temperature is lowered, the kinetic energy is lowered and there is greater tendency for ordering of the cations resulting in the separation of crystalline phases with definite stoichiometry. Cooling NaF–LnF_3 mixtures reflects this tendency by exhibiting the exsolution behavior which occurs as is indicated by the lower temperature phase boundary of the cubic phase. A somewhat opposite tendency is introduced as the reduction in polarizability of the lanthanide (with increasing atomic number of Ln) tends to allow increasing compositional variability in the low-temperature hexagonal and orthorhombic crystalline phases.

Stoichiometry of 5Na·9LnF$_3$.—The formula of this phase has been established by entirely empirical microscopic and X-ray diffraction analytical methods which are considered to be accurate within ±0.5 mole %. Investigation of the structure of the orthorhombic form of the compound has not yet advanced to the point that the exact stoichiometry is certain. Accordingly, confirmation of the formula of this compound necessitates completion of the structural investigation currently in progress.

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Contrasting Behavior of Boron Trifluoride and Phosphorus Pentafluoride toward Sulfolane[1]

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Sulfolane forms a 1:1 complex with boron trifluoride. The complex has $\delta^{19}F = +144.1$ ppm (δ relative to CCl_3F) and $\delta^{11}B = +19.2$ ppm (δ relative to trimethyl borate). In contrast to this, sulfolane forms no stable solid complex with phosphorus pentafluoride, though the ^{19}F resonance shows evidence of interaction and of P–F bond breaking.

Introduction

Sulfolane has been found to be a good aprotic solvent, dissolving molecular and ionic substances[3] without being attacked by even such strongly reactive species as the nitronium ion.[4] In this laboratory it has been used for nmr studies of pyridine–Lewis acid adducts[5] because its very low proton basicity ($pK_{BH^+} = -12.88$)[6] suggested that it might be a very weak Lewis base, unable to displace a strong base, such as pyridine, from its adducts with Lewis acids.

However, despite some reported failure[7] to prepare adducts of Lewis acids with sulfones, Lindqvist and Einarsson[8a] have prepared solid adducts of dimethyl and diphenyl sulfones with antimony tri- and pentachloride, the structure of $Me_2SO_2 \cdot SbCl_5$ having been determined,[8b] and Langford and Langford[9] succeeded in preparing weak hygroscopic complexes of sulfolane itself with anhydrous cobalt(II) salts. More recently Laughlin[10] has found that 1 mole of methyl *n*-dodecyl sulfone dissolved in benzene would take up 1 mole of boron trifluoride, though he could isolate no solid complex, and Drago, *et al.*,[11] found spectroscopic evidence for charge-transfer interaction with iodine. Lastly, in a footnote, Alder and Whiting[12] observed that sulfolane and boron trifluoride react to give a solid product.

These findings suggested that although sulfones are such weak Brønsted bases that they are not protonated in 100% H_2SO_4, they may be good Lewis bases. Accordingly, it was decided to investigate the action of boron trifluoride and phosphorus pentafluoride on sulfolane.

Experimental Section

Sulfolane (kindly supplied by the Shell Chemical Co., Shell Center, London S.E.1, U. K.) was purified in 500-ml batches by first treating with 25 ml of "100 volume" hydrogen peroxide and 25 ml of 96% H_2SO_4, which together oxidize any sulfoxide present. The remaining hydrogen peroxide and water were distilled off under vacuum and then the main body of solvent was collected by vacuum distillation, bp 90–100° (4–7 mm), dry nitrogen being passed through the vacuum leak. This sulfolane, now water-

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[1] Tetrahydrothiophene 1,1-dioxide; tetramethylene sulfone.

[2] ICI Research Fellow. This work was supported by the University of Sheffield. Thanks are expressed to the Shell Chemical Co. for a gift of sulfolane.

[3] R. S. Drago in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965.

[4] (a) S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961); (b) J. Jones and J. Jones, *Tetrahedron Letters*, **31**, 2117 (1964).

