243. *Mixed Halides of Phosphorus*(V). *Part II.* Dichlorotrifluorophosphorane.*

By T. Kennedy and D. S. Payne.

Dichlorotrifluorophosphorane PF_3Cl_2 has been re-examined and its vapour pressure, melting point, infrared spectra, and conductance in acetonitrile are reported. A slow transformation into tetrachlorophosphonium hexafluorophosphate ($[PCl_4^+][PF_6^-]$) has been observed. Vapour-phase hydrolysis leads to high-boiling oxyfluorides and hydrogen chloride.

DICHLOROTRIFLUOROPHOSPHORANE, the product of reaction between phosphorus trifluoride and chlorine, has been examined on several occasions. Moissan [1] and Poulenc [2] established its composition and certain of its physical and chemical properties. Electron-diffraction studies [3] have shown the molecule to have a trigonal bipyramidal structure, with the three fluorine atoms in the equatorial positions and the two chlorine atoms in the polar positions; both the P–Cl (2·05 ± 0·03 Å) and the P–F (1·59 ± 0·03 Å) distances appear somewhat longer than those found in other phosphorus halides. The kinetics of the formation reaction have been briefly reported by Wilson.[4] By the fluorination of phosphorus pentachloride with arsenic trifluoride, Kolditz [5] obtained a compound of identical composition but differing from dichlorotrifluorophosphorane in being clearly ionic in nature, namely tetrachlorophosphonium hexafluorophosphate, $[PCl_4^+][PF_6^-]$. We have

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* Part I of this series appeared as " The Reaction between Phosphorus Trichloride and Bromine. Part I," by Harris and Payne, *J.*, 1956, 4613.

[1] Moissan, *Ann. Chim. Phys.*, 1885, **6**, 433, 438.

[2] Poulenc, *Compt. rend.*, 1891, **113**, 75.

[3] Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836.

[4] Wilson, *ibid.*, 1958, **80**, 1338.

[5] Kolditz, *Z. anorg. Chem.*, 1956, **284**, 144.

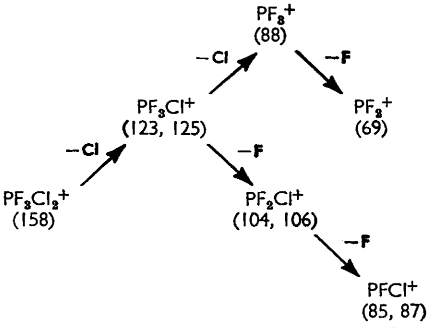
examined the molecular compound PF_3Cl_2 as part of a systematic study of mixed halides of phosphorus(v) and now report further on its chemical and physical properties.

The reaction of phosphorus trifluoride and chlorine in approximately equimolar amounts proceeds slowly in the gas phase at room temperature, but rapidly at lower temperatures in the liquid phase. Irradiation with ultraviolet light failed to accelerate the gas-phase reaction. In every preparation yields were below theoretical and varying amounts of a white solid were obtained. An *X*-ray powder photograph of this solid showed strong lines due to $[PCl_4^+][PF_6^-]$ together with weak lines of $[PCl_4^+][F^-]$. Analysis showed the relative molar amounts to be 9 : 1. On storage the white solid sometimes volatilised and on occasions re-formed as distinct crystals on the walls of the vessel. Separation of the dichlorotrifluorophosphorane from the excess of phosphorus trifluoride always present, and from traces of phosphorus oxyfluoride and silicon tetrafluoride, was accomplished by repeated fractionation at low temperatures in a vacuum line employing taps greased with Florube W. In the initial stages of the work the purification was followed by vapour-pressure checks; later, however, the infrared spectra of gas samples were employed for this purpose.

TABLE 1.

Expt. No.	Temp.	Press. (mm. Hg)	Expt. No.	Temp.	Press. (mm. Hg)	Expt. No.	Temp.	Press. (mm. Hg)	Expt. No.	Temp.	Press. (mm. Hg)
III	−10°	416·33	II	−35°	121·82	I	−45°	73·76	III	−50°	58·79
III	−15	336·84	III	−40	96·70	I	−50	58·35	II	−55	44·19
II	−20	257·25	II	−40	97·70	I	−50	57·39	II	−60	31·00
II	−25	204·69	III	−45	68·39	II	−50	58·90	I	−60	32·10
II	−30	161·68									

