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

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Adducts of the general formula $R_3PO\,.\,BF_3$ react with BF_3 to give $R_3PO\,.\,BF_3\,.\,BF_3$. 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

$PhPOF_2$ is known to react with BCl_3 to give $PhPOCl_2$ and BF_3.[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): $POCl_3$, $PhPOF_2$, $PhPOCl_2$, Ph_2POF, Ph_2OCl, $(CH_3O)_3PO$(TMP), n–$(C_4H_9O)_3PO$ (TBP), Ph_3PO (TPO), $[(CH_3)_2N]_3PO$(HMPA).

Experimental Section

$PhPOF_2$ and Ph_2POF were prepared from the respective chlorides with Na_2SiF_6.[2] Ph_2POCl was obtained by oxidation of Ph_2PCl with Cl_2 followed by solvolysis with SO_2.[3] The commercial products of $POCl_3$, $PhPOCl_2$, TMP, TBP, HMPA were distilled prior to use ($\varkappa < 10^{-7}$ ohm^{-1} cm^{-1} at 25°). Ph_3PO was purified by recrystallization from absolute benzene.

Nitrobenzene was purified chromatographically (Al_2O_3),[4] dried over $CaCl_2$ and fractionally distilled under dry N_2. It was further purified by means of molecular sieves (Linde A 4); b.p. 79.8°/9 mm, $\varkappa = 3.10^{-8}$ ohm^{-1} cm^{-1}, water content: 9.10^{-4} mole/1.

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 ^{19}F) and at 25 Mc (^{31}P). For ^1H-resonance $(CH_3)_4Si$ (TMS, 1%) and for ^{19}F-resonance CCl_3F (10%) was used as internal standard while the ^{31}P-resonance spectra were recorded with 85% H_3PO_4 as external standard. The samples containing different BF_3-donor molar ratios were recorded in the absence of a solvent.

Conductometric titrations of BF_3 with the donor were carried out in nitrobenzene under dry N_2 at 25°. Molar conductivities (λ_m) are based on the concentration of BF_3, measured in mole BF_3 per 1000 ml nitrobenzene.

Results

In the BF_3 systems of $POCl_3$, $PhPOF_2$, $PhPOCl_2$, Ph_2POF and Ph_2POCl the chemical shift of the ^{31}P-signals is decreased by increase in BF_3-concentration (Figure 1) while the ^{19}F-signals of $PhPOF_2$ and Ph_2POF are shifted upfield (Figure 2) to the same extent as the ^{31}P-signals are shifted downfield (Table I).

In the systems TMP–BF_3, TBP–BF_3, HMPA–BF_3 (Table I) signals for the free donor and the complex were detected separately. In the system TMP–BF_3, the ^1H-signals of the complex are shifted downfield (B_H) with respect to free TMP, while the ^{31}P-signal undergoes a highfield shift. The ^{31}P-signals of the three halogen free donors (TMP, TBP, HMPA) are very broad unresolved multiplets.

In the system TBP–BF_3 only the ^{31}P-signals are sufficiently separated. B_P may be attributed to the complex TBP . BF_3. The signal D_H is shifted slightly downfield with increasing BF_3 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 ($CH_3 = A$, $-CH_2-P = 0 = D$). The chemical shift of the other ^1H-signals are nearly independent of the BF_3 concentration.

The ^1H-spectra of the system HMPA–BF_3 show two doublets, A_H for free HMPA and B_H for the complex