[5] J. G. Jones, Abstracts of Chemical Society (London), Anniversary Meetings, Glasgow, 1965, p X6.

[6] S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 113 (1964).

[7] F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).

[8] (a) T. Lindqvist and P. Einarsson, *Acta Chem. Scand.*, **13**, 420 (1959); (b) quoted by Lindqvist in "Inorganic Adduct Molecules of Oxo-Compounds," Springer-Verlag, Berlin, 1963.

[9] C. H. Langford and P. O. Langford, *Inorg. Chem.*, **1**, 184 (1962).

[10] R. G. Laughlin, *J. Org. Chem.*, **25**, 864 (1960).

[11] R. S. Drago, B. Wayland, and R. L. Carlson, *J. Am. Chem. Soc.*, **85**, 3125 (1963).

[12] R. W. Alder and M. C. Whiting, *J. Chem. Soc.*, 4707 (1964).

white, was redistilled *in vacuo* from crushed sodium hydroxide, as described by Burwell and Langford.[13] Boron trifluoride and phosphorus pentafluoride were used directly from lecture bottles purchased from The Matheson Co., East Rutherford, N. J.

Complex preparation was carried out in a Kel-F vacuum pressure vessel fitted with Kel-F valves and a detachable Kel-F top. This was connected to a copper vacuum line fitted with a Monel vacuum pressure gauge as described in two recent publications.[14]

Sulfolane was loaded into the Kel-F vessel under dry nitrogen, and the capped vessel was connected to the vacuum line. The reaction vessel was pumped out, and then the volatile fluoride was gradually admitted to the stirred reaction mixture. In each case the reaction mixture grew hot as volatile fluoride was absorbed. When no further volatile fluoride appeared to be absorbed, 2 atm of excess pressure was left above the reaction mixture for 1 hr. This procedure gave a solid white mass of square platelike crystals from sulfolane and boron trifluoride, but in the case of phosphorus pentafluoride the sulfolane remained liquid, with only a very small quantity of fine white needles suspended in the fluid. Excess pressure of volatile fluoride was the nreleased, and the sealed reaction vessel was taken from the vacuum line and opened in the drybox. The sulfolane–boron trifluoride complex remained as a white solid, but the small needlelike crystals suspended in the sulfolane–phosphorus pentafluoride reaction mixture quickly disappeared when the excess pressure of phosphorus pentafluoride was released.

Quantitative Experiments.—In these, a dry glass vial fitted with a small Teflon-covered magnetic stirrer and containing a known weight of sulfolane was loaded into the Kel-F reaction vessel and treated with volatile fluoride as already described. After 1 hr, the Kel-F vessel was opened in the drybox and the inner glass vessel was sealed with a gastight polyethylene cap. Then the inner vessel and its contents were weighed, and thus the combined weight of boron trifluoride or dissolved weight of phosphorus pentafluoride could be determined.

Nmr Experiments.—Solutions of the boron trifluoride complex in sulfolane or dichloromethane were prepared and put into nmr tubes in the drybox. The saturated solution of phosphorus pentafluoride in sulfolane was loaded directly into nmr tubes in the drybox. In all cases the tubes were sealed with Teflon tape. Trichlorofluoromethane was used as the internal standard in ^{19}F resonance measurements, and trimethyl borate as the external standard in ^{11}B resonance measurements. ^{19}F measurements were made at 60 Mcps, ^{11}B and ^{31}P measurements at 20 Mcps on an AEI RS.2 spectrometer, using calibration by field-modulated side bands.

Infrared Measurements.—These were performed on the boron trifluoride complex, using Perkin-Elmer Infracords with NaCl and KBr optics. The best spectra were obtained by using the freshly prepared complex in potassium chloride disks.

