793. *Sulphoxides. Part I. The Oxidation of Tervalent Phosphorus Compounds by Dimethyl Sulphoxide* *

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Dimethyl sulphoxide oxidises tervalent phosphorus compounds to phosphoryl compounds, and dimethyl sulphide is formed. The influence of phosphorus substituents on reactivity has been investigated, and the following order was observed: $P(NMe_2)_3 > PBu^n_3 > PPh_3 < P(OEt)_3 < P(OMe)_3 < P(OCH_2{\cdot}CH_2Cl)_3 < Ph_2PCl < PhPCl_2 \leqslant MeO{\cdot}PCl_2 \simeq P(OPh)_3 < PCl_3$. Reaction mechanisms are discussed.

Dimethyl sulphoxide is a well-known polar solvent and electron donor, but its use as an oxidising agent has received attention only comparatively recently.[1] A preliminary account of our work on the oxidising and hydroxylating properties of dimethyl sulphoxide has appeared.[2] Reaction of dimethyl sulphoxide with tervalent phosphorus compounds involves oxidation to the phosphoryl compound and the formation of dimethyl sulphide,

$$Me_2SO + R_3P \longrightarrow Me_2S + R_3PO$$

A subsequent reaction occurs in the presence of phosphorus–halogen bonds. Oxidation is followed by hydroxylation of the phosphorus–halogen bonds to give hydroxy-derivatives of quinquevalent phosphorus together with chloromethyl methyl sulphide,

$$Me_2SO + P^V{-}Cl \longrightarrow P^V{-}OH + Me{\cdot}S{\cdot}CH_2Cl$$

This Paper is concerned with the first of these reactions: the oxidation of phosphorus(III) to phosphorus(V) by means of dimethyl sulphoxide.

The oxidation reaction has considerable value in the preparation of phosphoryl compounds in high yields. The reaction takes place smoothly in the absence of a solvent; alternatively, a suitable solvent, such as methylene chloride, can be used with the more reactive compounds. Side-reactions are not observed, and the volatile dimethyl sulphide is readily removed. Reaction of dimethyl sulphoxide with tris(dimethylamino)phosphine, tri-n-butylphosphine, triphenylphosphine, triethyl phosphite, trimethyl phosphite, tris-(2-chloroethyl) phosphite, diphenylchlorophosphine, phenyldichlorophosphine, methyl phosphorodichloridite, triphenyl phosphite, and phosphorus trichloride, gives, respectively, tris(dimethylamino)phosphine oxide, tri-n-butylphosphine oxide, triphenylphosphine oxide, triethyl phosphate, trimethyl phosphate, tris-(2-chloroethyl) phosphate, diphenylchlorophosphine oxide, phenyldichlorophosphine oxide, methyl phosphorodichloridate, triphenyl phosphate, and trichlorophosphine oxide.

Semiquantitative data show that the rates of reaction decrease along the following series: $PCl_3 > P(OPh)_3 \simeq MeO{\cdot}PCl_2 \geqslant PhPCl_2 > Ph_2PCl > P(OCH_2{\cdot}CH_2Cl)_3 > P(NMe_2)_3 > P(OMe)_3 > P(OEt)_3$; $P(OMe)_3 > PBu^n_3 > PPh_3$ (cf. Table 2); trimethyl phosphite is common to both series. The fastest reaction occurs with phosphorus trichloride and the slowest with triphenylphosphine. The details are described in the Experimental section.

Tervalent phosphorus compounds form dative σ-bonds to suitable electron acceptors, and vacant $3d$-orbitals of the phosphorus atom can accept electrons from suitable σ- or π-electron donors. The σ-donor properties have been investigated by studying the ability of tervalent phosphorus compounds to quaternise with alkyl halides,[3,4] and by measuring

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[1] See, *e.g.*, W. O. Ranky and D. C. Nelson, " Organic Sulphur Compounds," ed. N. Kharasch, Pergamon, Oxford, 1961, vol. I, ch. 17; H. H. Szmant, *ibid.*, ch. 16; " Dimethyl Sulphoxide, Reaction Medium and Reactant," Crown Zellerbach Corporation, Carmas, Washington, 1962.

