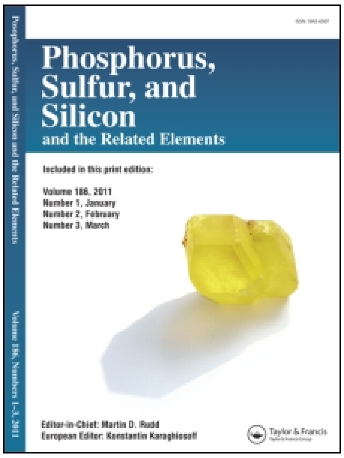

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REACTION OF THIOPHOSPHORYL FLUORIDE AND THIOPHOSPHORYL CHLORIDE WITH DIMETHYL SULPHOXIDE

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REACTION OF THIOPHOSPHORYL FLUORIDE AND THIOPHOSPHORYL CHLORIDE WITH DIMETHYL SULPHOXIDE

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Solid complexes of thiophosphoryl fluoride and thiophosphoryl chloride with dimethyl sulphoxide (DMSO) have been prepared and characterized.

Thiophosphoryl fluoride and thiophosphoryl chloride have been found to behave as Lewis acids towards pyridine and corresponding 1 : 1 complexes have been isolated and characterized.[1] Similar complexes are readily formed with dimethyl sulphoxide (DMSO) which are isolated and characterized by chemical analysis and infrared spectra. These reactions are exothermic.

EXPERIMENTAL

A known amount of pure thiophosphoryl fluoride (≈200 mg) is taken in a reaction vessel provided with vacuum stopcocks and ground glass joints. The vessel is cooled in liquid nitrogen. Dry DMSO (≈1 g) is introduced into the reaction vessel. After an interval of ten minutes, the contents are allowed to attain room temperature (25°C) gradually. Formation of a yellow solid is noted. Excess DMSO is removed at the pump. As the adduct is susceptible to moisture, it is preserved under vacuum or in an atmosphere of nitrogen.

The solid does not have a sharp melting point, but melts over a range of 100–110°C.

A similar yellow product is obtained with thiophosphoryl chloride and DMSO. It melts in the range of 70–75°C.

It has been observed that these complexes are insoluble in most of the common organic solvents.

The composition of these adducts are determined by hydrolytic reaction: a known amount (≈150 mg) of the adduct is treated with 25 ml of sodium hydroxide (2N) containing cadmium hydroxide suspension. As the hydrolytic reaction is found to be very slow at room temperature, it is hastened by warming to 80°C. After the completion of the reaction, (2 hr), the products of hydrolysis are found to contain phosphate, fluoride/chloride, sulphide, sulphite and thiosulphate. These products are estimated quantitatively by standard methods.[3] The analytical results are presented in Table I.

TABLE I

Alkaline hydrolysis of DMSO/$P(S)X_3$ adducts

Adduct taken	Trial no.	Amount of the adduct taken in mg	Sulphide[a] in mg	Sulphite[a] in mg	Thiosulphate[a] in mg	Total sulphur in mg		Total phosphorus in mg		Total fluoride/ chloride in mg	
						Expt.	Cald.	Expt.	Cald.	Expt.	Cald.
Thiophosphoryl fluoride-DMSO	1	141.00	7.76 (34.02%)	0.78 (3.42%)	14.22 (62.34%)	22.76	22.81	21.95	22.04	40.50	40.61
	2	212.00	11.66 (34.02%)	1.18 (3.43%)	21.32 (62.23%)	34.16	34.30	30.05	33.13	60.75	60.99
Thiophosphoryl chloride-DMSO	1	206.80	15.30 (57.061)	0.80 (2.98%)	10.65 (39.75%)	26.75	26.80	25.75	25.89	88.80	89.04
	2	310.20	23.00 (57.22%)	1.10 (2.74%)	16.00 (39.80%)	40.10	40.20	38.65	38.84	132.70	133.50

[a] Expressed as milligrams of sulphur.

TABLE II

Infrared absorption frequencies (cm^{-1}) of DMSO, PSF$_3$, PSCl$_3$ and their complexes

	νS=O	ν_{asy}C–S	ν_{asy}C–S	νP=S	νP–F/P–Cl	
DMSO	1050	700	670	—	—	—
PSF$_3$	—	—	—	700	955	995
PSCl$_3$	—	—	—	750	430	550
PSF$_3$:DMSO	1020	690	650	640	860	940
PSCl$_3$:DMSO	990	685	640	690	420	530

The infrared spectra of the adducts in nujol are recorded on a Carl–Zeiss UR10 Spectrophotometer and their characteristic absorption frequencies are presented in Table II.

RESULTS AND DISCUSSION

The analytical results in Table I show that every mole of thiophosphoryl halide (Fluoride/Chloride) is associated with one mole of DMSO.

The infrared spectra data, in Table II, shows bathochromic shifts of νS=O and νC–S in the adducts. This indicates that DMSO is coordinated through oxygen to thiophosphoryl halide. Other DMSO complexes also show such bathochromic shifts.[4] If coordination had occurred through sulphur instead of oxygen of DMSO then a hypsochromic shift of νS=O and νC–S should have been observed. Shifts in νP–F/νP–Cl and νP=S to lower regions in the adducts clearly indicate that phosphorus of thiophosphoryl halide has coordinated with oxygen of DMSO.

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