

**678.** *The Structures of the Phosphoryl Chloride–Boron Trichloride Complex and Similar Compounds.*

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The infrared spectra of the compounds  $\text{POCl}_3\cdot\text{BCl}_3$ ,  $\text{Ph}_2\text{POCl}\cdot\text{BCl}_3$ , and  $\text{Ph}_3\text{PO}\cdot\text{BCl}_3$  have been re-examined and certain frequencies have been assigned. It is concluded that the structures are all oxygen-co-ordinated, and not ionic. Changes in the P=O frequency in several adducts of phosphoryl chloride are discussed and compared with changes in the  $\text{C}\equiv\text{N}$  frequency in similar acetonitrile adducts.

It has recently been postulated that the phosphoryl chloride–boron trichloride complex is an ionic species;<sup>1</sup> this argument is based on changes in the P–Cl and P=O frequencies, the position of the B–Cl frequencies, and there being no B–O frequency in the infrared spectrum. In this paper we hope to provide convincing evidence that this compound is

<sup>1</sup> Gerrard, Mooney, and Willis, *J.*, 1961, 4255.

an oxygen-co-ordinated adduct, by re-examination of the infrared spectrum, some of its chemical reactions, and its relationship to similar compounds of known structure.

Several adducts of phosphoryl chloride have previously been prepared; the P=O frequencies of some of them are shown in Table 1, together with certain other phosphoryl

TABLE 1.

P=O and C≡N Frequencies.

	P=O or C≡N	$\Delta\nu$ in complex	$\Delta\nu$ (BCl <sub>3</sub> ) minus $\Delta\nu$ (complex)		P=O or C≡N	$\Delta\nu$ in complex	$\Delta\nu$ (BCl <sub>3</sub> ) minus $\Delta\nu$ (complex)
Ref.	(cm. <sup>-1</sup> )	(cm. <sup>-1</sup> )	$\Delta\nu$ (complex)	Ref.	(cm. <sup>-1</sup> )	(cm. <sup>-1</sup> )	$\Delta\nu$ (complex)
POCl <sub>3</sub> .....	1290	—	—	Ph <sub>2</sub> POCl .....	1236	—	—
POCl <sub>3</sub> , BCl <sub>3</sub> ...	1290	0	—	Ph <sub>2</sub> POCl, BCl <sub>3</sub>	1187	-49	—
POCl <sub>3</sub> , AlCl <sub>3</sub> ...	1260	-30	30	MeCN .....	5	2248	—
POCl <sub>3</sub> , GaCl <sub>3</sub>	2	1290	0	MeCN, BCl <sub>3</sub> ...	5	2357	109
(POCl <sub>3</sub> ) <sub>2</sub> , SnCl <sub>4</sub>	3	1215	-75	(MeCN) <sub>2</sub> , AlCl <sub>3</sub>	5	2340	92
(POCl <sub>3</sub> ) <sub>2</sub> , TiCl <sub>4</sub>	3	1205	-85	(MeCN) <sub>2</sub> , TiCl <sub>4</sub>	5	2304	56
POCl <sub>3</sub> , BF <sub>3</sub> ...	4	1298	+8	(MeCN) <sub>2</sub> , SnCl <sub>4</sub>	5	2303	55
Ph <sub>3</sub> PO .....	1192	—	—	MeCN, BF <sub>3</sub> ...	5	2359	111
Ph <sub>3</sub> PO, BCl <sub>3</sub> ...	1115	-77	—				-2