[2] S. K. Ray, R. A. Shaw, and B. C. Smith, *Nature*, 1962, **196**, 372.

[3] G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, 1964, **18**, 38.

[4] Collated from P. C. Crofts, *Quart. Rev.*, 1958, **12**, 341; G. M. Kosolapoff, " Organophosphorus Compounds," Wiley, New York, 1950, p. 24.

the basicity towards perchloric acid in nitromethane solution.[5,6] Donor strength depends on the characteristics of the acceptor and on the method used for comparison, but for a limited series of phosphines it has been shown that there is an overall correlation between basicity and reactivity in simple quaternisation reactions.[7]

The order of increasing π-acceptor behaviour of tervalent phosphorus compounds can be related to the order of increasing carbonyl-bond order in phosphinometal(0) carbonyls, and extensive compilations and discussions of stretching frequencies and force constants are available.[5,8,9]

The most complete quantitative information about substituents attached to phosphorus has been obtained from a study of the basic strengths of cyclic phosphazenes.[10] This gives an electron-availability series for phosphorus compounds, which can be summarised by the following order of substituents: $NMe_2 > Alk > Ph > OEt > OMe > OPh > Cl$. This is also the order of decreasing σ-donor strength and increasing π-acceptor strength. This order differs significantly from the order of reactivity of tervalent phosphorus compounds with dimethyl sulphoxide which is: $P(NMe_2)_3 > PBu^n_3 > PPh_3 < P(OEt)_3 < P(OMe)_3 < P(OCH_2{\cdot}CH_2Cl)_3 < Ph_2PCl < PhPCl_2 \leqslant MeO{\cdot}PCl_2 \simeq P(OPh)_3 < PCl_3$. The rate of reaction decreases with decreasing electron-availability until triphenylphosphine, and then increases with decreasing electron-availability. The reactivity of triphenylphosphine in the series $PPh_3 < Ph_2PCl < PhPCl_2 < PCl_3$ is surprisingly low compared with the reactivity of trimethyl phosphite in the series $P(OMe)_3 < MeO{\cdot}PCl_2 < PCl_3$ (cf. Table 2).

It is suggested that differences in rehybridisation effects alone are of insufficient importance to account for the observed differences in the reactivity series reported here, and that two different features in the reaction mechanism would account better for the observed behaviour. Reaction mechanisms can be discussed in terms of the nucleophilic and electrophilic properties of tervalent phosphorus. Initial reaction with dimethyl sulphoxide may occur at oxygen or sulphur by a number of different mechanisms. All three atomic centres contain lone pairs of electrons, and biphilic mechanisms [11] are intrinsically possible.

Phosphorus trichloride has negligible donor but strong acceptor properties. The rapid reaction with dimethyl sulphoxide presumably occurs *via* electrophilic attack by phosphorus on oxygen, which is at the negative end of the sulphur–oxygen dipole. This type of mechanism has been suggested for the oxidation of tervalent phosphorus compounds by pyridine-*N*-oxides and, for a given *N*-oxide, the reactivity increases in the order of decreasing electron supply to phosphorus.[12] The reactivity decreases when an electron-withdrawing group is substituted in the pyridine ring, *e.g.*, in 4-nitropyridine 1-oxide.[12,13] Electrophilic attack by phosphorus on oxygen may involve an intermediate with a dative σ-bond from oxygen to sp^3d-hybridised phosphorus,[12] of the type that may occur in the 1 : 1 molecular addition compounds formed between trimethylamine and phosphorus trichloride or phosphorus tribromide.[14] If no intermediate is involved, the transition state of this mechanism cannot be distinguished from that of a biphilic

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[5] L. S. Meriwether and M. L. Fiene, *J. Amer. Chem. Soc.*, 1959, **81**, 4200.

[6] C. A. Streuli, personal communication.