The vapour pressure from static measurements is shown in Table 1. The vapour-pressure equation found by the method of least squares, $\log_{10} p_{\text{mm.}} = -1228/T + 7{\cdot}264$, gives ΔH for vaporisation = 5·66 kcal. and a value of 20·2 for Trouton's constant. The extrapolated b. p. at 760 mm. is 7·1°. The m. p. lies within the range −125° to −130°. Molecular-weight measurement gave a value of 159 ± 1 at 20° (Calc. for PF_3Cl_2: 158·9), thus establishing the unimolecular nature of the vapour at room temperature. Infrared spectra were obtained at various pressures, a stainless-steel gas cell with potassium bromide windows and lubricated with Kel-F fluorocarbon grease being used. The details of the spectra obtained at 5 mm. pressure are as follows: peaks (cm.$^{-1}$), 932 s, 899 s, 870 s, 675 s, 668 s, 635 s, 564 m, 500 m, 492 m, and 432 w. At 40 mm. and 80 mm., additional peaks at 415 m and 530 s were observed. No attempt has been made to correlate these frequencies with the trigonal bipyramidal model of the molecule. The presence of silicon tetrafluoride and phosphorus oxyfluoride as impurities was clearly apparent through the strong peak of the former at 1024 cm.$^{-1}$ and the triplet of the latter at 1415 cm.$^{-1}$. In connection with later studies a sample of pure dichlorotrifluorophosphorane was examined mass spectroscopically at an ionisation energy of 15 ev; the mass peaks shown in Table 2 were obtained and can be interpreted according to the scheme:



(Mass nos. are indicated in parentheses)

TABLE 2. *Mass spectrum of* PF_3Cl_2 *at* 15 ev.

Mass peak	Strength	Assignment	Mass peak	Strength	Assign ment	Mass peak	Strength	Assignment
35	s	Cl^+	87	w	$PClF^+$	123	vs	PF_3Cl^+
37	s	Cl^+	88	s	PF_3^+	125	s	PF_3Cl^+
69	vw	PF_2^+	103	m	PF_2Cl^+	158	vw	$PF_3Cl_2^+$
85	w	$PClF^+$	106	vs	PF_2Cl^+ +(?)			

The species with mass number of 106 cannot be exclusively PF_2Cl^+ because of the lower relative peak height of mass 103, which is the adjacent peak corresponding, within the limits of experimental error, to the other chlorine isotope (^{35}Cl). It would be convenient to relate this peak at 106 in part to hydrolysis products such as phosphorus oxyfluoride or silicon tetrafluoride both of mass 104, but the difference in mass number is outside the error of experiment and there is no evidence of hydrogen chloride or of other related fragments being present. Attempts to assign the major part of this strong peak at 106 have therefore not been successful and must await further mass-spectrometric studies of compounds of this type. The ionisation process leads largely to loss of chlorine. Loss of fluorine appears only to occur from a monochloro-fragment, there being no evidence for $PF_2Cl_2^+$ or later fragments in the spectra.

Reference has already been made to a rearrangement leading to the formation of $[PCl_4^+][PF_6^-]$ from PF_3Cl_2; a study of this change and further studies on the pyrolysis reaction in general will be reported later. However, it is appropriate to comment that the speed of the rearrangement of dichlorotrifluorophosphorane to the ionic form can be greatly reduced by rigorous drying of the apparatus, and in the experiments reported in this paper this has always been done.

The molar conductance of a solution of dichlorotrifluorophosphorane in carefully purified acetonitrile at 20° is 9·63 mho $cm.^{-1}$ $mole^{-1}$ at a concentration of 0·04542M and 9·31 mho $cm.^{-1}$ $mole^{-1}$ at 0·09053M. Immediately after preparation of the solutions the conductance increased slightly with time, equilibrium being established only after 1—2 hr. The conductance of liquid dichlorotrifluorophosphorane was found to be less than 10^{-7} mho $cm.^{-1}$.

The hydrolysis of dichlorotrifluorophosphorane vapour with an equimolecular quantity of water gave a high-boiling oxyfluoride together with hydrogen chloride. No evidence in support of the reaction $PF_3Cl_2 + H_2O \longrightarrow POF_3 + 2HCl$ was obtained.

