533. *Oxidation of Dialkyl Sulphides and Trisubstituted Phosphines by Dinitrogen Tetroxide; Molecular Addition Compounds with Dialkyl Sulphoxides.*

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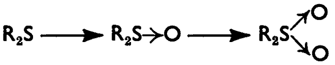
Alkyl sulphides are readily oxidised by liquid dinitrogen tetroxide to the sulphoxides, and there is no further oxidation to sulphone. Because of its anhydrous and volatile nature, dinitrogen tetroxide is an excellent oxidant in the preparation of sulphoxides. Tributyl- and triphenyl-phosphine are similarly oxidised to the phosphine oxides. Molecular addition compounds of dimethyl, diethyl, di-*n*-propyl, and di*iso*propyl sulphoxides with dinitrogen tetroxide have been studied by thermal analysis; 1 : 1 compounds predominate, and the possible structures are discussed. Neither diethyl sulphone nor the phosphine oxides give addition compounds with dinitrogen tetroxide, and sulphur is therefore considered to be the donor atom in compounds with sulphoxides.

In view of the readiness with which dinitrogen tetroxide forms molecular addition compounds with ethers,[1] and with other compounds (*e.g.*, esters, aldehydes, ketones [2]) in which oxygen can act as an electron donor, it was of interest to determine whether sulphur compounds show similar behaviour. However, it was not possible to investigate compound formation with the dialkyl sulphides since they undergo vigorous oxidation by dinitrogen tetroxide. On addition of small quantities of the tetroxide to diethyl sulphide at $-70°$ a red colour appeared; at this temperature oxidation is negligible and the colour is probably due to the formation of an addition compound analogous to that formed with diethyl ether. As the temperature is increased, nitric oxide is evolved at an increasing rate, and the sulphide is converted completely into the sulphoxide. Similar behaviour was observed with the other alkyl sulphides mentioned in this paper. Oxidation of organic sulphur compounds by " nitrous fumes " has been reported,[3] and Horner and Hübenett [4] have recently used a dinitrogen tetroxide–carbon tetrachloride mixture to oxidise methyl phenyl sulphide to the sulphoxide.

A unique feature in the oxidising properties of dinitrogen tetroxide is its ability to restrict a reaction to a single oxidation stage only, when further oxidation would appear to be possible. The preparation of substituted aromatic aldehydes $R{\cdot}C_6H_4{\cdot}CHO$ by oxidation of the corresponding alcohols with dinitrogen tetroxide is superior to many other methods in simplicity and in yield;[5] both sodium hyponitrite and sodium α-oxyhyponitrite ($Na_2N_2O_3$) are oxidised [6] rapidly to the compounds β-$Na_2N_2O_3$ and $Na_2N_2O_4$. Addition of a single oxygen atom to an alkyl sulphide is another example of this unusual property, since the complete oxidation



is not a difficult process, and low melting points recorded in earlier literature (*e.g.*, 8° for Me_2SO) [7] are probably due to the presence of sulphone. Douglas [8] gives 18·5° for the melting point of pure dimethyl sulphoxide; our product melted at 19—20°. The alkyl sulphoxides are hygoscopic and difficult to crystallise when moist; di-*n*-butyl sulphoxide, for example, crystallises when anhydrous, but liquefies rapidly on absorption of moisture.[9] The ease with which sulphoxides have been found to crystallise in this work is attributed to the completely anhydrous nature of dinitrogen tetroxide. Oxidation of sulphoxide to

