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Reaction of Phosphoryl-Compounds with Boron(III)-fluoride

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Adducts of the general formula $R_3PO \cdot BF_3$ react with BF_3 to give $R_3PO \cdot BF_3 \cdot BF_3$. NMR- and conductometric studies show that both adducts are ionized in nitrobenzene. Ionization is promoted by increase in donor strength of the PO-compound. Rapid intermolecular exchange of BF_3 is found at 25° with the adducts of phosphoryl donors with the exception of TMP and of HMPA-complex.

Introduction

PhPOF₂ is known to react with BCl₃ to give PhPOCl₂ and BF₃.¹ This work has now been extended by means of NMR and conductometric techniques, to include phosphoryl compounds of various donor properties, namely (with increasing donor strength): POCl₃, PhPOF₂, PhPOCl₂, Ph₂POF, Ph₂POCl, (CH₃O)₃PO (TMP), n-(C₄H₉O)₃PO (TBP), Ph₃PO (TPO), [(CH₃)₂N]₃PO(HMPA).

Experimental Section

PhPOF₂ and Ph₂POF were prepared from the respective chlorides with Na₂SiF₆.² Ph₂POCl was obtained by oxidation of Ph₂PCL with Cl₂ followed by solvolysis with SO₂.³ The commercial products of POCl₃, PhPOCl₂, TMP, TBP, HMPA were distilled prior to use ($\kappa < 10^{-7}$ ohm⁻¹ cm⁻¹ at 25°). Ph₃PO was purified by recrystallization from absolute benzene.

Nitrobenzene was purified chromatographically (Al₂O₃),⁴ dried over CaCl₂ and fractionally distilled under dry N₂. It was further purified by means of molecular sieves (Linde A 4); b.p. 79.8°/9 mm, $\kappa = 3.10 \cdot 10^{-8}$ ohm⁻¹ cm⁻¹, water content: $9.10 \cdot 10^{-4}$ mole/l.

(1) V. Gutmann, J. Imhof, and F. Mairinger, *Mh. Chem.* 99, 1615 (1968).

(2) V. Gutmann, P. Heilmayr, and K. Utvary, *Mh. Chem.* 92, 196 (1961).

(3) E. L. Gefter, *Zhur. Obschei. Khim.* 28, 1338 (1958); ref. C 130, 9202 (1959).

(4) F. F. Cheshko, L. K. Bydylo, V. P. Naumenko, and O. E. Shvechenko, *Zhur. Priklad. Khim.* 34, 908 (1961); ref. CA 55, 21002 g (1961).

Boron(III) fluoride was used without any further purification. The NMR-spectra were recorded with a RS 2-spectrometer (Associated Electric Ind., England) at 60 Mc (¹H and ¹⁹F) and at 25 Mc (³¹P). For ¹H-resonance (CH₃)₄Si (TMS, 1%) and for ¹⁹F-resonance CCl₃F (10%) was used as internal standard while the ³¹P-resonance spectra were recorded with 85% H₃PO₄ as external standard. The samples containing different BF₃-donor molar ratios were recorded in the absence of a solvent.

Conductometric titrations of BF₃ with the donor were carried out in nitrobenzene under dry N₂ at 25°. Molar conductivities (λ_m) are based on the concentration of BF₃, measured in mole BF₃ per 1000 ml nitrobenzene.

Results

In the BF₃ systems of POCl₃, PhPOF₂, PhPOCl₂, Ph₂POF and Ph₂POCl the chemical shift of the ³¹P-signals is decreased by increase in BF₃-concentration (Figure 1) while the ¹⁹F-signals of PhPOF₂ and Ph₂POF are shifted upfield (Figure 2) to the same extent as the ³¹P-signals are shifted downfield (Table I).

In the systems TMP-BF₃, TBP-BF₃, HMPA-BF₃ (Table I) signals for the free donor and the complex were detected separately. In the system TMP-BF₃, the ¹H-signals of the complex are shifted downfield (B_H) with respect to free TMP, while the ³¹P-signal undergoes a highfield shift. The ³¹P-signals of the three halogen free donors (TMP, TBP, HMPA) are very broad unresolved multiplets.