Results and Discussion

Sulfolane–BF$_3$.—The quantitative experiments showed that these combined together in a 1:1 mole ratio to produce square, white plates of a stable but very hygroscopic complex. *In vacuo* the complex slowly lost boron trifluoride, reverting to sulfolane. It melted at 37°, nearly 9° higher than sulfolane itself, and lost boron trifluoride rapidly above its melting point. The complex dissolved freely in benzene, dichloromethane, and chloroform, but not in petroleum ether, carbon tetrachloride, or chlorofluorocarbon fluids.

TABLE I

Solvent	Complex molarity	δ, ppm from internal CCl_3F
Sulfolane	2.9	+142.5
	1.45	144.5
	0.725	143.9
	Av	143.6 ± 0.8
Dichloromethane	0.764	144.3
	0.508	145.3
	0.384	145.2
	Over-all av	+144.1

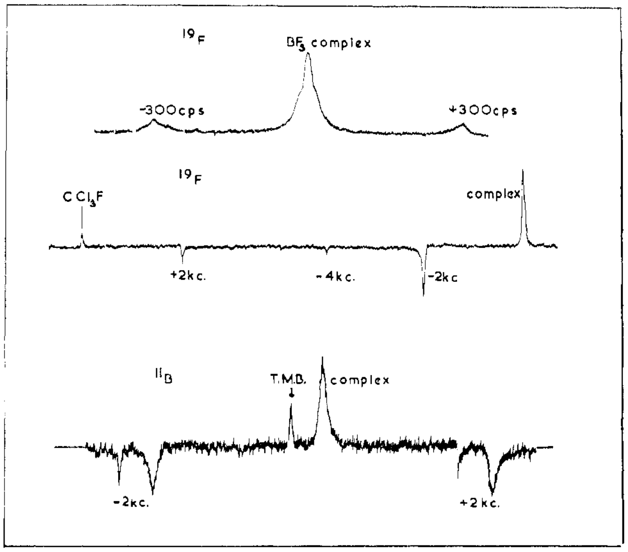

Figure 1.—^{19}F and ^{11}B nmr spectra of sulfolane–BF_3 complex in sulfolane.

Further evidence for complex formation is provided by the ^{19}F nmr results (Table I, Figure 1). The ^{19}F resonance is shifted substantially to high field of boron trifluoride itself ($\delta = +129$ ppm[15]), as in other boron trifluoride complexes. The present upfield shift on complex formation is less than that in the formation of BF_3–ether complexes[15] ($\delta = +153$ ppm) and the BF_3–pyridine complex[15] ($\delta = +149.4$ ppm). Brownstein's results indicate that there is no general relationship between the ^{19}F shifts of BF_3–donor complexes and their heats of formation; the pyridine complex with a large heat of formation (−50.6 kcal/mole or even the lower value of −30 kcal/mole now preferred[16]) has a lower positive ^{19}F shift (149.4 ppm) than the ether complexes (~153 ppm) with their lower heats of formation (12–13 kcal/mole).

The ^{19}F resonance of the complex in sulfolane solution can be described as an incompletely resolved quartet, with quadrupole broadening[17] and perhaps some broadening due to an exchange process. This cannot be a slow exchange process, because if it were, ^{19}F signals characteristic of both free and complexed boron trifluoride would be observed. On the other hand, one signal which varies little with concentration is consistent with a rapid exchange between "bound" and "free" boron trifluoride molecules, with the degree of

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[13] R. L. Burwell and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959).

[14] (a) H. H. Hyman in "Non-Aqueous Solvent Systems" T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965; (b) M. Kilpatrick and J. G. Jones in "The Chemistry of Non-Aqueous Solvents," Vol. II, J. J. Lagowski, Ed., Academic Press Inc., New York, N. Y., to be published.

[15] S. Brownstein, A. M. Eastham, and G. A. Latremouille, *J. Phys. Chem.*, **67**, 1028 (1963).

[16] F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

[17] J. Bacon, R. J Gillespie, and J W. Quail, *Can. J. Chem.*, **41**, 3063 (1963).