[7] W. A. Henderson and C. A. Streuli, *J. Amer. Chem. Soc.*, 1960, **82**, 5791; W. A. Henderson and C. A. Buckler, *ibid.*, p. 5794.

[8] R. B. King, *Inorg. Chem.*, 1963, **2**, 963.

[9] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J.*, 1959, 2323; T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Amer. Chem. Soc.*, 1961, **83**, 3200; R. Poilbane and M. Bigorgne, *Bull. Soc. chim. France*, 1962, 1301; F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

[10] D. Feakins, W. A. Last, and R. A. Shaw, *Chem. and Ind.*, 1962, 510; *J.*, 1964, 4464; D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *Chem. and Ind.*, 1963, 164; *J.*, 1965, 2804.

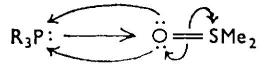
[11] R. G. Pearson, H. B. Gray, and F. Basolo, *J. Amer. Chem. Soc.*, 1960, **82**, 787.

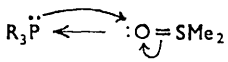
[12] F. Ramirez, personal communication; F. Ramirez and A. Aguiar, Abs. 134th Meeting Amer. Chem. Soc., 1958, p. 42*N*; A. Aguiar, *Diss. Abs.*, 1960, **21**, 437.

[13] T. R. Emerson and C. W. Rees, *J.*, 1964, 2319.

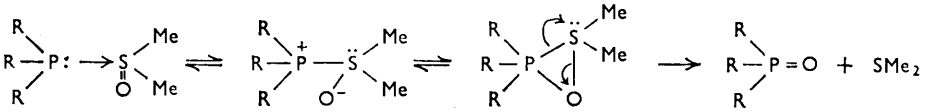
[14] R. R. Holmes, *J. Phys. Chem.*, 1960, **64**, 1295; *J. Amer. Chem. Soc.*, 1960, **82**, 5285.

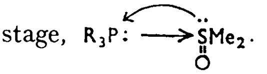
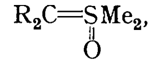
mechanism. The relative importance of the components, dative π-bonds from oxygen to phosphorus and a dative σ-bond from phosphorus to oxygen, or a dative σ-bond from oxygen to phosphorus and a dative π-bond from phosphorus to oxygen, depend on the substituents.





Tris(dimethylamino)phosphine and trialkylphosphines are strong electron donors and poor acceptors. The reactions with dimethyl sulphoxide presumably occur *via* nucleophilic attack by phosphorus on sulphur, which is at the positive end of the sulphur–oxygen dipole. Reaction intermediates may be involved in the scheme shown below, in which reaction is completed by concurrent or successive rupture of the sulphur–oxygen and phosphorus–sulphur bonds.[15]



The lone pair of electrons on sulphur may contribute to a biphilic mechanism in the first stage,  $R_3P\!:\longrightarrow \underset{O}{\overset{\cdot\cdot}{S}}Me_2$. Compounds having related structures,  $R_2C{=}\underset{O}{S}Me_2$, have been shown to exist and have been isolated in a number of cases.[16] Tervalent phosphorus compounds form stable addition compounds with many electron-acceptors, and this type of mechanism is preferred for the oxidation of phosphines by sulphur dioxide.[17] Initial attack on carbonyl carbon is also believed to occur in the Perkov reaction.[18] Oxygen transfer between phosphine oxides and phosphines has been explained in terms of nucleophilic attack by phosphorus on oxygen; [12] by analogy, an alternative mechanism may involve nucleophilic attack by phosphorus(III) on phosphorus(V).