In the system TBP-BF₃ only the ³¹P-signals are sufficiently separated. B_P may be attributed to the complex TBP · BF₃. The signal D_H is shifted slightly downfield with increasing BF₃ concentration owing to solvent effects. Two lines of the signal D_H are lost in the noise so that this signal appears as a quartet instead of the expected hextet (CH₃ = A, -CH₂-P = O = D). The chemical shift of the other ¹H-signals are nearly independent of the BF₃ concentration.

The ¹H-spectra of the system HMPA-BF₃ show two doublets, A_H for free HMPA and B_H for the complex

Table I. Some NMR data for the BF_3 -systems with PhPOF_2 , Ph_2POF , TMP , TBP and HMPA

Donor	X	NMR	N	M	δ	J	M	δ	J	M	δ	M	δ	J
PhPOF_2	0.0	^{19}F	2	2	65.0	1100 PF								
	0.0	^{31}P	3	3	-11.4	1100 PF								
	0.75	^{19}F	3	2	69.1	1127 PF	1	142						
Ph_2POF	0.0	^{19}F	2	2	-15.3	1125 PF								
	0.0	^{31}P	2	2	73.8	1010 PF								
	1.11	^{19}F	6	2	-39.6	1010 PF								
TMP	0.0	^1H	2	2	87.0	1050 PF	2	88.4	1080 PF	1	135.2	1	143	
	0.0	^{31}P	m	m	3.70	11 PH								
	0.42	^1H	4	2	-2.59	11 PH	2	4.21	11 PH					
TBP	0.0	^{31}P	m	m	0.0									
	0.0	^1H	m	3	0.904		m	1.01		m	1.50	4	3.95	7.2 HHP
	0.96	^1H	m	3	0.6		m	1.06		m	1.67	4	4.27	6.4 HHP
HMPA	0.0	^{31}P	m	m	0.6		m	6.56						
	0.0	^1H	2	2	2.51	10.4 PH								
	0.33	^1H	4	2	-23.0	10.0 PH	2	2.71	11.4 PH					
	0.33	^{31}P	m	m	2.57									
	0.33	^{31}P	m	m	-23.6									

X = mole ratio BF_3/donor , N = total number of signal lines in the spectrum, M = multiplet-structure (1 = single peak, 2 = doublet etc.), δ = chem. shift in ppm (Varian scale for ^1H), J = coupling constant cycl./sec., m = unresolved multiplet(s) A, B, C, D.. symbols for the signals or group of lines in the spectrum.

$\text{HMPA} \cdot \text{BF}_3$. The signal B_H of the complex appears downfield with respect to the ^1H -signals of the free HMPA.

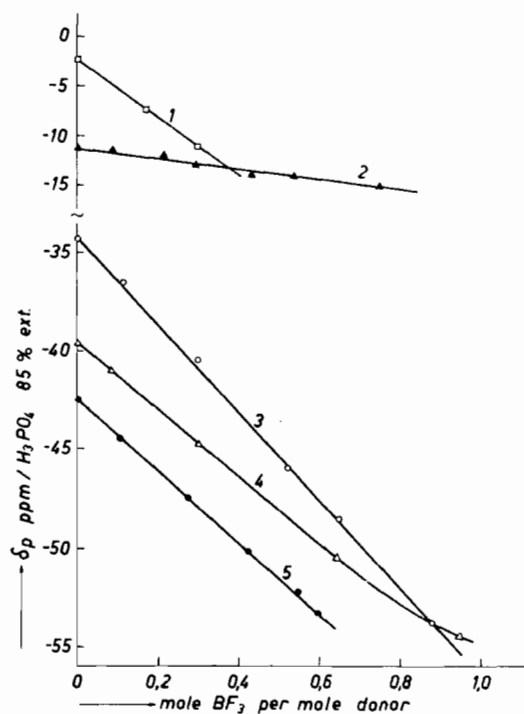


Figure 1. ^{31}P chemical shift vs. mole ratio $\text{BF}_3:\text{D}$ in the systems $\text{POCl}_3\text{-BF}_3$ (1), $\text{PhPOF}_2\text{-BF}_3$ (2), $\text{PhPOCl}_2\text{-BF}_3$ (3), $\text{Ph}_2\text{POF-BF}_3$ (4) and $\text{Ph}_2\text{POCl-BF}_3$ (5).