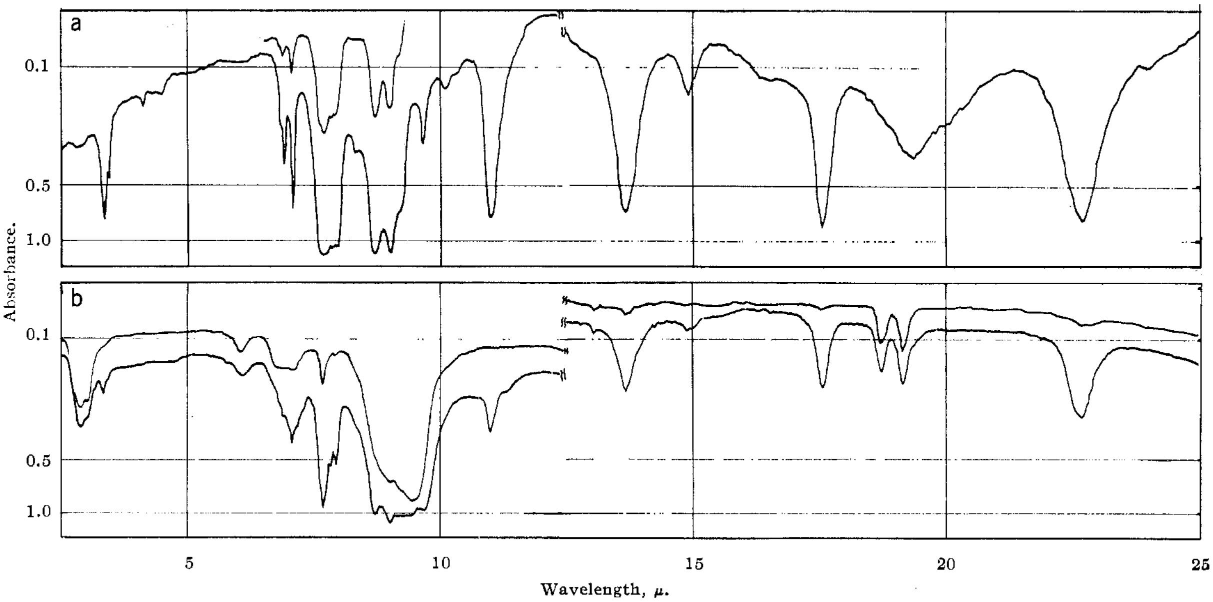

Figure 2.—(a) Infrared spectrum of sulfolane. (b) Infrared spectrum of BF_3–sulfolane complex in a KCl disk.

dissociation varying little in the concentration range studied, thus preserving constant mole fractions of bound and free molecules.

The ^{11}B resonance of a sulfolane solution of the complex was a broad single peak 19.2 ppm upfield from external trimethylborate, with peak position independent of concentration; this is 12.6 ppm to high field of uncomplexed boron trifluoride.[18]

In view of the quadrupole moment of the ^{11}B nucleus and the unsymmetrical nature of the boron environment in the complex, the broadness, 90 cps at half-height, of the ^{11}B resonance is not surprising. A boron shift of +19.2 ppm for the sulfolane complex can be compared with ones of +17 to +21 ppm for other boron trifluoride complexes.[18,19] A recent article[20] has claimed that ^{11}B chemical shifts in complexes can be taken as a measure of ligand donor strengths. While this may be true for a limited series of ligands, figures already in the literature prove it to be generally untrue. For example, tetrahydrofuran forms a more stable complex with boron trifluoride than does diethyl ether ($\Delta H_f = -13.4$ kcal/mole as against -10.9 kcal/mole) and has a greater positive shift (+19.0 ppm as against +18.2 ppm). On the other hand, from the figures of Gates, *et al.*,[20] the ^{11}B shift of the pyridine–BF_3 complex can be estimated as only +16.6 ppm[21] relative to trimethyl borate, despite the very high heat of formation of the pyridine complex. In our own case, the ^{19}F shift seems to give the sulfolane complex as considerably less stable than the tetrahydrofuran complex, yet the ^{11}B chemical shift would seem to indicate that it is slightly more stable.