Kolditz[6] has recently discussed the relation of molecular to ionic states in the phosphorus halides. Dichlorotrifluorophosphorane is of particular interest because of the striking difference between the two forms—on the one hand, the ionic $[PCl_4^+][PF_6^-]$, a white solid subliming with decomposition at 135°, with a value of 90·9 mho $cm.^{-1}$ $mole^{-1}$ for the molar conductance in acetonitrile solution at 0·0420M, and on the other, the covalent form with a b. p. of 7·1° and an unusually low m. p. of —125° to —130°, with a molar conductance of *ca.* 9 mho $cm.^{-1}$ $mole^{-1}$ in acetonitrile, the pure liquid being virtually a non-conductor. The evidence presented here supports emphatically the molecular nature of dichlorotrifluorophosphorane, but the conductance data show that in acetonitrile solvolysis is sufficient to bring about limited ion formation. It seems possible that in this medium the rearrangement reported for the gas occurs, but the magnitude of the molar conductance (values should be doubled to compare with $[PCl_4^+][PF_6^-]$) shows that this has not occurred to completion, if at all. The ions responsible for the conductance have not been identified, but a simple ionisation process such as $2PX_5 \rightleftharpoons PX_4^+ + PX_6^-$, where X represents either chlorine or fluorine, following the scheme observed with the simple phosphorus halides in this solvent,[7] would seem to be more favoured than the rearrangement. The slight slow initial increase in conductance with time has been observed before in such systems and may indicate the rate of the ionisation process.

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[6] Kolditz, *Z. anorg. Chem.*, 1957, **293**, 147.

[7] Payne, *J.*, 1953, 1052; Harris and Payne, *J.*, 1956, 3038, 4167.

EXPERIMENTAL

Preparation.—Dichlorotrifluorophosphorane is prepared by mixing approximately equal volumes of phosphorus trifluoride and chlorine, care being taken to have a slight excess of phosphorus trifluoride in the final mixture, since this can be removed more easily than excess of chlorine. Phosphorus trifluoride was initially prepared by Hoffman's method,[8] *viz.*, $PCl_3 + AsF_3 \longrightarrow PF_3 + AsCl_3$, but it was later found that phosphorus trifluoride could be prepared more conveniently by the method of Chatt and Williams [9] using zinc fluoride in place of arsenic trifluoride. The phosphorus trichloride was obtained by fractionation of a good commercial sample in a 2-ft. column packed with glass Fenske rings at a reflux ratio of 20 to 1, the fraction of b. p. 74·4—74·5° being retained for use. The crude dichlorotrifluorophosphorane was purified in vacuum by allowing it to distil slowly into a trap immersed in a toluene slush bath (−96°), the impurities passing through being condensed in a liquid-air trap; 12—15 distillations were required to produce pure material. Apiezon and silicone greases were attacked by dichlorotrifluorophosphorane. Florube W and Kel-F greases, being the only ones found to be stable, were used throughout this work.

Analysis.—A known amount of dichlorotrifluorophosphorane was hydrolysed by an excess of 0·1N-sodium hydroxide, the phosphorus being estimated volumetrically, and the chlorine gravimetrically [Found: P, 19·4, 19·3; Cl, 44·2, 43·9; F (by diff.), 36·4, 36·8. Calc. for PF_3Cl_2: P, 19·5; Cl, 44·6; F, 35·9%].

Vapour-pressure Measurements.—These were carried out in an all-glass system, a spiral gauge being used as a null instrument. Considerable difficulty was encountered in obtaining reproducible results; in particular, a change in vapour pressure slowly occurred which could not be explained in terms of reaction with any part of the apparatus or the admission of inadvertent traces of water. The lack of reproducibility may be connected with the ready formation of $[PCl_4^+][PF_6^-]$, since it was observed that samples, even those kept at low temperatures, could not be evaporated without leaving a trace of a white residue, which appeared by the circumstances of its formation and its volatility to be $[PCl_4^+][PF_6^-]$. Satisfactory results for the vapour pressure were eventually obtained by limiting the time taken for equilibrium to be established before a pressure measurement was made to about 30 min. and by employing several highly purified specimens in the course of the complete series of observations. Purity checks were carried out by reference to the infrared spectra, a sensitive detector of the most likely impurities, namely, silicon tetrafluoride and phosphorus oxyfluoride. The homogeneity of the sample was further checked by the successive removal of the vapour phase and the separate examination of these fractions.

Molecular-weight Measurements.—These were carried out by using a vapour-density bulb fitted with a tap greased with Florube W, in combination with the spiral gauge pressure-measuring system.