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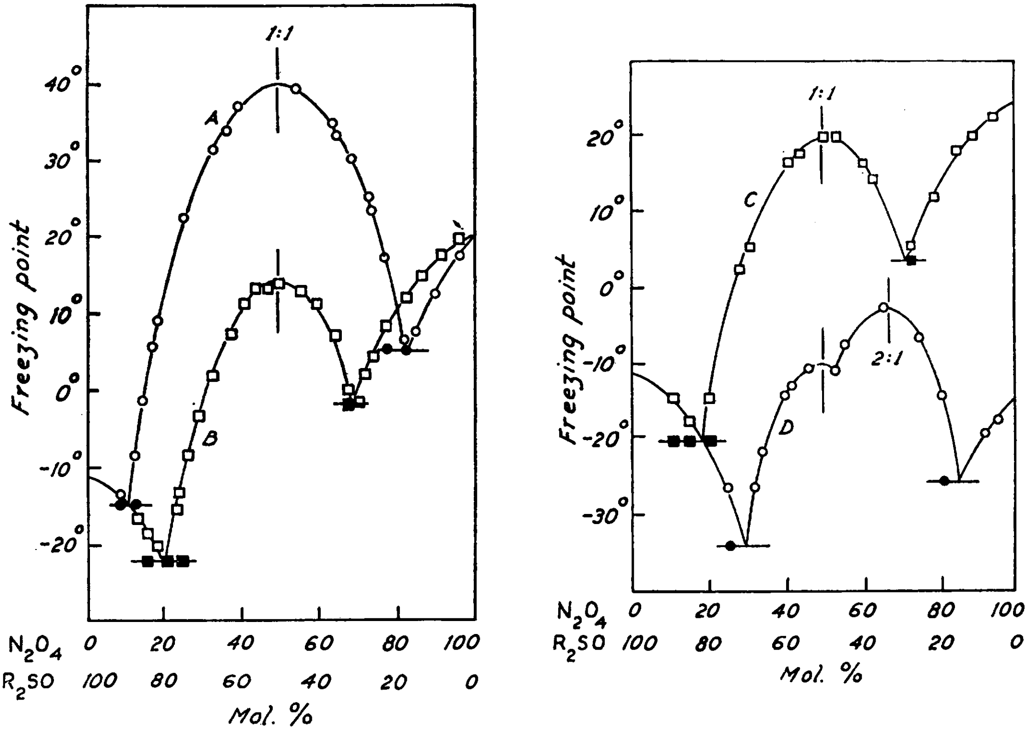
[1] Rubin, Shechter, and Sisler, *J. Amer. Chem. Soc.*, 1952, **74**, 877; Whanger and Sisler, *ibid.*, 1953, **75**, 5188.
[2] Addison and Sheldon, *J.*, 1956, 1941.
[3] Pummerer, *Ber.*, 1910, **43**, 1407.
[4] Horner and Hübenett, *Annalen*, 1953, **579**, 193.
[5] Field and Grundy, *J.*, 1955, 1110.
[6] Addison, Gamlen, and Thompson, *J.*, 1952, 346.
[7] Strecker and Spitala, *Ber.*, 1926, **59**, 1754.
[8] Douglas, *J. Amer. Chem. Soc.*, 1946, **68**, 1072.
[9] Edwards and Stenlake, *J.*, 1954, 3272.

sulphone is slight even on prolonged contact. Mixtures of sulphoxide with dinitrogen tetroxide developed a pale green colour (due to a small amount of dinitrogen trioxide) after 24 hours, but even after several weeks the sulphoxide could be recovered almost unchanged.

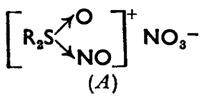
Triphenylphosphine and tri-*n*-butylphosphine are oxidised vigorously by dinitrogen tetroxide at room temperature (the latter the more vigorously) to the corresponding phosphine oxides; in this case no further oxidation stage is involved. Oxidation of the tributylphosphine was still rapid at —70°.

Molecular Addition Compounds.—The stability of the sulphoxide–dinitrogen tetroxide mixtures enabled thermal analysis to be carried out, and phase diagrams for four sulphoxides are shown in Figs. 1 and 2. Obvious 1 : 1 compounds are formed in the solid state, and only in the case of di*iso*propyl sulphoxide (curve *D*) is a 2 : 1 compound observed. Since 'onium donors normally give 2 : 1 compounds,[2] there are unusual features in the structure of the sulphoxide compounds, and it is relevant here to draw comparison with the addition compound with nitric acid, Me_2SO,HNO_3. This compound, prepared by the action of concentrated nitric acid on dimethyl sulphide,[10] crystallises from aqueous solution and has been assumed to be a salt $Me_2SOH^+ NO_3^-$. If sound evidence was available for this ionic formulation, the dinitrogen tetroxide compounds might be regarded, by analogy, as ionic compounds of type (*A*); however, the published experimental results reveal no clear evidence for this ionic formulation. The electrical conductivity of the compound in water is nearly the same as for an equivalent amount of nitric acid;[11] pH measurements show it to be completely dissociated into its components in water,[12] and it is not associated in

FIGS. 1 *and* 2. *Addition compounds of* N_2O_4 *and* R_2SO.