Infrared Results.—The infrared spectra of sulfolane itself between silver chloride plates and of the sulfolane–BF_3 complex in a KCl disk are presented in Figure 2, and the assignments are presented in Table II.

TABLE II

Freq for complex, cm^{-1}	Assignment	Freq for sulfolane, cm^{-1}
3400	HF, etc., from hydrolysis	...
2930	C—H str	2990 2900
1440	CH_2 scissoring	1450
1400		1410
1290 1265 sh 1245 sh	S=O asym str	1300 1270 1250
1150–1020, max at 1040	B—F asym str + B—O + SO sym	
	S=O sym str	1150 1110
910	CH_2 rocking	910
771	ν_1 B—F sym str	...
735	>C—C< vibration	735
670	C—S str	670
570	Out-of-plane C—C def + C—S—C bending	570
534 521	ν_4 bending of B—F	...
	O=S=O bending	517
440	SO_2 rocking	440

The symmetric and asymmetric stretching frequencies of sulfones have recently been discussed by Bavin,[22] *et al.*, and the partial infrared spectra of some unsaturated thiophene 1,1-dioxides have been presented by Krug and Yen.[23]

The assignments in Table II also lean heavily on a theoretical and experimental investigation of dimethyl sulfone by Fujimori.[24]

The main features of the complex absorption are: (1) A strong, broad band at 3200–3400 cm^{-1}, assigned to hydrogen fluoride liberated on hydrolysis of the complex. (2) Strong, new broad absorption centered

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(18) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

(19) T. P. Omak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1333 (1959).

(20) P. N. Gates, E. J. McLauchan, and E. F. Mooney, *Spectrochim. Acta*, **21**, 1445 (1965).

(21) Gates, *et al.*, give the shift as +10.0 ppm relative to uncomplexed BF_3. If this is taken as being +6.6 ppm from trimethyl borate, the pyridine–BF_3 complex must have $\delta^{11}B$ as +16.6 ppm relative to trimethyl borate.

(22) P. M. G. Bavin, E. W. Gray, and A. Stephenson, *Spectrochim. Acta*, **16**, 1312 (1959).

(23) R. E. Krug and T. F. Yen, *J. Org. Chem.*, **21**, 1083 (1956).

(24) K. Fujimori, *Bull. Chem. Soc. Japan*, **32**, 1374 (1959).

at 1100 cm^{-1}, due to boron–fluorine stretching, analogous to the ν_3 mode of the fluoborate ion. This must, of course, be coupled with B–O stretching modes, which occur in the same region.[25] (3) A broad band in sulfolane, centered at 520 cm^{-1} and ascribed to an O=S=O bending mode, disappears and is replaced by a doublet at 521 and 534 cm^{-1}, recognizable as analogous to the degenerate ν_4 B–F bending mode in BF_4^-. The doublet is a consequence of the change of symmetry around the boron atom from T_d to C_{3v}. (4) Complex formation brings about slight ($\sim$10 cm^{-1}) lowering of the S=O stretching frequencies. Thus, there is good infrared evidence for complex formation.

The Action of Phosphorus Pentafluoride on Sulfolane.—It has been stated that phosphorus pentafluoride is a slightly weaker Lewis acid than boron trifluoride[26] so its failure to form a solid complex with sulfolane at room temperature is not too surprising. Combining weight experiments at 20° indicate that sulfolane takes up 50% of the phosphorus pentafluoride needed to form a 1:1 complex.