The chemical shift of coordinated BF_3 found in the range 140-150 ppm/ CCl_3F is independent of the BF_3 concentration but is slightly altered by variation of the donor.

The low solubility of $\text{Ph}_3\text{PO} \cdot \text{BF}_3$ in inert solvents made an investigation of this system by NMR impossible.

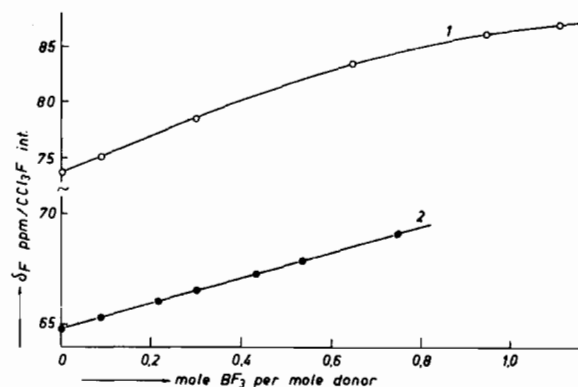


Figure 2. ^{19}F chemical shift vs. mole ratio $\text{BF}_3:\text{D}$ in the systems $\text{Ph}_2\text{POF-BF}_3$ (1) and PhPOF-BF_3 (2).

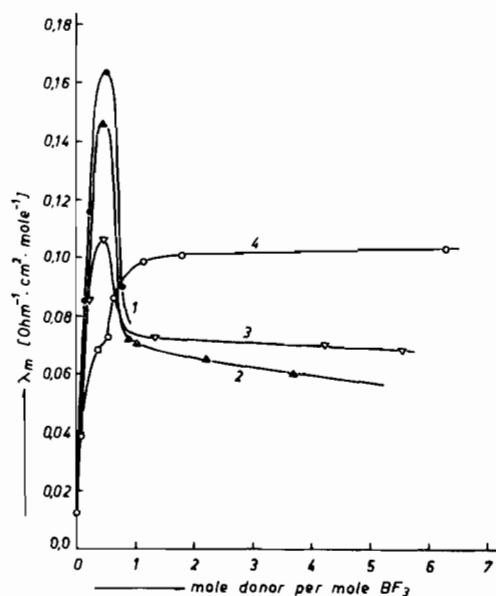


Figure 3. Molar conductance vs. mole ratio $\text{Ph}_2\text{POCl}:\text{BF}_3$ in nitrobenzene $c_{\text{BF}_3} = 0.317 \text{ m}$ (1), $c_{\text{BF}_3} = 0.296 \text{ m}$ (2), $c_{\text{BF}_3} = 0.174 \text{ m}$ (3), $c_{\text{BF}_3} = 0.0854 \text{ m}$ (4).

The molar conductances in nitrobenzene reach a maximum at a molar ratio of 0.5 mole donor per mole BF_3 (Figure 3, 4, 5).

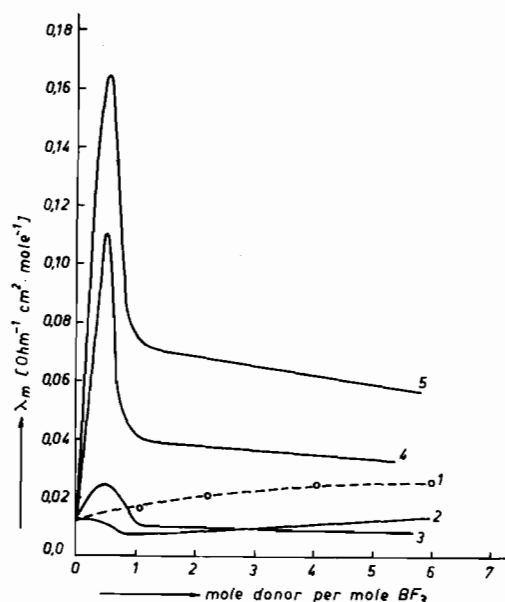


Figure 4. Molar conductance vs. mole ratio D. BF_3 in nitrobenzene at $c_{\text{BF}_3} = 0.3$. $\text{POCl}_3\text{-BF}_3$ (1), $\text{PhPOF}_2\text{-BF}_3$ (2), $\text{PhPOCl}_2\text{-BF}_3$ (3), $\text{Ph}_2\text{POF-BF}_3$ (4) and $\text{Ph}_2\text{POCl-BF}_3$ (5).

