515. *The Liquid Hydrogen Chloride Solvent System. Part V.*[1] *Solubilities and Reactions of Some Compounds Containing Doubly Bonded Oxygen.*

By M. E. Peach and T. C. Waddington.

The conductivities of several compounds containing nitrosyl, nitryl, phosphoryl, sulphonyl, and sulphinyl groups have been measured. The basic strengths of these compounds and others discussed in earlier papers are related to the negative inductive effects of the various substituent ligands. Compounds acting as solvobases have been titrated conductimetrically with boron trichloride. The behaviour of some oxyacids and oxyacid anhydrides in liquid hydrogen chloride has been studied.

This paper describes, initially, the basic properties of alkyl, aryl, and halogen substituents attached to nitro-, phosphoryl, sulphonyl, and sulphinyl groups. The halogen compounds could ionize either by protonation of the oxygen or by loss of a chloride ion. The basic strength of all these compounds is then discussed in terms of the magnitude of the negative inductive effect of the substituent ligand: from this the possibility that chloro-compounds owe their basic strength to protonation of their oxygen atoms is considered. In sulphuric acid the sulphones are considerably less basic than the sulphoxides:[2] this has also been observed in liquid hydrogen chloride.

The reactions of strong aquoacids and of acid anhydrides are then discussed. The use of methanesulphonic, trifluoromethanesulphonic, and sulphuric acid has been investigated without success. The reactions of dinitrogen tetroxide, phosphorus pentoxide, and sulphur dioxide are compared with those in sulphuric acid and some previously described in hydrogen chloride. The non-reactivity of these oxides is presumably due to their insolubility.

Experimental

The apparatus and techniques used have been described;[1] after conductimetric titrations with the solvoacid boron trichloride the product was isolated after removal of the excess of boron trichloride and solvent at −85°. Any gas evolved as the mixture warmed to room temperature was measured and this is quoted below as moles per mole of starting material.

Chloride was determined either by the Volhard method or gravimetrically: boron was estimated acidimetrically as the mannitol–borate complex. The free sulphur dioxide in compounds that were readily hydrolysed to sulphurous acid was analysed by dissolving them in an excess of standard iodine solution and estimating the excess with thiosulphate solution. Carbon, hydrogen, and nitrogen were determined by combustion.

Phosphoryl fluoride was prepared by treatment of phosphoryl chloride with antimony trifluoride, antimony pentachloride being used as a catalyst. Trifluoromethanesulphonic acid was prepared by heating its barium salt with concentrated sulphuric acid.[3]

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[1] Peach and Waddington, Part IV, *J.*, 1962, 600.

[2] Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40.

[3] Haszeldine and Kidd, *J.*, 1954, 4228.

Infrared spectra were taken on a Perkin–Elmer double-beam continuously recording spectrometer with either rock-salt or potassium bromide optics: less important spectra were recorded on a Perkin–Elmer Infracord instrument.

Conductivities.—These results are shown in Table 1.

TABLE 1.

Specific and molar conductances of compounds in liquid hydrogen chloride at −95°.

Compound	Concn. (mole/l.)	Spec. conductance (ohm^{-1} cm.$^{-1}$)	Molar conductance (ohm^{-1} cm.$^{-1}$ mole^{-1})	Compound	Concn. (mole/l.)	Spec. conductance (ohm^{-1} cm.$^{-1}$)	Molar conductance (ohm^{-1} cm.$^{-1}$ mole^{-1})
$HO\cdot NO_2$	Satd.	$0\cdot17 \times 10^{-6}$	—	Ph_2SO_2	0·21	$0\cdot11 \times 10^{-3}$	0·51
$PhNO_2$	0·31	$0\cdot49 \times 10^{-3}$	0·16	$Me\cdot SO_3H$	Satd.	$0\cdot90 \times 10^{-5}$	—
$MeNO_2$	Satd.	$0\cdot13 \times 10^{-5}$	—	$CF_3\cdot SO_3H$	Satd.	$0\cdot20 \times 10^{-5}$	—
Me_3NO,HCl	0·26	$0\cdot21 \times 10^{-2}$	8·0	$Cl\cdot SO_3H$	0·38	$0\cdot27 \times 10^{-5}$	0·007
$NOCl$	0·93	$0\cdot70 \times 10^{-6}$	0·00075	H_2SO_4	Satd.	$0\cdot14 \times 10^{-6}$	—
NO_2	Satd.	$0\cdot20 \times 10^{-6}$	—	Ph_3PO	0·22	$0\cdot22 \times 10^{-2}$	9·61
$SOMe_2$	Satd.	$0\cdot12 \times 10^{-2}$	—	Ph_2POCl	0·25	$0\cdot59 \times 10^{-2}$	28·9
$SOPh_2$	Satd.	$0\cdot15 \times 10^{-2}$	—	H_3PO_4	Satd.	$1\cdot77 \times 10^{-6}$	—
$SOCl_2$	0·39	$0\cdot27 \times 10^{-6}$	0·0007	POF_3	0·25	$0\cdot36 \times 10^{-5}$	0·015
SO_2	Satd.	$0\cdot15 \times 10^{-6}$	—	$POCl_3$	0·48	$0\cdot94 \times 10^{-4}$	0·20
SO_2Cl_2	Satd.	$0\cdot17 \times 10^{-6}$	—	P_4O_{10}	Satd.	$0\cdot82 \times 10^{-6}$	—
Me_2SO_2	0·23	$0\cdot47 \times 10^{-4}$	0·20				

