time curves cannot therefore be reliably extrapolated to zero time, but they are consistent with an initial ν' value of 2·0 and they have been extrapolated to this value in the Figure. The fact that the sulphonation apparently stops or at least becomes very slow

Variation of ν' for diphenyl sulphoxide with time.
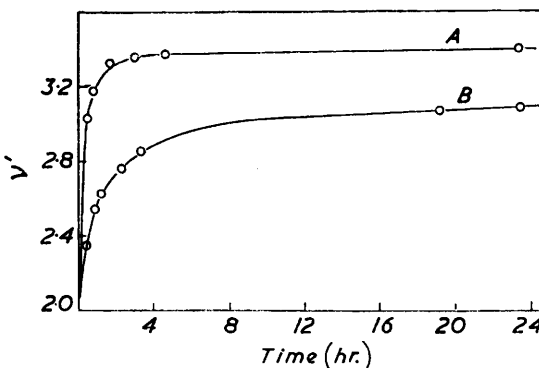
before completion may be attributed to the water formed in the reaction since the rate of sulphonation is known to decrease very rapidly with increasing concentration of water in the region of 100% H_2SO_4.[11] In the more concentrated solution (expt. B) the initial reaction is slower and the limiting value of ν' is smaller than in the more dilute solutions (expt. A). Both these observations are consistent with a greater change in the solvent composition in the more concentrated solution corresponding to the larger amount of water liberated by the sulphonation.

Diphenyl sulphoxide is sulphonated much more readily than diphenyl sulphone which is quite stable in sulphuric acid at room temperature. Presumably the deactivating inductive effect of the sulphoxide group is counterbalanced by the conjugation of the unshared pair of electrons on the sulphur with the aromatic ring (II).[12] (The conjugation of the S=O double bond with the aromatic ring appears to be rather slight.[12,13])
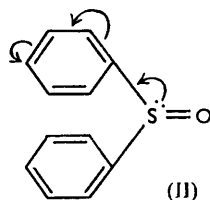
The introduction of a nitro-group into one of the aromatic rings is apparently sufficient to deactivate both rings towards sulphonation, as 4-nitrodiphenyl sulphoxide gave a stable pink solution and a constant ν' value of 2·07 which is presumably due mainly to protonation of the sulphoxide group. Some protonation of the nitro-group would be expected,[2] but the actual contribution that this makes to the observed ν' value cannot be found from the cryoscopic measurements. The colour of the solution of 4-nitrodiphenyl sulphoxide in

[11] Cowdrey and Davies, *J.*, 1949, 1871.
[12] Koch, *J.*, 1950, 2892.
[13] Koch and Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7.

sulphuric acid deepened considerably at room temperature during several days. As this colour change was not accompanied by any change in the freezing point of the solution, it cannot be due to change in the total number of solute particles. We cannot offer any explanation of this observation. 4 : 4'-Dinitrodiphenyl sulphoxide gave an orange solution and a constant ν' value of 2·04, which is not significantly different from that given by 4-nitrodiphenyl sulphoxide. Again the colour of the solution deepened and after several days was deep red. The observed ν' value is presumably due to extensive protonation of the sulphoxide group together with a small amount of protonation of the nitro-groups.

Sulphones.—Our present results extend the earlier work of Gillespie,[2] who obtained a ν' value for diphenyl sulphone of 1·20. It may be seen from Table 1 that the introduction of a nitro-group into the *para*-position of one of the aromatic rings causes ν' to increase to 1·35 and the introduction of a second nitro-group into the *para*-position of the other ring causes a slight decrease to 1·28. Both substances gave pale yellow solutions and could be recovered on dilution with water. These results are consistent with the interpretation that the sulphone group is partially protonated and that the nitro-groups are slightly protonated and reduce the basicity of the sulphone group to some extent.

Our results do not agree with those obtained by Szmant and Brost who found *i*-values of 1·5 for 4-nitrodiphenyl sulphone and 2·0 for 4 : 4'-dinitrodiphenyl sulphone and postulated that nitro-groups increase the basicity of the sulphone group in order to explain their results. We have pointed out above, however, that the accuracy of Szmant and Brost's *i* values is doubtful.

Our results and conclusions are in accord with the results of a theoretical molecular-orbital treatment of sulphones by Koch and Moffitt,[13] who showed that there is only slight conjugation between the S=O double bonds and the aromatic rings in diphenyl sulphone. They are also supported by the infrared spectroscopic measurements of Barnard, Fabian, and Koch,[4] who found that the S=O bond vibration frequencies are the same in methyl phenyl and diphenyl sulphoxide as in *cyclo*hexyl methyl sulphoxide. A similar result was obtained for the corresponding sulphone derivatives. They concluded that there was little conjugation of either the sulphoxide or the sulphone group with the aromatic rings. Leandri, Mangini, and Passerini[15] have reached a similar conclusion from ultraviolet absorption spectra measurements, although in the photo-excited state there appears to be more conjugation.

It may finally be noted that the sulphones we have studied are considerably weaker bases than the corresponding sulphoxides. Barnard, Fabian, and Koch[14] have shown that sulphoxides form stronger hydrogen bonds than sulphones and they attribute this to the greater basicity of sulphoxides. They also found on the basis of force constants that the S=O bond in sulphoxides is weaker than in sulphones. These observations are in accord with the view that, because of the greater electronegativity of the sulphur atom in sulphones than in sulphoxides, the bonds in the former are less polar and stronger than in the latter. The greater resulting negative charge on the oxygen atom of the sulphoxides than on the oxygen atoms of sulphones accounts for the greater basicity of the former.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES.
    UNIVERSITY COLLEGE, LONDON, W.C.1.
[Present address (R. C. P.) : ISTITUTO CHIMICA ORGANICA INDUSTRIALE UNIVERSITA,
    CATANIA, ITALY.]   [*Received, May 1st,* 1956.]

[14] Barnard, Fabian, and Koch, *J.*, 1949, 2442.
[15] Leandri, Mangini, and Passerini, *Gazzetta*, 1954, **84**, 73.