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

Donor	X	NMR	N	M	$^A\delta$	J	M	$^B\delta$	J	M	$^C\delta$	M	$^D\delta$	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						
	0.75	^{31}P	3	3	−15.3	1125 PF								
Ph_2POF	0.0	^{19}F	2	2	73.8	1010 PF								
	0.0	^{31}P	2	2	−39.6	1010 PF								
	1.11	^{19}F	6	2	87.0	1050 PF	2	88.4	1080 PF	1	135.2	1	143	
TMP	0.0	^1H	2	2	3.70	11 PH								
	0.0	^{31}P	m	m	−2.59									
	0.42	^1H	4	2	3.82	11 PH	2	4.21	11 PH					
	0.42	^{31}P	m	m	0.0									
TBP	0.0	^1H	m	3	0.904		m	1.01		m	1.50	4	3.95	7.2 HHP
	0.0	^{31}P	m	m	0.6									
	0.96	^1H	m	3	0.955		m	1.06		m	1.67	4	4.27	6.4 HHP
	0.96	^{31}P	m	m	0.6		m	6.56						
HMPA	0.0	^1H	2	2	2.51	10.4 PH								
	0.0	^{31}P	m	m	−23.0									
	0.33	^1H	4	2	2.57	10.0 PH	2	2.71	11.4 PH					
	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.

HMPA . BF_3. The signal B_H of the complex appears downfield with respect to the ^1H-signals of the free HMPA.

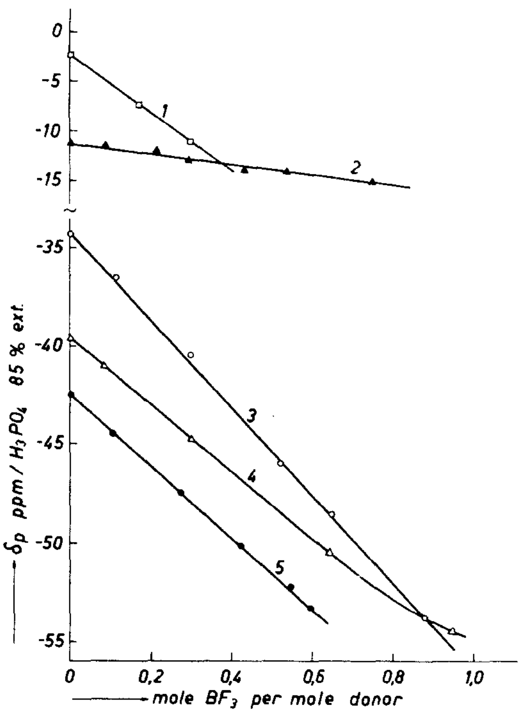


Figure 1. ^{31}P chemical shift *vs.* mole ratio BF_3: D in the systems $POCl_3$–BF_3 (1), $PhPOF_2$–BF_3 (2), $PhPOCl_2$–BF_3 (3), Ph_2POF–BF_3 (4) and Ph_2POCl–BF_3 (5).

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 Ph_3PO . BF_3 in inert solvents made an investigation of this system by NMR impossible.

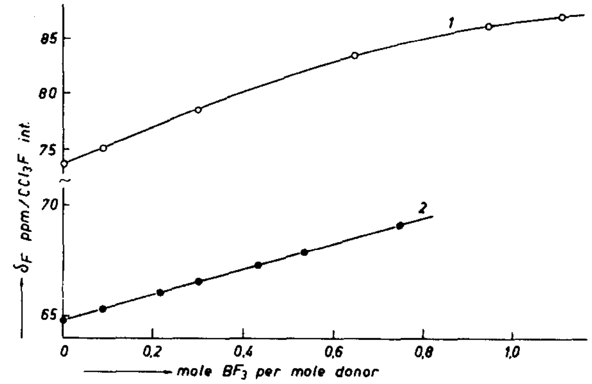


Figure 2. ^{19}F chemical shift *vs.* mole ratio BF_3: D in the systems Ph_2POF–BF_3 (1) and $PhPOF$–BF_3 (2).