Organic Derivatives.—Nitromethane was sparingly soluble in liquid hydrogen chloride, giving a colourless solution as it does in sulphuric acid,[2] and a white precipitate. With boron trichloride a white product was obtained, which melted to a colourless liquid just below room temperature. Analysis showed that a very unstable adduct had been formed.

Nitrobenzene, previously reported to be insoluble,[4] was observed to be completely soluble, forming a colourless solution which became yellow on addition of boron trichloride: nitrobenzene forms a yellow solution in sulphuric acid in which it is also more basic than nitromethane.[2] The product at room temperature was a mixture of liquid and solid which fumed in a dry box: this was analysed as the partially decomposed adduct, which is a yellow solid with a vapour pressure of 95 mm. at 25·5°.[5]

Trimethylamine oxide hydrochloride gave a colourless solution: a titration against boron trichloride was inconclusive owing to the small change in conductivity, but the curve had the same general shape as for the triphenylphosphine oxide–boron trichloride titration (see Figure). The white solid isolated at −85° was the *trimethylamine oxide–boron trichloride adduct* (Found: B, 5·0; Cl, 55·0; N, 7·3. $C_3H_9BCl_3NO$ requires B, 5·6; Cl, 55·4; N, 7·2%). The infrared spectrum showed B–Cl peaks at 832, 700, and 665 cm.$^{-1}$, a B–O frequency at 990 cm.$^{-1}$, and loss of O–H peaks at 3400 and 1638 cm.$^{-1}$.

Triphenylphosphine oxide gave a pale yellow solution, after evaporation of which the pale yellow hydrochloride remained (Found: Cl, 11·2 Calc. for $C_{18}H_{16}ClOP$: Cl, 11·3%). The infrared spectrum was very little different from that of the phosphine oxide and it was impossible to assign, with certainty, any O–H bands. The shape of the conductimetric titration curve against boron trichloride (Figure) suggested that ions were formed initially and then the adduct, both before the 1 : 1 molar ratio was reached. This was confirmed by analysis of the pale yellow solid product as a mixture of the adduct and the tetrachloroborate, which slowly decomposed into the adduct. The product partially melted and decomposed at 45—50°, leaving a solid which melted entirely at 203—204°: the melting point of the adduct is 207—208°.[6]

Dimethyl sulphoxide was fairly soluble, giving a colourless solution and white precipitate which dissolved on addition of boron trichloride. The conductimetric titration curve had a sharp break when the molar ratio is 1·0 : 1·0 (Figure); the product isolated was the unstable adduct (Found: Cl, 55·5. Calc. for $C_2H_6BCl_3OS$: Cl, 54·5%), which decomposed in a dry box to a yellow crystalline material. The adduct is known to be unstable.[7, 8]

[4] Maas and McIntosh, *J. Amer. Chem. Soc.*, 1911, **33**, 70.

[5] Brown and Holmes, *J. Amer. Chem. Soc.*, 1956, **78**, 2173.

[6] Frazer, Gerrard, and Patel, *J.*, 1960, 726.

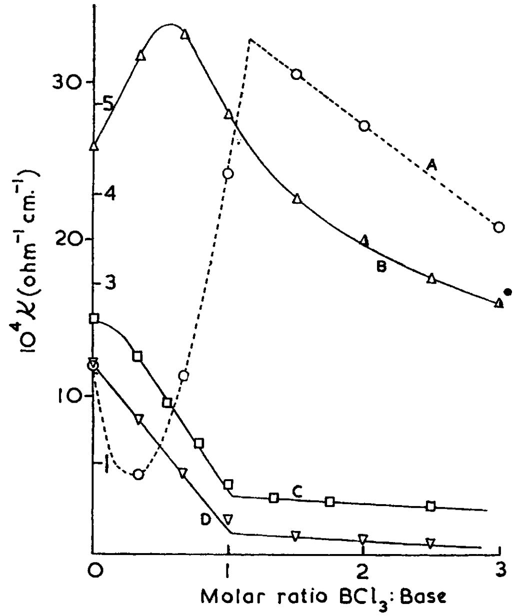
[7] Cotton and Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.