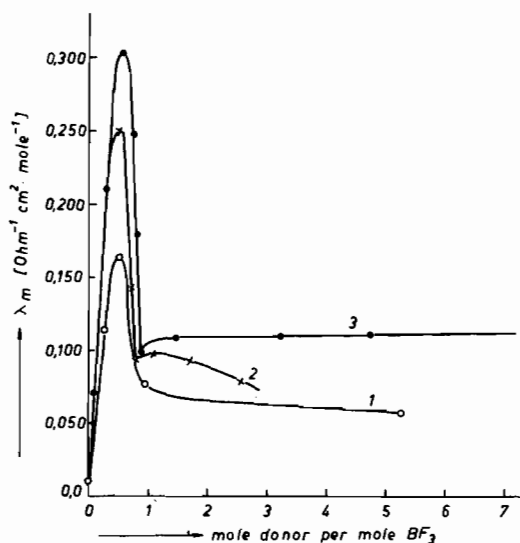


Figure 5. Molar conductance vs. mole ratio D. BF_3 in nitrobenzene at $c_{\text{BF}_3} = 0.3$. $\text{Ph}_2\text{POCl-BF}_3$ (1), TBP-BF_3 (2) and TMP-BF_3 (3).

The dependence of the molar conductance on the BF_3 concentration in the system $\text{Ph}_2\text{POCl-BF}_3$ is shown in Figure 3. It can be seen that the maximum conductivity (at the mole ratio $\text{D}:\text{BF}_3 = 0.5$) is increased by increasing the BF_3 concentration in contrast to the behaviour expected for a weak electrolyte. On the other hand, the conductance at mole ratio 1:1 is increased by decreasing the BF_3 concentration and thus shows the behaviour typical of a weak electrolyte.

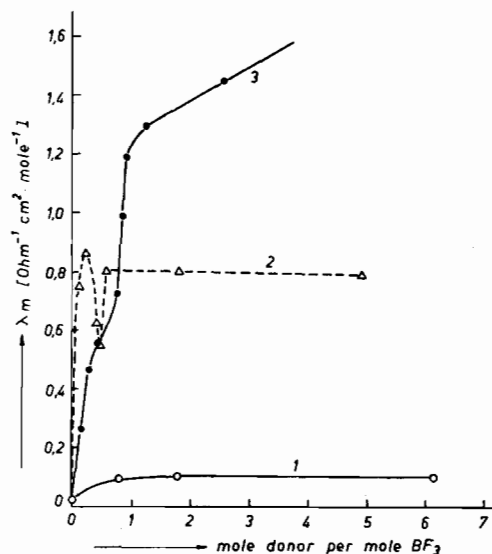


Figure 6. Molar conductance vs. mole ratio D. BF_3 in nitrobenzene at $c_{\text{BF}_3} = 0.085$. $\text{Ph}_2\text{POCl-BF}_3$ (1), HMPA-BF_3 (2) and $\text{Ph}_3\text{PO-BF}_3$ (3).

The titrations for the $\text{POCl}_3\text{-}$, $\text{PhPOF}_2\text{-}$, $\text{PhPOCl}_2\text{-}$, $\text{Ph}_2\text{POF-}$, $\text{Ph}_2\text{POCl-}$ (Figure 4), TBP- , TMP- , (Figure 5) BF_3 systems were all carried out at the same BF_3 concentration (0.300 mole $\text{BF}_3/1$ nitrobenzene). The conductances at the maximum depend on the nature of the donor. No maximum is found in the system $\text{POCl}_3\text{-BF}_3$ (dotted line in Figure 4), possibly owing to hydrolysis of POCl_3 . The $\text{BF}_3\text{-Ph}_3\text{PO}$ system had to be measured at low BF_3 concentration and showed the same type of curve as Ph_2POCl at the same concentration.

