# **807.** *Mixed Halides of Phosphorus*(V). *Part III.*[1] *Tetrachlorophosphonium Pentachlorofluorophosphate.*

By T. KENNEDY and D. S. PAYNE.

The preparation of $[PCl_4]^+[PCl_5F]^-$ by the decomposition of $[PCl_4]^+[PF_6]^-$ in carbon tetrachloride is described.

THE preparation of molecular chlorofluorophosphoranes and their corresponding ionic forms has been achieved by addition of halogen to phosphorus(III) halides [1,2] and by partial substitution of fluorine for chlorine in phosphorus(V) halides, a suitable fluorinating agent and solvent system being used.[3] Disproportionation of the resulting dichlorotrifluorophosphorane and tetrachlorophosphonium hexafluorophosphate can lead to further members of the series, and it is largely this aspect of the subject with which the present paper deals.

Pyrolysis of dichlorotrifluorophosphorane was reported by Moissan[4] to proceed at 200°C according to the scheme $5PCl_2F_3 \longrightarrow 2PCl_5 + 3PF_5$; in fact, however, above 150° it gives tetrachlorofluorophosphorane and phosphorus pentafluoride. Although this

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[1] Part II, Kennedy and Payne, *J.*, 1959, 1228.

[2] Booth and Bozarth, *J. Amer. Chem. Soc.*, 1933, **55**, 3890; 1939, **61**, 2927.

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

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

appears an obvious route for the preparation of tetrachlorofluorophosphorane, it is not so, since the reaction is complicated, first, by combination of the molecular $PCl_4F$ with $PF_5$ to give tetrachlorophosphonium hexafluorophosphate and, secondly, by the change of the molecular $PCl_4F$ into the ionic tetrachlorophosphonium fluoride; and the reaction is further complicated by an attack on the glass of the apparatus by phosphorus–fluorine compounds. Pyrolysis of tetrachlorophosphonium hexafluorophosphate in arsenic trichloride solution yields tetrachlorophosphonium fluoride and phosphorus pentafluoride,[5] but further examination of this reaction under different conditions has led to the recognition of other products. For example, when the hexafluorophosphate is heated alone at 100° under reduced pressure, the product is dichlorotrifluorophosphorane, although again the reaction is complicated by attack on the glass, which results in the formation of silicon fetrafluoride, phosphoryl trifluoride, phosphoryl chlorodifluoride, etc. The action of heat on tetrachlorophosphonium hexafluorophosphate suspended in boiling carbon tetrachloride led to phosphorus pentafluoride and dichlorotrifluorophosphorane; a white residue remained which gave an *X*-ray powder photograph containing lines corresponding to tetrachlorophosphonium fluoride along with a number of unidentified lines. Sublimation in dry air at 80—85° removed the tetrachlorophosphonium fluoride completely, leaving a residue of composition $PCl_{4\cdot5}F_{0\cdot5}$. The appearance and the mode of formation of this substance suggested an ionic nature, and a dimeric formula $P_2Cl_9F$ seemed likely. A mass-spectrometric examination of the vapour gave the results shown in Table 1 (in a previous publication [6] $P_2Cl_9F$ was incorrectly included amongst the list of species assigned to peaks found).

TABLE 1. *Mass spectrum of* $[PCl_4]^+[PCl_5F]^-$ *vapour at* 50 ev.

| Mass nos. (obs.) | Assignment | Mass nos. (calc.) | Mass nos. (obs.) | Assignment | Mass nos. (calc.) |
|---|---|---|---|---|---|
| 31 | $P^+$ | 31 | 152—156 | $P_2Cl_2F^+$ | 151—155 |
| 35, 37 | $Cl^+$ | 35, 37 | 166—173 | $PCl_4^+$ | 171—179 |
| 66, 69 | $PCl^+$ | 66, 68 | 183—186 | $P_2Cl_3F^+$ | 186—192 |
| 85, 87 | $PClF^+$ | 85, 87 | 258—266 | $P_2Cl_5F^+$ | 256—266 |
| 102—106 | $PCl_2^+$ | 101—105 | 280—290 | $P_2Cl_6F^+$ | 291—303 |
| 117, 119 | $P_2ClF^+$ | 116, 118 | 305—318 | $P_2Cl_7F^+$ | 326—340 |
| 133, 135 | $P_2Cl_2^+$ | 132—136 | 358—376 | $P_2Cl_8F^+$ | 361—377 |
| 136—140 | $PCl_3^+$ | 136—142 | | | |