[8] Lappert and Smith, *J.*, 1961, 3224.

Diphenyl sulphoxide, purified by sublimation, was incompletely soluble, forming a colourless solution. A titration with boron trichloride (Figure) gave a sharp break in the curve at molar ratio 1·0 : 1·0: the white solid product was the diphenyl sulphoxide–boron trichloride adduct (Found: B, 3·1; Cl, 33·0. Calc. for $C_{12}H_{10}BCl_3OS$: B, 3·4; Cl, 33·3%).

Dimethyl sulphone gave a colourless solution. A conductimetric titration with boron trichloride gave a curve with a sharp break when the molar ratio was 1·0 : 1·0; the product was the unstable boron trichloride adduct (Found: B, 4·4; Cl, 46·0; Cl/B, 10·3. Calc. for $C_2H_6BCl_3O_2S$: B, 5·1; Cl, 50·3; Cl/B, 9·9%).

Diphenyl sulphone dissolved to a colourless weakly basic solution: the titration curve with boron trichloride (Figure) was similar to that of dimethyl sulphone with boron trichloride. The white solid product was the unstable adduct, which decomposed overnight in a dry box or under a vacuum at room temperature (Found: B, 2·9; Cl, 29·5; Cl/B, 10·3. Calc. for $C_{12}H_{10}BCl_3O_2S$: B, 3·2; Cl, 31·7; Cl/B, 9·9%). The infrared spectrum had a B–O peak at 1030 and B–Cl frequencies at 785, 740, and 700 cm.$^{-1}$.



Conductimetric titration, with BCl_3, of (A) 0·22M-diphenyl sulphoxide, (B) 0·22M-dimethyl sulphoxide, (C) 0·22M-diphenyl sulphone (inner scale), and (D) 0·26M-triphenylphosphine oxide.

Halogen Compounds.—Phosphoryl fluoride was soluble, giving a colourless solution. No residue was obtained on evaporation of the solvent at −95°. As phosphoryl chloride and phosphoryl chlorofluorides are involatile at this temperature no solvolysis of the phosphoryl fluoride could have occurred. No reaction was observed with boron trichloride.

Diphenylphosphinyl chloride dissolved to a colourless highly conducting solution. In a reaction with boron trichloride the product isolated was the *boron trichloride–diphenylphosphinyl chloride adduct* (Found: B, 2·9; Cl, 40·3. $C_{12}H_{10}BCl_4OP$ requires B, 3·1; Cl, 40·1%).

Phosphoryl chloride dissolved to a colourless solution. Unsuccessful attempts were made to prepare the ion PCl_3OH^+ at room temperature by treating phosphoryl chloride with chloro- and trifluoromethane-sulphonic acid.

Sulphuryl chloride, purified by pumping at −63·5° (to remove hydrogen chloride) and vacuum-distilled at −10°, was sparingly soluble, forming a colourless solution and a white precipitate, which dissolved on addition of boron trichloride. A trace of white solid product was obtained at −85° from the boron trichloride reaction, but this volatilized to less than 0·1 mole of gas at room temperature.

Aquoacids.—Nitric (95% fuming), phosphoric (90% "AnalaR"), sulphuric (98% "AnalaR"), methanesulphonic and trifluoromethanesulphonic acid were all either sparingly soluble or insoluble. No oxidation of the solvent occurred with nitric acid as the solution remained colourless and chlorine gives a yellow solution.[9] Conductivity titrations against the solvobase tetramethylammonium chloride were attempted with sulphuric and methanesulphonic acid. With sulphuric acid the liquid separated into two layers at concentrations as low as 0·03M; with methanesulphonic acid only a slight change in conductivity occurred during the titration. The free acid was precipitated from an equimolar mixture of tetramethylammonium chloride and trifluoromethanesulphonic acid.

Oxyacid Anhydrides.—Dinitrogen tetroxide, phosphorus pentoxide (H form), and sulphur dioxide were all sparingly soluble. Sulphur dioxide gave no product with boron trichloride at −85°; dinitrogen tetroxide gave a yellow-orange product with boron trichloride, which volatilized, at room temperature, to boron trichloride and dinitrogen tetroxide. Conductivity titrations of sulphur dioxide against tetramethylammonium chloride produced a straight line showing no break at the molar ratio 1 : 1. The product contained a negligible amount of sulphur dioxide. In an attempted reaction of phosphorus pentoxide with tetramethylammonium chloride the unchanged oxide was recovered.