EXPERIMENTAL

Dimethyl sulphoxide, b. p. 189°, was purified by distillation. Tris(dimethylamino)phosphine, b. p. 162°, was prepared from phosphorus trichloride and dimethylamine.[19] Tri-n-butylphosphine, b. p. 111°/12 mm., was prepared from phosphorus trichloride and n-butylmagnesium bromide.[20] Triethyl phosphite, b. p. 50°/12 mm., trimethyl phosphite, b. p. 110—112°, tris-(2-chloroethyl) phosphite, b. p. 112°/3 mm., and methyl phosphorodichloridite, b. p. 95°, were prepared by Dr. W. Hewertson and Mr. P. Ward in this laboratory. Diphenylchlorophosphine, b. p. 89°/0·05 mm., and phenyldichlorophosphine, b. p. 105°/19 mm., were gifts from the Victor Chemical Works. Triphenylphosphine, m. p. 80°, was recrystallised from carbon tetrachloride. Triphenyl phosphite, b. p. 210°/1 mm., and the other tervalent phosphorus compounds were purified by distillation immediately before use. Organic solvents were dried by conventional methods.

Oxidation Reactions.—Reactions were carried out in an atmosphere of dry nitrogen. The experimental details are recorded in Table 1. Method (*a*) refers to reactions in the absence of solvent and method (*b*) to reactions in methylene chloride.

Dimethyl sulphide, b. p. 34—36° (lit.,[21] 37·2°/758 mm.), was characterised by its infrared spectrum and by preparation of the addition compound tris(mercuric chloride)–bis(dimethyl

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[15] R. F. Hudson, Reaction Mechanisms Symposium, *Chem. Soc. Special Publ.*, No. 19, 1965, 93.

[16] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 867; H. König and H. Metzger, *Z. Naturforsch.*, 1963, **18**b, 987; *Tetrahedron Letters*, 1964, **40**, 3003.

[17] B. C. Smith and G. H. Smith, unpublished results.

[18] P. A. Chopard, V. M. Clark, A. J. Kirby, and R. F. Hudson, *Tetrahedron*, 1965, in the press.

[19] H. Nöth and H. J. Vetter, *Chem. Ber.*, 1963, **96**, 1109.

[20] W. C. Davies and W. J. Jones, *J.*, 1929, 33.

[21] W. Strecker and R. Spitaler, *Ber.*, 1926, **59**, 1754.

TABLE 1

Preparation of phosphoryl compounds

Me_2SO	Phosphorus(III) compound			Phosphoryl compound	
(mole)	PR_3	(mole)	Method	R_3PO	(%)
0·14	$P(NMe_2)_3$	0·14	*a*	$(Me_2N)_3PO$	48
0·08	PBu^n_3	0·08	*a*	Bu^n_3PO	28
0·28	PPh_3	0·02	*a*	Ph_3PO	61
0·14	$P(OEt)_3$	0·14	*a*	$(EtO)_3PO$	79
0·14	$P(OMe)_3$	0·14	*a*	$(MeO)_3PO$	76
0·14	$P(OCH_2{\cdot}CH_2Cl)_3$	0·14	*a*	$(ClCH_2{\cdot}CH_2O)_3PO$	47
0·26	Ph_2PCl	0·26	*b*	Ph_2ClPO	89
0·66	$PhPCl_2$	0·70	*b*	$PhCl_2PO$	98
0·14	$MeO{\cdot}PCl_2$	0·14	*a*	$MeO{\cdot}Cl_2PO$	75
0·10	$P(OPh)_3$	0·10	*a*	$(PhO)_3PO$	98
0·20	PCl_3	0·20	*a*	Cl_3PO	58