The presence of an obvious series of ion species derived from a parent $P_2Cl_9F$ unit supported the dimeric formulation, although it was difficult to reconcile the occurrence of these units in the vapour phase with the idea of an essentially ionic structure. However, phosphorus pentachloride (tetrachlorophosphonium hexachlorophosphate) likewise gave a mass spectrum with a series of species originating from a $P_2Cl_{10}$ parent. In this case there was no doubt that the solid in fact consisted of $PCl_4^+$ and $PCl_6^-$ units. The detail of these molecular species is a subject for speculation and further work, but a chlorine bridge involving $d\pi$–$p\pi$ bonding leading to two octahedrally connected phosphorus atoms seems most likely. Association has been observed previously in the case of phosphorus pentachloride in carbon tetrachloride, although no details of the actual species involved are available.[7]

The molar conductance of $P_2Cl_9F$ in acetonitrile solution at 20° is 72·21, 68·53, and 66·13 ohm$^{-1}$ cm.$^2$ mole$^{-1}$ at 0·0227, 0·0433, and 0·0685 mole l.$^{-1}$, respectively. The values lie between those of phosphorus pentachloride and of tetrachlorophosphonium hexafluorophosphate, at comparable concentrations. Two probable ionic formulations may be written for the compound $P_2Cl_9F$; the first involves a fluorine-containing cation $PCl_3F^+$ and the hexachlorophosphate anion, the other a fluorine-containing anion $PCl_5F^-$ with the tetrachlorophosphonium cation. Kolditz and Feltz [8] reported the related compound

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

[6] Kennedy, Payne, Reed, and Snedden, *Proc. Chem. Soc.*, 1959, 133.

[7] Kolditz and Hass, *Z. anorg. Chem.*, 1958, **294**, 191.

[8] Kolditz and Feltz, *Z. anorg. Chem.*, 1957, **293**, 286.

$P_2Cl_9Br$ which has been formulated as $[PCl_4]^+[PCl_5Br]^-$. Quantitative electrolysis of an acetonitrile solution of $P_2Cl_9F$ showed the presence of phosphorus and fluorine in the anion, the value for the transport number being close to 0·5, thereby confirming the compound as tetrachlorophosphonium pentachlorofluorophosphate, $[PCl_4]^+[PCl_5F]^-$.

$P_2Cl_9F$ is stable up to 110° in the solid phase, but above this temperature disproportionation to phosphorus pentachloride and tetrachlorofluorophosphorane occurs, followed as the temperature is raised by dissociation of these compounds into chlorine and the corresponding trihalide. Data on these dissociations, obtained from pressure–temperature studies, lead to values of the equilibrium constant for the dissociation $PCl_4F(g) \rightleftharpoons PCl_2F(g) + Cl_2(g)$ as shown in Table 2. A plot of $\log_{10} K_p$ (mm.) against $1/T$(°K) is linear,

TABLE 2. $\log_{10} K_p$ *for* $PCl_4F \rightleftharpoons PCl_2F + Cl_2$ *as a function of temperature.*

| Temp. (°C) | 133·8 | 148·0 | 163·5 | 182·3 | 193·5 | 212·5 |
|---|---|---|---|---|---|---|
| $\log_{10} K_p$ (mm.) | −0·6120 | −0·6630 | +0·1701 | +0·4060 | +0·7593 | +0·9393 |

giving a value of 11 kcal. mole$^{-1}$ for $\Delta H$. This compares with a value of 22 kcal. mole$^{-1}$ for the thermal dissociation of phosphorus pentachloride.