DISCUSSION

It is now possible to discuss the values of the equivalent conductivities of the bases measured in this and earlier papers. If the basic action of the compounds is due to protonation, then in a given series of related compounds the changes in basicity would be expected to parallel the changes in the negative inductive effect of the various ligands. The basicity of the compounds may be regarded as being measured by their equivalent conductivity at comparable dilutions. The negative inductive effect of several ligands, found from the dissociation constants of substituted acetic acids,[10] are shown in Table 2. Table 3 shows the equivalent conductivities of the series of basic compounds from this paper and Parts III and IV. Comparison of these two Tables show that, in general, the equivalent conductivities parallel changes in the negative inductive effect. The exceptions are ethyl benzoate, diphenyl sulphide, the sulphones, and diphenylphosphinyl chloride. In the case of ethyl benzoate the situation is complicated by the possibility of protonation of the ethoxide-oxygen as well as the carbonyl-oxygen. With aromatic compounds protonation of the aromatic nucleus may occur; this gives highly coloured compounds and solutions.[11] Coloured solutions in liquid hydrogen chloride are formed by anisole (pale pink), diphenyl sulphide (purple), triphenylphosphine oxide (pale yellow), and diphenylphosphoryl chloride (yellow). Protonation of the aromatic nucleus therefore may account for the anomalous conductivities of diphenyl sulphide and diphenylphosphinyl chloride. In the series X_3PO

TABLE 2.

$K_{classical}$ for substituted acetic acids, $X{\cdot}CH_2{\cdot}CO_2H$.[10]

X	Me	H	Ph	OMe	I	Br	Cl	F
10^5K	1·34	2·1	5·60	33·5	75	138	155	217

TABLE 3.

Variation of equivalent conductivities with ligands.

(Solutions of approximately the same strength.)

XYO

X	Y = Me	H	Ph
Me	0·43	0·13	0·021
H	0·13	—	0·019
Ph	0·021	0·019	0·0017

XYS

X	Y = Me	Ph
Me	11·8	—
H	0·054	0·030
Ph	—	0·15

X_2SO_2

X	
Me	0·20
Ph	0·51
Cl	—

X_3PO

X	
Ph	9·61
Cl	0·20
F	0·015

Ph·COX

X	
Ph	7·15
Cl	0·046
OEt	0·74

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[9] Peach and Waddington, unpublished observation.

[10] Turner and Harris, " Organic Chemistry," Longmans, Green and Co., London, 1952, p. 364.

[11] Peach and Waddington, *J.*, 1961, 1238.

triphenylphosphine oxide can only act as a base by protonation and since phosphoryl fluoride is not solvolysed it must ionize by protonation: $F_3PO + 2HCl \longrightarrow F_3POH^+ + HCl_2^-$. Phosphoryl chloride can ionize either by loss of a chloride ion to give $POCl_2^+$ or by protonation to Cl_3POH^+. The fact that its equivalent conductivity parallels the size of the negative inductive effect of the chloride group suggests that it is in fact protonated.

Sulphuryl and thionyl chloride have no basic properties in the solvent whereas the corresponding phenyl and methyl sulphones and sulphoxides are moderately strong bases: this is due to the high negative inductive effect of the chlorine, that prevents protonation of the oxygen.

Dinitrogen pentoxide reacts with liquid hydrogen chloride to give nitryl chloride and nitric acid.[12] This reaction is expected from the formulation as nitronium nitrate: $NO_2^+NO_3^- + HCl \longrightarrow NO_2Cl + HNO_3$. Dinitrogen tetroxide, which ionizes as nitrosyl nitrate in many solvents, might similarly be expected to form nitrosyl chloride and nitric acid. If this occurred, addition of boron trichloride would produce nitrosyl tetrachloroborate,[13] a stable orange-red solid, m. p. 25°. As this is not observed it must be concluded that the oxide is too insoluble to react.

All the oxyacids studied, including even the strongest, trifluoromethanesulphonic, failed to act as solvoacids in the system. This casts doubt on the formulation of the reported [14] compounds $HCl,HClO_4$ and HCl,H_2SO_4 as salts of the cation H_2Cl^+ and leads one to suspect that in the preparation of chlorosulphonates in the solvent [15] the actual salt formation may have taken place after the removal of the solvent at low temperature. None of the oxyacid anhydrides studied (SO_2, P_2O_5, N_2O_4) acted as solvoacids in the solvent. This is surprising, in view of the ready formation of fluorosulphinates [16] and fluorophosphates [17] in liquid hydrogen fluoride from the corresponding oxides, but may be due to the insolubility of the oxides in liquid hydrogen chloride.

The authors acknowledge the kind gift of diphenylphosphinyl chloride from Dr. F. G. Mann, F.R.S., and one of them (M. E. P.) acknowledges a maintenance grant from the D.S.I.R.

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD, CAMBRIDGE.

[*Received, January 22nd*, 1962.]

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[17] Sidgwick, " Chemical Elements and their Compounds," Oxford Univ. Press, Oxford, 1950, p. 748.