A, Me_2SO; *B*, Et_2SO; *C*, $Pr^n{}_2SO$; *D*, $Pr^i{}_2SO$.



(*A*)

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[10] Saizew, *Annalen*, 1867, **144**, 150.

[11] Hantzsch and Hibbert, *Ber.*, 1907, **40**, 1508.

[12] Nylén, *Z. anorg. Chem.*, 1941, **246**, 227.

chloroform solution whereas ionic nitrates (*e.g.*, tetra-alkylammonium nitrates) show association.[13] The freezing points of aqueous solutions of two sulphoxides are given in Table 1. Phase diagrams constructed from these values show no breaks, so that the proton affinity of the sulphoxides is insufficient to give rise to compound formation with water. There is therefore no reason to favour an ionic structure for the dinitrogen tetroxide complexes. The equilibria between ionic and molecular compounds

$$R_2SO,N_2O_4 \rightleftharpoons R_2SO + N_2O_4 \rightleftharpoons R_2SO,NO^+ \ NO_3^-$$

may well occur in the liquid state, as with other 'onium donors,[2] but the properties of the liquid mixtures indicate that very little of the ionic form can be present; the specific conductivity does not exceed 10^{-4} ohm^{-1} cm.$^{-1}$, and the rates of reaction with metals are little more than the rates with dinitrogen tetroxide alone.

In considering a structure for the molecular addition compounds it is necessary to determine whether the sulphur or the oxygen atom acts as electron donor to the tetroxide. When bonded in the form R–O–R or $R_2C{=}O$, electron donation by the oxygen atom is sufficiently strong to give addition compounds.[2] However, in compounds $R_2S^+{-}O^-$, the oxygen atom is bonded in yet another way, and may have different electron-donor properties. The sulphur atom has an electron pair available for donation in the sulphoxide, but not in the sulphone, and any compound formation between dinitrogen tetroxide and a sulphone will therefore depend upon the donor properties of oxygen bonded in this manner. Similar conditions apply in the compounds $R_3P^+{-}O^-$. Mixtures of the tetroxide with diethyl sulphone and with tri-*n*-butylphosphine oxide have therefore been studied by thermal analysis, and the freezing points are given in Table 2.

TABLE 1. *Freezing points of sulphoxide–water mixtures.*

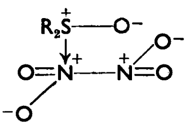
Mol. % of Me_2SO	100	80	68	54	45·5		
Freezing point	20°	7·5°	−3·5°	−20·5°	−42·5°		
Mol. % of Et_2SO	100	78	65	54·5	44·5	37	30
Freezing point	20°	12°	4°	−3·5°	−15°	−26°	−35°

TABLE 2. *Freezing points of mixtures with dinitrogen tetroxide.*

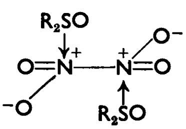
Mol. % of Et_2SO_2	100	65·5	57	42	37	27·5	0		
Freezing point	74°[13]	50·5°	41°	23°	4°	−23°	−11·3°		
Eutectic	26 mol. % at −27·5°								
Mol. % of Bu_3PO	100	91	82	61·5	48	46	38·5	25·5	14·5
Freezing point	67·4°	61·4°	51°	22°	−7°	−13°	−27°	−28°	−16·5°
Eutectic	33 mol. % at −37°								

In each case the phase diagram is a simple eutectic system, and the absence of compound formation indicates that an oxygen atom bonded in this way is not a sufficiently strong donor with respect to dinitrogen tetroxide to be responsible, in itself, for compound formation. The 1 : 1 molecular addition compounds with sulphoxides are therefore represented as in (I), with the sulphur atoms primarily responsible for electron donation. In the 1 : 1 compounds, electron donation by a second sulphoxide molecule (as in II) is considered to be inhibited by partial charge transfer from the oxygen atom which is brought into close proximity with the N_2O_4 molecule on formation of the 1 : 1 compound. This type of association is only possible when the lattice structure permits the S–O bond to be in