The ^{19}F spectrum of phosphorus pentafluoride dissolved in sulfolane has a chemical shift of +62.2 ppm to high field of CCl_3F and is a single broad peak showing complete loss of phosphorus–fluorine splitting (Figure 3). Solutions of our sample of PF_5 in other polar solvents such as alcohol, acetone, and acetic anhydride showed spectra typical of a phosphorus pentafluoride–solvent complex,[27] with no distinction between axial and equatorial fluorine due to rapid exchange of the form[26] $PF_5 \cdot \text{base} \rightleftharpoons PF_5 + \text{base}$, but with the phosphorus–fluorine splitting preserved. (For example, PF_5 in ethanol has $\delta^{19}F = +70.1$ ppm relative to CCl_3F; $J_{P-F} = 706$ cps. PF_5 does not dissolve in an inert solvent to an extent sufficient for its ^{19}F resonance to be detected unless high pressures or low temperatures, both inaccessible to this author, are employed.)

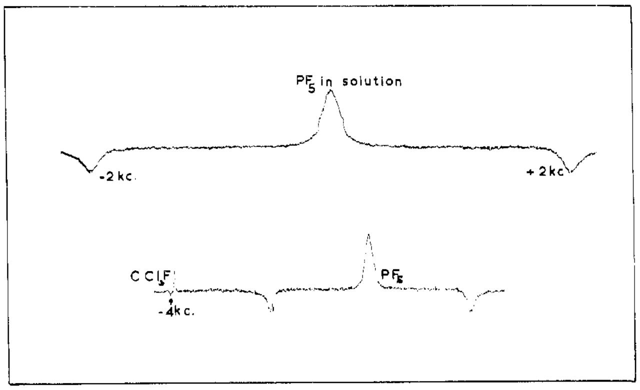

Figure 3.—^{19}F nmr spectra of a saturated solution of PF_5 in sulfolane.

The loss of phosphorus–fluorine splitting could be accounted for in terms of ionization of the phosphorus pentafluoride, with rapid fluorine exchange between ionic and molecular phosphorus(V) fluoride species (eq 1). Similar ionization has recently been encountered with solutions of phosphorus pentachloride in acetonitrile and nitrobenzene.[28]

$$\text{sulfolane} + PF_5 \rightleftharpoons PF_4^+(\text{solv}) + F^-(\text{solv}) \qquad (1a)$$

$$\text{sulfolane} + 2PF_5 \rightleftharpoons PF_4^+(\text{solv}) + PF_6^-(\text{solv}) \qquad (1b)$$

If the approximate fast-exchange formula[29] (eq 2)[30]

$$\tau^{-1} = 4\pi\Delta\nu_0^2/\delta'\nu \qquad (2)$$

is applied to the broad ^{19}F resonance with its line width at half-height of 200 cps, then the average exchange lifetime of a fluorine nucleus is 2.76×10^{-5} sec.

Investigation of ^{31}P resonance proved unsuccessful, no signal being detected owing to PF_5 dissolved in sulfolane. This may have been because the resonance was too broad or because of the much lesser sensitivity of the nmr spectrometer toward ^{31}P relative to ^{19}F.

Further investigation of the action of sulfolane on PF_5, in an inert solvent and at lower temperatures, appears worthwhile. The present investigations establish that sulfolane is not such an inert solvent as had been thought.

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(25) B. P. Susz and P. Chaladon, *Helv. Chim. Acta*, **41**, 699 (1958).

(26) E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960).

(27) S. Johnson, Ph.D. Thesis, Purdue University, June 1963.

(28) V. P. Petro, J. Howatson, and S. G. Shore, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965, p 33-O.

(29) E. F. Caldin, "Fast Reactions in Solution," Blackwell Scientific Publications, Oxford, U. K., 1964, Chapter 11.

(30) The assumptions used in this calculation are: (a) $\tau \ll T_2$; (b) ν_0 = 740 cps, the average value of J_{P-F} in PF_6 complexes (E. L. Muetterties and W. D. Phillips, *Advan. Inorg. Chem. Radiochem.*, **4**, 245 (1962)); (c) $\delta\nu' = 200 - 10 = 190$ cps, 10 cps being taken as the PF_5 line width in the absence of exchange.