sulphide), m. p. 150° (lit.,[22] 151°). The phosphoryl compounds had the following physical constants: tris(dimethylamino)phosphine oxide, b. p. 80°/1 mm. (lit.,[23] 76°/1 mm.), n_D^{25} 1·4572 (lit.,[23] 1·4570); tri-n-butylphosphine oxide (Found: C, 65·8; H, 12·4; P, 14·2. Calc. for $C_{12}H_{27}OP$: C, 66·0; H, 12·4; P, 14·2%), m. p. 58—60°, b. p. 90°/0·06 mm. (lit.,[20] 300°/760 mm.); triphenylphosphine oxide, m. p. and mixed m. p. 137—140°; triethyl phosphate, b. p. 100°/13 mm. (lit.,[24] 99·2°/13 mm.), n_D^{20} 1·4060 (lit.,[24] 1·40616); trimethyl phosphate, b. p. 70°/10 mm. (lit.,[23] 79°/12 mm.), n_D^{25} 1·3956 (lit.,[24] 1·3950); tris-(2-chloroethyl) phosphate, b. p. 144—146°/0·5 mm. (lit.,[25] 180—182°/2—3 mm.), n_D^{20} 1·4728 (lit.,[25] 1·4731); diphenylchlorophosphine oxide (Found: C, 61·0; H, 4·0. Calc. for $C_{12}H_{10}ClOP$: C, 60·9; H, 4·2%), b. p. 132—135°/0·3 mm. (lit.,[26] 138—139°/0·15 mm.); phenyldichlorophosphine oxide (Found: C, 37·0; H, 2·9; P, 15·2. Calc. for $C_6H_5Cl_2OP$: C, 36·9; H, 2·6; P, 15·9%), b. p. 91°/4·5 mm. (lit.,[27] 104°/4 mm.); methyl phosphorodichlorodate (Found: C, 8·2; H, 2·0; Cl, 47·0. Calc. for $CH_3Cl_2O_2P$: C, 8·0; H, 2·0; Cl, 47·7%), b. p. 58—60°/12 mm. (lit.[28] 62—64°/15 mm.); triphenyl phosphate, m. p. 50—51° (lit.,[29] 50°); and trichlorophosphine oxide, b. p. 109—110°/760 mm. (lit.,[30] 105°), which formed the derivative trisanilinophosphine oxide, m. p. and mixed m. p. 208—210°.

Reaction Temperatures.—The two series *A* and *B*, recorded in Table 2, are characteristic temperatures at which fixed percentages of dimethyl sulphide were evolved in given times at comparable stages in the reactions carried out in the absence of solvent. The course of each reaction was followed by measuring the volume of dimethyl sulphide. It is not intended that too much significance should be placed on the exact numerical values, although the temperatures are probably reproducible to ±5°. *A*. The phosphorus compound was cooled to −80°. Dimethyl sulphoxide was added dropwise. The mixture was allowed to warm up slowly in a solvent-bath until reaction occurred. The temperature at which 10% of the reaction (from 15—25%) occurred in ½ hr. was recorded. *B*. A different scale was used for the less-reactive compounds. The reagents were mixed at room temperature and warmed

TABLE 2

Comparable temperatures for the reaction $PR_3 + Me_2SO \longrightarrow R_3PO + Me_2S$

PR_3	*A*	PR_3	*A*	PR_3	*B*
PCl_3	10°	$P(OCH_2{\cdot}CH_2Cl)_3$	105°	$P(OMe)_3$	90°
$P(OPh)_3$	45	$P(NMe_2)_3$	145	PBu^n_3	100
$MeO{\cdot}PCl_2$	45	$P(OMe)_3$	160	PPh_3	225
$PhPCl_2$	50	$P(OEt)_3$	175		
Ph_2PCl	85				

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[22] W. F. Faragher, J. C. Morrell, and S. Comay, *J. Amer. Chem. Soc.*, 1929, **51**, 2776.

[23] G. M. Kosolapoff, "Organophosphorus Compounds," Wiley, New York, 1950, p. 313.

[24] Ref. 23, p. 258.

[25] Ref. 23, p. 260.

[26] W. A. Higgins, P. W. Vogel, and W. G. Craig, *J. Amer. Chem. Soc.*, 1955, **77**, 1864.

[27] A. D. F. Toy, *J. Amer. Chem. Soc.*, 1948, **70**, 186.

[28] Ref. 23, p. 241.

[29] S. Sugden, J. B. Reed, and H. Wilkins, *J.*, 1925, 1539.

[30] N. N. Greenwood and K. Wade, *J.*, 1957, 1516.

gradually. Temperatures were recorded at which 2% of the reaction (in the range 6—12%) occurred in 1 hr.

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