frequencies and the C≡N frequency in some acetonitrile adducts. The phosphoryl frequency is found to decrease in the adducts. The decrease from the free P=O value in the series POCl<sub>3</sub>, BCl<sub>3</sub>; Ph<sub>2</sub>POCl, BCl<sub>3</sub>; Ph<sub>3</sub>PO, BCl<sub>3</sub> is 0—49—77 cm.<sup>-1</sup>; the change in frequency in the diphenylphosphinic chloride-boron trichloride adduct is very roughly two-thirds of the difference between the P=O frequency changes in the phosphoryl chloride and the triphenylphosphine oxide adduct. The difference between the P=O frequency in phosphoryl chloride adducts where *d* $\pi$ -*p* $\pi$  bonding can occur, and in the boron trichloride adduct, where it cannot, is of the same order of magnitude as the difference in the C≡N frequency in corresponding acetonitrile adducts. The nitrile complexes can only be nitrogen-co-ordinated, and the phosphoryl complexes might, therefore, be expected to be oxygen-co-ordinated.

It is notable that in the aluminium and the gallium trichloride adducts, where next to the boron trichloride adduct the *d*-orbitals are least available for bonding, the shifts in the P=O frequency are least. However, in stannic and titanium tetrachloride vacant *d*-orbitals are readily available on the metal atom, and hence the  $\pi$ -electrons of the P=O bonds can readily co-ordinate into the *d*-shell of the metal, producing a *p* $\pi$ -*d* $\pi$  bond between the oxygen and the tin or titanium, with subsequent delocalization of the  $\pi$ -electrons across the P-O-M bonds, increasing the M-O bond strength, but weakening the P=O bond. This weakening is reflected by a decrease in the P=O frequency in the infrared spectra.

Examination of the crystal structures of (POCl<sub>3</sub>)<sub>2</sub>TiCl<sub>4</sub><sup>6</sup> and POCl<sub>3</sub>, SbCl<sub>5</sub><sup>7</sup> has shown that these compounds are oxygen-co-ordinated. The Raman spectra of the phosphoryl chloride adducts with aluminium and gallium trichloride, in the liquid state, have also been interpreted as being due to an oxygen-co-ordinated species Cl<sub>3</sub>P<sup>O</sup>\MCl<sub>3</sub>.<sup>2</sup>

The infrared spectrum of the phosphoryl chloride-boron trichloride complex has been re-examined and is shown in the Figure, together with the boron trichloride adducts of triphenylphosphine oxide and diphenylphosphinic chloride; some frequency assignments are shown in Table 2. The infrared spectrum of the phosphoryl chloride-boron trichloride adduct prepared in liquid hydrogen chloride is not the same as that given by Gerrard

<sup>2</sup> Gerding, Koningstein, and van der Worm, *Spectrochim. Acta*, 1960, **16**, 881.

<sup>3</sup> Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4778.

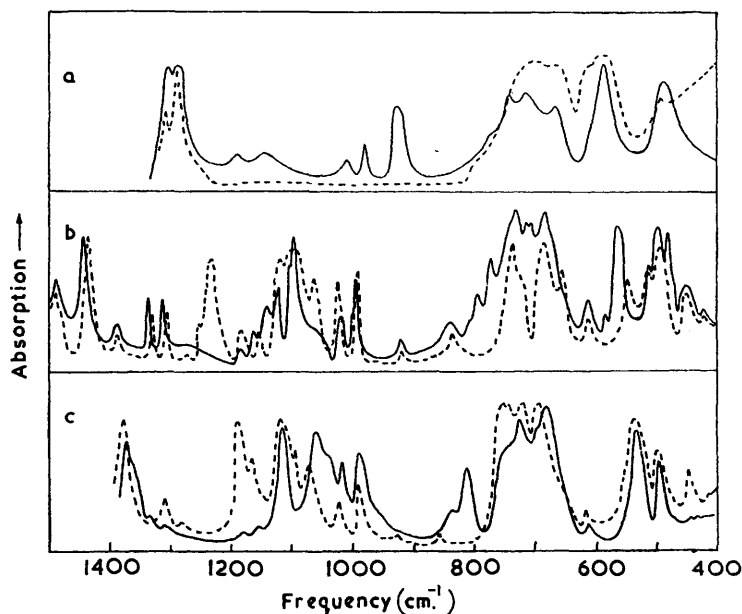
<sup>4</sup> Waddington and Klanberg, *J.*, 1960, 2339.