(I)



(II)



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[13] Walden, *Bull. Acad. St. Petersbourg.*, 1915, 509; *Chem. Zentr*, 1925, **96**, 1674.

the same direction as the N–N bond. The phase diagrams for the dipropyl sulphoxides (Fig. 2) show that a change in shape of the alkyl group results in a change from a 1 : 1 (*n*-propyl) to a predominant 2 : 1 (*iso*propyl) compound. Unless the electronic distribution in the sulphoxide group varies appreciably with the structure of the alkyl group, the change in compound ratio must be a lattice effect. It is feasible that in the 2 : 1 compound with di*iso*propyl sulphoxide, the stable lattice structure requires that the S–O and the N–N bonds are at a wide angle to one another; the oxygen atom is then so far removed that electron transfer to the second NO_2 unit is no longer possible. Under these conditions the normal 'onium donor (2 : 1) compound (II) would be found.

EXPERIMENTAL

Preparations of Sulphoxides.—A 250 ml. flask containing 100 g. of dialkyl sulphide was connected, through twin necks, to a phosphoric oxide guard-tube and to a 100 ml. flask containing an excess of liquid dinitrogen tetroxide. The sulphide was cooled in alcohol–solid carbon dioxide, and the tetroxide was added slowly either by distillation or by careful pouring. At low temperatures, oxidation proceeds smoothly, but care is needed at higher temperatures; reaction and evolution of nitric oxide are very vigorous if the liquids are mixed near 0°. The product was the liquid sulphoxide containing much tenaciously held dinitrogen tetroxide, but distillation at low pressure gave a 90% yield of the colourless liquid sulphoxide solidifying over a temperature range of about 4°. Some decomposition occurs during distillation, so that further distillation did not increase the purity of the sulphoxide. Fractional crystallisation is a suitable method of purification, and the products, once distilled, were cooled slowly until about one quarter of the products had crystallised. This fraction had the following properties:

Dimethyl sulphoxide: m. p. 19—20°, b. p. 80°/18 mm.

Diethyl sulphoxide: m. p. 19—20°, b. p. 95°/18 mm. (Found: C, 44·7; H, 9·5; S, 31·2. Calc. for Et_2SO: C, 45·3; H, 9·45; S, 30·2%).

Di-*n*-propyl sulphoxide: m. p. 24·5—25·5°, b. p. 80°/3 mm. (Found: C, 53·1; H, 10·5. Calc. for $C_6H_{14}OS$: C, 53·6; H, 10·5%).

Di*iso*propyl sulphoxide: m. p. −17° to −14·5°, b. p. 60°/3 mm.

When the trisubstituted phosphines were oxidised by excess of liquid dinitrogen tetroxide, the products crystallising from solutions were solid solutions of phosphine oxides with dinitrogen tetroxide. The N_2O_4 mol. fraction in the crystals was 0·38 for tributylphosphine oxide, and 0·55 for triphenylphosphine oxide. The tetroxide is tenaciously held, and was removed from the crystals only slowly in a vacuum at room temperature. Crystals containing triphenylphosphine oxide were therefore melted at 100°, the dinitrogen tetroxide being then given off. The residue, recrystallised from aqueous alcohol, gave pure triphenylphosphine oxide as a colourless solid, m. p. 156—157° (lit.[14] 156·5—157°). The gold chloride addition compound crystallised from a concentrated solution of the components as deep yellow plates, m. p. 177·5—178·5° (lit.,[15] 179°). The product of a similar oxidation of tri-*n*-butylphosphine distilled at 150°/1·5 mm., and gave colourless hygroscopic needles of the oxide, m. p. 67·0—67·4° (Found: C, 65·0; H, 12·3. Calc. for $C_{12}H_{27}OP$: C, 66·1; H, 12·5%). Tributylphosphine was prepared from *n*-butyl bromide by a Grignard reaction described by Davies and Jones,[16] who also report a slightly low C value on analysis of the tributylphosphine oxide.

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[14] Stelling, *Z. phys. Chem.*, 1925, **117**, 170.
[15] Pickard and Kenyon, *J.*, 1906, **89**, 262.
[16] Davies and Jones, *J.*, 1929, 33.