Discussion

The NMR-spectra of the system $\text{Ph}_2\text{POF-BF}_3$ and $\text{PhPOF}_2\text{-BF}_3$ (Table I) show multiplet structures caused by the coupling of phosphorus with fluorine. The ^{19}F -signal of Ph_2POF and PhPOF_2 shows a doublet, the ^{31}P -signal of Ph_2POF a doublet and that of PhPOF_2 a triplet within the investigated composition range. The ^{19}F and the ^{31}P chemical shift of the donor depends strongly on the mole ratio $\text{BF}_3:\text{D}$ (Figure 1, 2). This is evidence for the presence of donor-acceptor compounds. According to IR-measurements adduct formation in the system $\text{PhPOF}_2\text{-BF}_3$ is known to occur through O-coordination,⁵ and this is in accordance with the NMR results, which exclude the formation of $[\text{Ph}_2\text{PO}]^+[\text{BF}_4]^-$ and $[\text{PhPOF}]^+[\text{BF}_4]^-$, for which ^{31}P should give a single peak in the system $\text{Ph}_2\text{POF-BF}_3$ and doublet in the system $\text{PhPOF}_2\text{-BF}_3$. The absence of ionized units in the adduct $\text{PhPOF}_2\text{-BF}_3$ is also seen from the results presented in Figure 7.

The fluorine chemical shift of Ph_2POF is increased by addition of BF_3 . At 25° the system is saturated with BF_3 at a mole ratio $\text{BF}_3:\text{D} = 1.1:1$. In the range of excess BF_3 (between the molar ratios 1:1 and 1.1:1) a second doublet appears in the ^{19}F -spec-

(5) V. Gutmann and E. Wychera, *Mh. Chem.* 96, 828 (1965).

trum (88.4 ppm/CCl₃F), which is shifted upfield with respect to the doublet of Ph₂POF · BF₃ (87.0 ppm/CCl₃F). In this composition range a second ¹⁹F-signal for coordinated BF₃ is found, namely at 135 ppm with respect to CCl₃F. This signal is shifted downfield with respect to BF₃ in Ph₂POF · BF₃ (142 ppm/CCl₃F), just as the ¹⁹F-signal of [B₂F₇]⁻ occurs at lower field⁶ than that of [BF₄]⁻, and must be attributed to a species which contains more than 1 mole BF₃ per mole Ph₂POF.

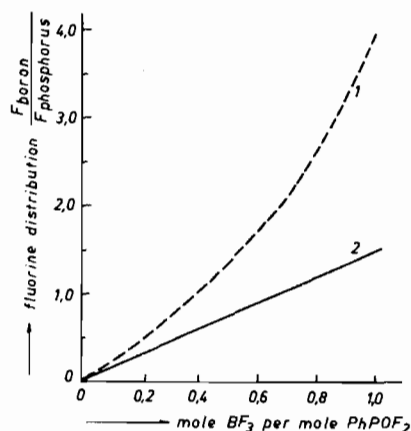
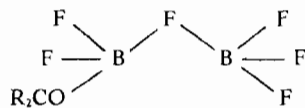


Figure 7. Fluorine distribution of $F_{\text{boron}}/F_{\text{phosphorus}}$ vs. mole ratio BF₃ · PhPOF₂, expected for [PhPOF]⁺[BF₄]⁻ (1), found and calcd. for PhPOF₂ · BF₃ (2).

Such compounds have been described in systems of the type R₂CO–BF₃ which have been formulated as:⁷

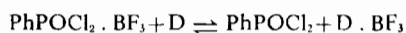


The [B₂F₇]⁻ ion is known to lose one mole of BF₃ easily⁶ and likewise Ph₂POF · BF₃ · BF₃ could not be isolated.