<sup>5</sup> Coever and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

<sup>6</sup> Bränden and Lindqvist, *Acta Chem. Scand.*, 1960, **14**, 726.

<sup>7</sup> Lindqvist and Bränden, *Acta Chem. Scand.*, 1958, **12**, 134.

*et al.*<sup>1</sup> There is only a very slight change in the P-Cl frequencies in the adducts. If there were a change in hybridization to  $\text{POCl}_2^+$  a greater change in this frequency would be expected, as is shown by the P-Cl frequencies in  $\text{PCl}_4^+$  (584, 650  $\text{cm}^{-1}$ )<sup>4</sup> ( $sp^3$ ),  $\text{PCl}_5(g)$  (592, 465  $\text{cm}^{-1}$ , antisym. equatorial and axial)<sup>8</sup> ( $dsp^3$ ), and  $\text{PCl}_6^-$  (447  $\text{cm}^{-1}$ )<sup>9</sup> ( $d^2sp^3$ ); similarly,



Infrared spectra of: (a)  $\text{POCl}_2\cdot\text{BCl}_3$  (— our work, --- Gerrard *et al.*<sup>1</sup>); (b) —  $\text{Ph}_2\text{POCl}\cdot\text{BCl}_3$ , ---  $\text{Ph}_2\text{POCl}$ ; and (c) —  $\text{Ph}_3\text{PO}\cdot\text{BCl}_3$ , ---  $\text{Ph}_3\text{PO}$ .

the C-Cl frequency in carbon chloride compounds decreases by about 100  $\text{cm}^{-1}$  when the hybridization of the carbon changes from  $sp^2$  to  $sp^3$ .<sup>10</sup> The diphenylphosphinic chloride-boron trichloride complex still has a P-Cl frequency and must, therefore, be oxygen-co-ordinated,  $\text{Ph}_2\text{ClPO}\rightarrow\text{BCl}_3$ , and not ionic,  $\text{Ph}_2\text{PO}^+\text{BCl}_4^-$ . The frequencies associated

TABLE 2.

Frequency assignments in boron trichloride adducts.

	$\text{POCl}_2$	$\text{POCl}_2\cdot\text{BCl}_3$	$\text{Ph}_2\text{POCl}$	$\text{Ph}_2\text{POCl}\cdot\text{BCl}_3$	$\text{Ph}_3\text{PO}$	$\text{Ph}_3\text{PO}\cdot\text{BCl}_3$
P-Cl.....	484 588	490 588	518	518	—	—
B-Cl .....	—	670 715 743 775	—	706 716 774 795	—	685 728 815 840
B-O.....	—	1150 1190	—	1050 1105	—	1021 1065
P-O.....	1290	1290	1236	1187	1192	1115

with the B-Cl bonds in all the complexes are higher than those found for tetrachloroborates (660 and 700  $\text{cm}^{-1}$ )<sup>11</sup> and are within the broad range found for boron trichloride adducts (*ca.* 690—813  $\text{cm}^{-1}$ ).<sup>12</sup>

<sup>8</sup> Wilmshurst and Bernstein, *J. Chem. Phys.*, 1957, **27**, 661.

<sup>9</sup> Waddington and Klanberg, unpublished observation.

<sup>10</sup> Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1950, p. 330.

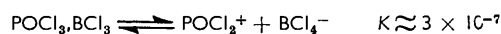
<sup>11</sup> Kynaston and Turner, *Proc. Chem. Soc.*, 1958, 304.

<sup>12</sup> Greenwood and Wade, *J.*, 1960, 1130.