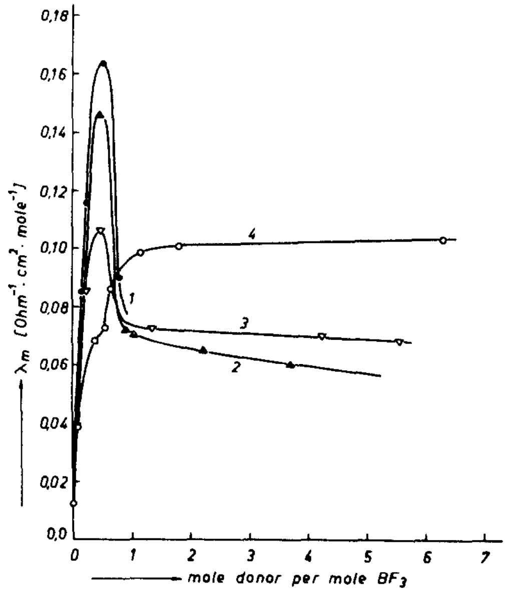


Figure 3. Molar conductance *vs.* mole ratio Ph_2POCl: BF_3 in nitrobenzene c_{BF_3} = 0.317 m (1), c_{BF_3} = 0.296 m (2), c_{BF_3} = 0.174 m (3), c_{BF_3} = 0.0854 m (4).

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).

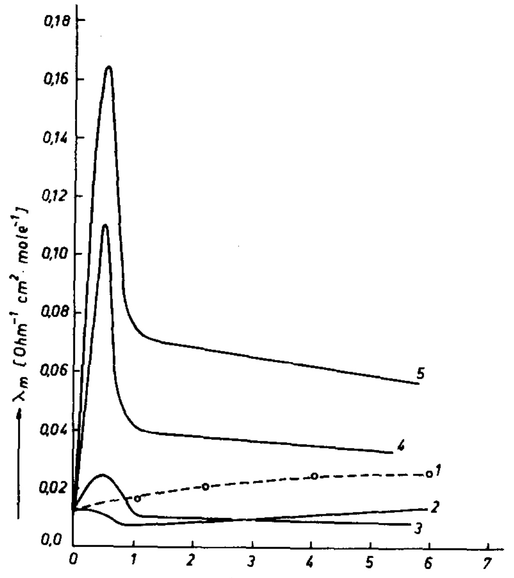


Figure 4. Molar conductance vs. mole ratio D . BF_3 in nitrobenzene at $c_{BF_3} = 0.3$. $POCl_3$–BF_3 (1), $PhPOF_2$–BF_3 (2), $PhPOCl_2$–BF_3 (3), Ph_2POF–BF_3 (4) and Ph_2POCl–BF_3 (5).

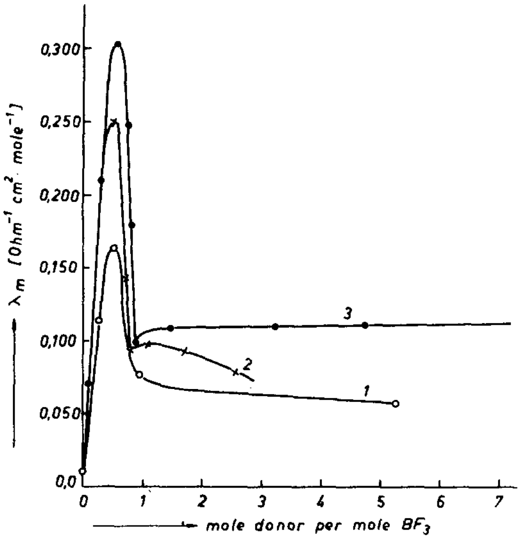


Figure 5. Molar conductance vs. mole ratio D . BF_3 in nitrobenzene at $c_{BF_3} = 0.3$. Ph_2POCl–BF_3 (1), TBP–BF_3 (2) and TMP–BF_3 (3).

The dependence of the molar conductance on the BF_3 concentration in the system Ph_2POCl–BF_3 is shown in Figure 3. It can be seen that the maximum conductivity (at the mole ratio $D:BF_3 = 0.5$ 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.