## EXPERIMENTAL

Volatile materials were handled throughout *in vacuo*, and non-volatile materials in a glove-box filled with dry nitrogen. Precautions were taken at every stage to exclude moisture. Samples of dichlorotrifluorophosphorane were prepared as described in Part II of this series,[1] and tetrachlorophosphonium hexafluorophosphate as described by Kolditz.[3] Infrared examinations were made by using a gas cell of 10 cm. path length with sodium chloride windows. Chloride and phosphorus analyses were carried out by standard methods. Fluoride was determined by the method of Popov and Knudson,[9] modified in small details only. The halide was first dissolved in acetonitrile, and the resulting solution was then treated with an excess of aqueous sodium hydroxide. Before proceeding with the addition of the perchloric acid and the distillation, the solution was evaporated to dryness. The lanthanum fluoride was separated by filtration, and the excess of lanthanum determined with the aid of cupferron. The method, including the addition of acetonitrile and sodium hydroxide and the evaporation to dryness, was checked by using a mixture of phosphate and fluoride in the ratio and amount to be expected in the actual analysis. Results agreed within 1%.

*Pyrolysis of Dichlorotrifluorophosphorane.*—Samples (4·0—4·5 mmoles) were sealed in an all-glass pressure-measuring system with a volume of *ca.* 300 ml. The whole apparatus was placed in an oil-filled thermostat, controlled to ±0·5°. Observations were made of the variation of pressure with temperature. The equilibrium was rapidly attained (within 30 min.) when all the material was in the gaseous phase; however, when a solid phase was present it was usually necessary for a longer time (2—5 hr.) to elapse before pressure measurements could be recorded. At the conclusion of an experiment the contents of the apparatus were examined—solids by analysis and *X*-ray powder photography, and volatile matter by analysis, molecular-weight determination, and infrared and mass spectroscopy. In a typical experiment (see Figure) a sample of pure dichlorotrifluorophosphorane was sealed in the apparatus and heated to 140°. Up to this temperature no change occurred, the pressure variation following the Charles's law line, *ab*. Above 140° an irreversible change occurred (line *bc*). On cooling from 210° (line *cdef*) the pressure fell linearly, but below 120° (point *d*) more rapidly, and at 70° a white solid was seen in the apparatus. On reheating, the pressure increase followed the line *fgdc*, and on cooling thereafter the pressure fell almost as before, along the line *cdef*. The fact that there was a slight difference (average value = +2—3 mm.) between the two descending-pressure curves is probably due to the reaction which occurs at the higher temperatures between phosphorus pentafluoride and glass, giving silicon tetrafluoride and phosphoryl fluoride. The broken line in the Figure shows the pressure calculated for the decomposition products according to Moissan;[4] in practice, the data can be best interpreted by assuming a mixture of phosphorus oxyfluoride and pentafluoride with tetrachlorofluorophosphorane and silicon tetrafluoride, the

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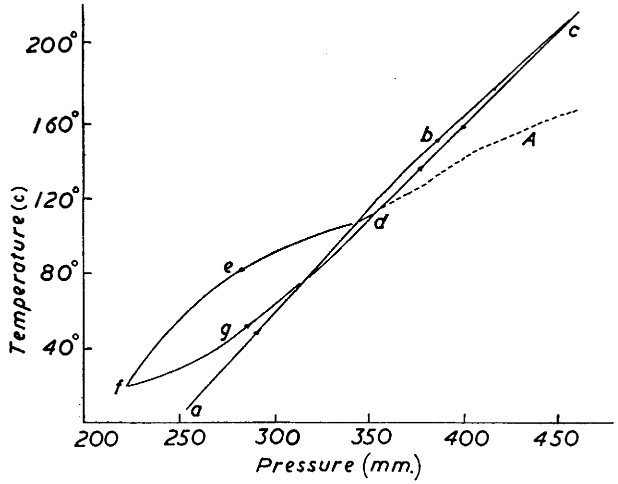
[9] Popov and Knudson, *Analyt. Chem.*, 1954, **26**, 892.

mixed halide undergoing thermal dissociation to dichlorofluorophosphine and chlorine. In the typical experiment outlined above, 1·05 mmoles of dichlorotrifluorophosphorane initially present were transformed into 0·566 mmole of volatile products of average molecular weight 125·8. This mixture consisted of 0·258 mmole of phosphoryl fluoride, 0·129 mmole of silicon tetrafluoride, 0·129 mmole of tetrachlorofluorophosphorane, and 0·051 mmole of phosphorus pentafluoride. On the basis of this gas mixture the solid should have consisted of 0·180 mmole of tetrachlorophosphonium fluoride and 0·216 mmole of tetrachlorophosphonium hexafluorophosphate, which was confirmed by a complete analysis of the solid.