The boron-oxygen frequencies, not found by Gerrard *et al.*,<sup>1</sup> are all in fact split; the splitting is, within experimental error, consistent with the Nettler ratio of 1.05 for the two atomic species of boron. When the lower B-O frequencies of 1150, 1050, and 1021 cm.<sup>-1</sup> (POCl<sub>3</sub>, BCl<sub>3</sub>, Ph<sub>2</sub>POCl, BCl<sub>3</sub>, and Ph<sub>2</sub>PO, BCl<sub>3</sub>) are used, the higher frequencies are calculated as 1206, 1102, and 1071 cm.<sup>-1</sup>, respectively; the observed values are 1190, 1105, and 1065 cm.<sup>-1</sup>. The <sup>11</sup>B-O frequencies ought to be more intense and occur at lower frequencies than the <sup>10</sup>B-O ones. The higher B-O frequencies of the triphenylphosphine oxide- and the diphenylphosphinic chloride-boron trichloride adduct appear as shoulders on more intense peaks and it is impossible to compare their relative intensities. The B-O frequencies of the phosphoryl chloride-boron trichloride adduct are too weak for intensity comparison. It was not possible to assign the frequencies at 1010, 975, and 936 cm.<sup>-1</sup> in the spectrum of the phosphoryl chloride-boron trichloride adduct, but they are certainly not due to phosphoryl chloride or the hydrolysis products, phosphoric and boric acid.

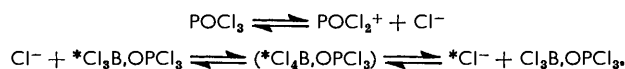
The infrared spectrum of the phosphoryl chloride-boron trifluoride adduct has been examined.<sup>4</sup> This would be expected to have a structure similar to that of the boron trichloride adduct, and, if the compound is ionized, as POCl<sub>2</sub><sup>+</sup>BF<sub>3</sub>Cl<sup>-</sup>, it ought to be possible to detect frequencies characteristic of the BF<sub>3</sub>Cl<sup>-</sup> ion. These frequencies were not observed.

Numerous chloride ion acceptors have been studied as solutions in liquid phosphoryl chloride, the ideal solvent for preparing the POCl<sub>2</sub><sup>+</sup> ion. The equilibrium constant for the dissociation of the boron trichloride adduct in this solvent has been found:<sup>13</sup>



and the dissociation constant of the antimony pentachloride complex is only  $4 \times 10^{-6}$ ;<sup>14</sup> antimony pentachloride is one of the strongest acids in phosphoryl chloride and would be expected to be appreciably ionized.

The rapid halogen isotopic exchange between boron trichloride and phosphoryl chloride in the complex has been examined.<sup>15</sup> The mechanism postulated is:



No evidence was found for the formation of a tetrachloroborate in this reaction.

All the evidence suggests that the phosphoryl chloride-boron trichloride complex is an oxygen-co-ordinated adduct and not an ionic species.

*Experimental.*—The phosphoryl chloride-boron trichloride adduct was prepared in liquid hydrogen chloride by treating phosphoryl chloride with an excess of boron trichloride, and removing the excess with the solvent (Found: Cl, 77.7. Calc. for BCl<sub>3</sub>OP: Cl, 78.6%). The boron trichloride adducts of triphenylphosphine and diphenylphosphinic chloride were prepared as reported previously.<sup>16</sup>

The infrared spectra were recorded on a Perkin-Elmer model 21 double-beam, continuously recording spectrophotometer with rock-salt or potassium bromide optics. Solids were finely powdered in an agate mortar and made into a mull, with either Nujol or hexachlorobutadiene; the liquids were smeared as thin films.

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<sup>13</sup> Baaz, Gutmann, and Hübner, *Monatsh.*, 1960, **91**, 694.

<sup>14</sup> Baaz and Gutmann, *Monatsh.*, 1959, **90**, 426.

<sup>15</sup> Herber, *J. Amer. Chem. Soc.*, 1960, **82**, 792.

<sup>16</sup> Peach and Waddington, *J.*, 1962, 3105.