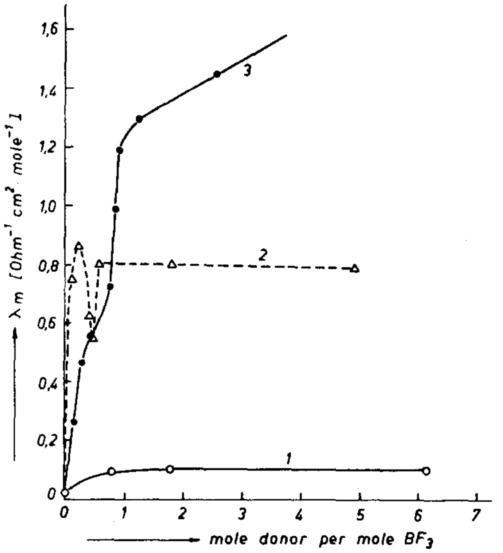


Figure 6. Molar conductance vs. mole ratio D . BF_3 in nitrobenzene at $c_{BF_3} = 0.085$. Ph_2POCl–BF_3 (1), HMPA–BF_3 (2) and Ph_3PO–BF_3 (3).

The titrations for the $POCl_3$–, $PhPOF_2$–, $PhPOCl_2$–, Ph_2POF–, Ph_2POCl– (Figure 4), TBP–, TMP–, (Figure 5) BF_3 systems were all carried out at the same BF_3 concentration (0.300 mole BF_3/1 nitrobenzene). The conductances at the maximum depend on the nature of the donor. No maximum is found in the system $POCl_3$–BF_3 (dotted line in Figure 4), possibly owing to hydrolysis of $POCl_3$. The BF_3–Ph_3PO 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 Ph_2POF–BF_3 and $PhPOF_2$–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 BF_3: D (Figure 1, 2). This is evidence for the presence of donor-acceptor compounds. According to IR-measurements adduct formation in the system $PhPOF_2$–BF_3 is known to occur through O-coordination,[5] and this is in accordance with the NMR results, which exclude the formation of $[Ph_2PO]^+[BF_4]^-$ and $[PhPOF]^+[BF_4]^-$, for which ^{31}P should give a single peak in the system Ph_2POF–BF_3 and doublet in the system $PhPOF_2$. BF_3 The absence of ionized units in the adduct $PhPOF_2$. 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 $BF_3:D = 1.1:1$. 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/CCl_3F), which is shifted upfield with respect to the doublet of $Ph_2POF . BF_3$ (87.0 ppm/CCl_3F). In this composition range a second ^{19}F-signal for coordinated BF_3 is found, namely at 135 ppm with respect to CCl_3F. This signal is shifted downfield with respect to BF_3 in $Ph_2POF . BF_3$ (142 ppm/CCl_3F), just as the ^{19}F-signal of $[B_2F_7]^-$ occurs at lower field[6] than that of $[BF_4]^-$, and must be attributed to a species which contains more more than 1 mole BF_3 per mole Ph_2POF.

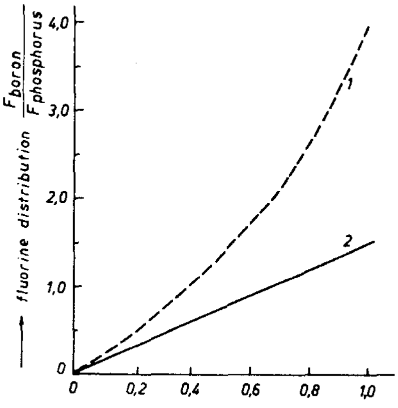
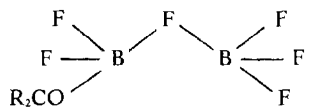


Figure 7. Fluorine distribution of $F_{boron}/F_{phosphorus}$ *vs.* mole ratio $BF_3 . PhPOF_2$, expected for $[PhPOF]^+[BF_4]^-$ (1), found and calcd. for $PhPOF_2 . BF_3$ (2).