Conductance Experiments in Acetonitrile.—These were carried out in an all-glass cell fitted with a pair of smooth platinum electrodes (area *ca.* 1 cm.^{2}, cell constant 0·324 cm.$^{-1}$) and maintained at a constant temperature by means of a water-bath. Solutions for conductance measurements were prepared by passing a known weight of pure sample in a slow stream of dry nitrogen into a weighed amount of solvent. The conductance was measured by a Mullard conductance bridge (Type E7566). Readings were taken immediately the dichlorotrifluorophosphorane had passed into solution, and observations on the variation of bridge reading with time were then carried out. The acetonitrile was purified essentially as by Smith and Witten's method.[10] However, immediately before use, the solvent was distilled *in vacuo* from *ca.* 20° to −183°. This served to remove phosphoric oxide, traces of which sublimed over from the desiccating agent during distillation at ordinary pressures. The purified material had a specific conductance of *ca.* 10^{-6} mho cm.$^{-1}$. The conductance of liquid dichlorotrifluorophosphorane was measured in an all-glass cell with small platinum electrodes, the cell being specially constructed to deal with small quantities of volatile material. Measurements were made by using the Mullard bridge.

Mass-spectrometer Studies.—These were carried out by use of a Metro Vick MS2 instrument. Measurements were made at 15 ev and at a pressure of 10^{-6} mm., samples being transferred to the apparatus by means of bulbs fitted with magnetic break seals.

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[8] Hoffman, " Inorganic Syntheses," McGraw-Hill, New York, 1953, Vol. IV, 140.

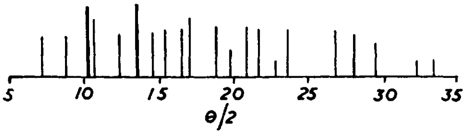
[9] Chatt and Williams, *J.*, 1951, 3065.

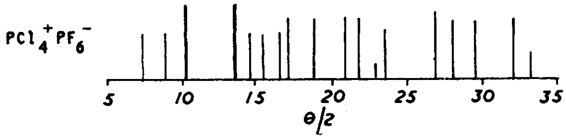
[10] Smith and Witten, *Trans. Faraday Soc.*, 1951, **47**, 1304.

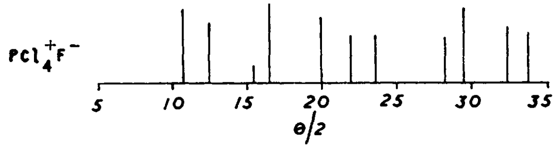
Infrared Spectra.—A Unicam double-beam instrument (S.P. 100) was used. Samples were contained in a stainless-steel gas cell of 10 cm. path length, fitted with KBr windows, and of capacity approximately 0·2 l. Spectra were observed at a number of pressures (measured by the spiral-gauge system already described).

Melting Point.—This was measured by surrounding a solidified sample of pure dichlorotrifluorophosphorane with an *iso*pentane slush bath (−160·5°) and allowing the bath temperature to rise slowly until the solid appeared just to melt, the procedure being repeated three times to obtain a reproducible range of melting.

The *X*-ray powder diagram of the solid obtained on storage of dichlorotrifluorophosphorane, taken with Cu-K_α radiation in a camera of diameter 11·45 cm., is shown below. Data for $[PCl_4^+][PF_6^-]$ [5] and $[PCl_4^+][F^-]$ [11] are shown for comparison.







Reaction with Water Vapour.—This experiment was carried out at room temperature (20°). A bulb of approximately 300 ml. capacity was filled to the pressure corresponding to the vapour pressure of water at the temperature of the experiment with dichlorotrifluorophosphorane. This was then removed, and the bulb refilled with water vapour to the same pressure by allowing it to come to equilibrium with liquid water. The two were then brought into contact, and the vapour phases allowed to react, the pressure of the system being observed by using the spiral-gauge system. After an initial pressure variation, the final pressure of the system corresponded to no net change in the volume of vapour present. The products of the reaction, present in part as droplets of liquid, were divided into a non-volatile and a volatile fraction; the former contained, as shown by examination of the hydrolysed material, only phosphorus and fluorine, the latter only chlorine. The evidence thus supports the reaction $PF_3Cl_2(g) + H_2O(g) \longrightarrow 2HCl(g) + (POF_3)_x(l)$.

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[11] Kolditz, *Z. anorg. Chem.*, 1956, **286**, 307.