In the ¹⁹F-spectra (except in the POCl₃–BF₃ system) only the signal of coordinated BF₃ is present (140–150 ppm/CCl₃F, POCl₃–BF₃ 135 ppm/CCl₃F).

The molar conductivities in nitrobenzene (Figure 4, 5, 6) at molar ratios of D:BF₃ = 0.5:1 (λ_{0.5}) and D:BF₃ = 1:1 (λ_{1.0}) are increased by increasing strength of the phosphoryl donor D indicating higher ionization by increasing donor properties (Table II), but POCl₃ and HMPA do not obey this rule.

The K_{DA} values derived from ³¹P–NMR measurements⁹ for the reactions



also increase with increasing values of DN_{SbCl₅}.

The ionization at mole ratios D:BF₃ = 1:0 may be regarded as due to autoionization



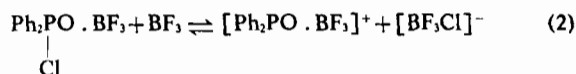
(6) J. J. Harris, *Inorg. Chem.* 5, 1627 (1966).

(7) R. J. Gillespie and J. S. Hartmann, *Can. J. Chem.* 46, 2147 (1968).

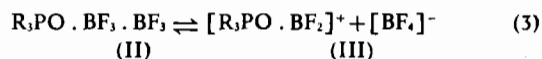
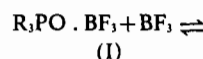
Table II. Conductances in Phosphoryldonor–BF₃ systems of different donor number⁸ at c ~ 0.3 mole BF₃/liter

D	DN _{SbCl₅}	K _{D.A}	λ _{0.5}	λ _{1.0}
PhPOF ₂	16.4	0.2 ± 0.05	0.011	0.0050
PhPOCl ₂	18.5	0.0	0.025	0.011
Ph ₂ POF	—	60 ± 5	0.110	0.040
Ph ₂ POCl	22.4	100 ± 10	0.165	0.075
TMP	23.0	—	0.300	0.110
TBP	23.7	—	0.250	0.095
Ph ₃ PO	ca. 33	—	0.890	—

which is expected to be promoted by increasing donor strength. The conductivity maximum in nitrobenzene solution at a mole ratio D:BF₃ = 0.5 cannot be attributed to an equilibrium such as



since the maximum is also found in the system TMP–BF₃ where such ionization is impossible. It may be explained, however, by assuming the following equilibria



which involve the partial ionization of the adduct (II) found by NMR in the system Ph₂POF–BF₃.

The dependence of the molar conductance on the concentration in the system Ph₂POCl–BF₃ (Figure 3) can now also be explained. The maximum at the mole ratio D:BF₃ = 0.5 is increased by increasing the concentration in contrast to the behaviour of a weak electrolyte and this must be due to dissociation of (II) into (I) and BF₃, which is favoured by dilution. The molar conductivities at molar ratios D:BF₃ > 1:1 are increased at low concentrations as expected for a weak electrolyte, such as (1).

In the BF₃ systems with POCl₃, PhPOF₂, PhPOCl₂, Ph₂POF, and Ph₂POCl the ³¹P-signals experience a downfield shift the more BF₃ is provided. This must be attributed to a fast intermolecular exchange of BF₃ as is known to occur in other D–BF₃ systems.^{10,12} On the other hand, separate ¹H-signals from the complex and free donor were detected in the systems containing the stronger donors TMP and HMPA. This shows that, in these systems, there is no intermolecular exchange of BF₃.

Acknowledgments. We wish to thank the « Fonds zur Förderung der wissenschaftlichen Forschung », Wien for financial support and Dr. T. M. Coffield, Ethyl Corporation for the supply of trimethylphosphate.

(8) V. Gutmann, « Coordination Chemistry in Non Aqueous Solutions », Springer-Verlag Wien - New York (1968).

(9) V. Gutmann and J. Imhof, unpublished results.

(10) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, 21, 279 (1953).

(11) H. M. McConnell, *J. Chem. Phys.*, 28, 430 (1958).

(12) A. H. Cowley and J. L. Mills, *J. Amer. Chem. Soc.* 91, 2911 (1969) and ref. therein.