Such compounds have been described in systems of the type $R_2CO–BF_3$ which have been formulated as:[7]



The $[B_2F_7]^-$– ion is known to loose one mole of BF_3 easily[6] and likewise $Ph_2POF . BF_3 . BF_3$ could not be isolated.

In the ^{19}F-spectra (except in the $POCl_3–BF_3$ system) only the signal of coordinated BF_3 is present (140-150 ppm/CCl_3F, $POCl_3–BF_3$ 135 ppm/CCl_3F).

The molar conductivities in nitrobenzene (Figure 4, 5, 6) at molar ratios of $D:BF_3 = 0.5:1$ ($\lambda_{0.5}$) and $D:BF_3 = 1:1$ ($\lambda_{1.0}$) are increased by increasing strength of the phosphoryl donor D indicating higher ionization by increasing donor properties (Table II), but $POCl_3$ and HMPA do not obey this rule.

The K_{DA} values derived from ^{31}P–NMR measurements[9] for the reactions

$$PhPOCl_2 . BF_3 + D \rightleftharpoons PhPOCl_2 + D . BF_3$$

also increase with increasing values of DN_{SbCl_5}.

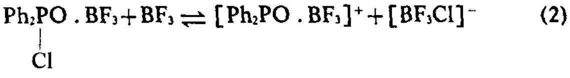
The ionization at mole ratios $D:BF_3 = 1:0$ may be regarded as due to autoionization

$$2\,D . BF_3 \overset{D}{\rightleftharpoons} BF_2^+ + [BF_4]^- \tag{1}$$

Table II. Conductances in Phosphoryldonor-BF_3 systems of different donor number[8] at c∼0.3 mole BF_3/liter

D	DN_{SbCl_5}	$K_{D.A}$	$\lambda_{0.5}$	$\lambda_{1.0}$
$PhPOF_2$	16.4	0.2 ± 0.05	0.011	0.0050
$PhPOCl_2$	18.5	0.0	0.025	0.011
Ph_2POF	—	60 ± 5	0.110	0.040
Ph_2POCl	22.4	100 ± 10	0.165	0.075
TMP	23.0	—	0.300	0.110
TBP	23.7	—	0.250	0.095
Ph_3PO	*ca.* 33	—	0.890	—

which is expected to be promoted by increasing donor strength. The conductivity maximum in nitrobenzene solution at a mole ratio $D:BF_3 = 0.5$ cannot be attributed to an equilibrium such as



$$\underset{\displaystyle Cl}{Ph_2PO} . BF_3 + BF_3 \rightleftharpoons [Ph_2PO . BF_3]^+ + [BF_3Cl]^- \tag{2}$$

since the maximum is also found in the system TMP–BF_3 where such ionization is impossible. It may be explained, however, by assuming the following equilibria

$$\underset{\text{(I)}}{R_3PO . BF_3} + BF_3 \rightleftharpoons$$

$$\underset{\text{(II)}}{R_3PO . BF_3 . BF_3} \rightleftharpoons \underset{\text{(III)}}{[R_3PO . BF_2]^+} + [BF_4]^- \tag{3}$$

which involve the partial ionization of the adduct (II) found by NMR in the system $Ph_2POF–BF_3$.

The dependence of the molar conductance on the concentration in the system $Ph_2POCl–BF_3$ (Figure 3) can now also be explained. The maximum at the mole ratio $D:BF_3 = 0.5$ 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 BF_3, which is favoured by dilution. The molar conductivities at molar ratios $D:BF_3 > 1:1$ are increased at low concentrations as expected for a weak electrolyte, such as (1).

In the BF_3 systems with $POCl_3$, $PhPOF_2$, $PhPOCl_2$, Ph_2POF, and Ph_2POCl the ^{31}P-signals experience a downfield shift the more BF_3 is provided. This must be attributed to a fast intermolecular exchange of BF_3 as is known to occur in other D–BF_3 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 BF_3.

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