*Pyrolysis of Tetrachlorophosphonium Hexafluorophosphate.*—A sample (3·5 mmoles) was sealed *in vacuo* in an all-glass pressure-measuring system (volume *ca.* 300 ml.), and the whole apparatus immersed in an oil-filled thermostat. Below 100° the pressure was only a few mm. of mercury. Above this temperature the solid vaporised and thereafter the system behaved as the dichlorotrifluorophosphorane already described. Molecular weights calculated from the pressure data in the range 100—150°, *i.e.*, before breakdown of dichlorotrifluorophosphorane at 150°, gave values of 160·7, 160·6, and 157·8 (Calc. for $P_2Cl_4F_6$, 317·8; for $PCl_2F_3$, 158·9).

Tetrachlorophosphonium hexafluorophosphate (37·3 g., 117·3 mmoles), heated in 38 ml. of boiling carbon tetrachloride for 8 hr., evolved phosphorus pentafluoride and dichlorotrifluorophosphorane. The remaining white solid, after separation by filtration, was dried *in vacuo* and then heated in dry air at 80—85° for several hours. Tetrachlorophosphonium fluoride present in the solid, together with any residual carbon tetrachloride, was removed by this treatment, which was continued until the *X*-ray powder diagram of the solid no longer showed the lines characteristic of the contaminant. Analysis of the resulting white solid gave Cl, 79·6, 80·8; P, 15·6, 15·8; F, 4·6, 4·6% ($PCl_{4.5}F_{0.5}$ requires Cl, 79·8; P, 15·5; F, 4·7%).



*Pressure changes on heating, cooling, and re-heating* $P_2Cl_9F$. *The broken line A is that calculated for* $2PCl_5 + 3PF_5$.

*Examination of* $P_2Cl_9F$.—Electrolytic conductance and transport experiments were carried out in purified acetonitrile by methods described previously.[10] A Metrovic MS2 instrument was used for the mass spectrometry, samples being examined at room temperature at an ionisation potential of 50 ev. *X*-Ray powder photographs were obtained with the sample enclosed in a thin-walled Pyrex capillary, an 11·45 cm. camera and Cu-$K_\alpha$ radiation being used with exposure times of 15—20 hr. Lines were observed at $\theta/2$ values of 7·80m, 9·41vs, 9·56w, 11·41m, 12·35m, 13·20m, 13·94w, 15·59g, 16·36s, 16·87m, 18·62m, 19·95m, 22·04m, 23·42w, 24·90w, 25·62w, 28·90m, 29·40w.

TABLE 3. *Molecular weight of* $P_2Cl_9F$ *in vapour phase* (*calculated for* $P_2Cl_9F$ 400·5).

| Temp. | 109·0° | 122·8° | 133·8° | 148·0° | 163·5° | 182·3° | 193·5° | 212·5° | 197·1° | 171·5° | 153·5° | 136·3° | 112·0° |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *M* ... | 198·4 | 185·7 | 176·0 | 166·6 | 155·3 | 143·0 | 137·6 | 131·2 | 135·2 | 145·4 | 153·4 | 162·9 | 173·1 |

Tetrachlorophosphonium pentachlorofluorophosphate (0·33 mmole) was sealed in the all-glass pressure-measuring system (volume *ca.* 300 ml.), and the pressure measured at a series

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[10] Harris and Payne, *J.*, 1956, 3038.

of temperatures up to 220°. Vaporisation was complete at about 110°; the molecular weight calculated for the data at this temperature and above is given in Table 3. If it is assumed that these values of the molecular weight at different temperatures arise from the breakdown of $P_2Cl_9F$ into phosphorus pentachloride and tetrachlorophosphonium fluoride, and that these compounds then undergo thermal dissociation, the equilibrium data for the dissociation of tetrachlorofluorophosphorane can be calculated from the pressure–temperature data with the aid of published data for the dissociation of phosphorus pentachloride.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW, W.2. [*Received, March* 15*th*, 1960.]