

### 832. Electron-impact Spectroscopy of Phosphorus Compounds. Part III.<sup>1</sup> Positive- and Negative-ion Formation from Phosphorus Trichloride and Phosphoryl Chloride.

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Phosphorus trichloride and phosphoryl chloride decompose on electron impact in the mass spectrometer, forming both positive- and negative-ion fragments. The ions  $\text{Cl}^-$  and  $\text{PCl}_2^-$  are formed in high abundance from both compounds. The ionisation-efficiency curves for negative ions indicate both resonance capture processes and ion-pair production. The observed appearance potentials, in conjunction with thermochemical data, suggest probable mechanisms of formation for several of the ionic products.

APPEARANCE potentials for formation of positive ions from phosphorus trichloride by electron impact in the mass spectrometer have been previously reported, and mechanisms for dissociation processes have been suggested.<sup>2,3</sup> In the present work, we attempted, at first, to use the appearance potentials for positive ions from phosphoryl chloride to indicate possible reaction paths. However, it was found that the observed appearance potentials could not be accounted for by formation of positive and neutral fragments only, but could

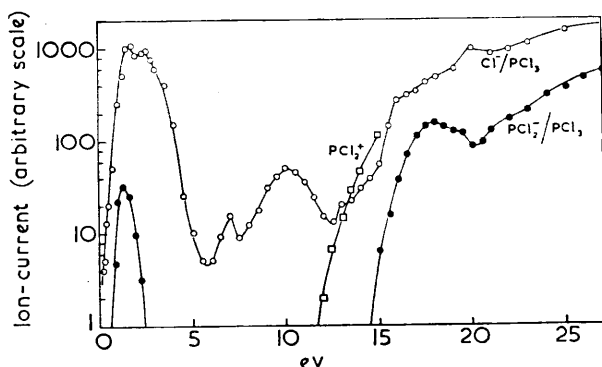
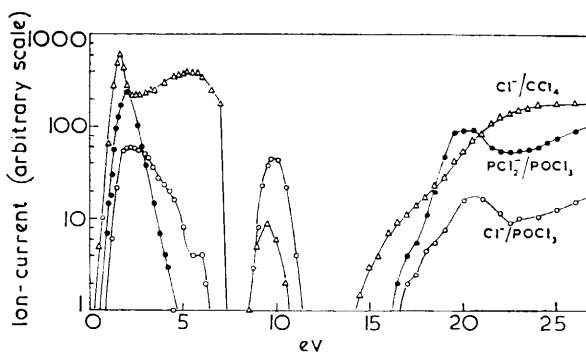


FIG. 1. Ionisation-efficiency curves for  $\text{Cl}^-$  ( $\circ$ ),  $\text{PCl}_2^-$  ( $\bullet$ ), and  $\text{PCl}_4^+$  ( $\square$ ) from electron impact on phosphorus trichloride.

FIG. 2. Ionisation-efficiency curves for  $\text{Cl}^-$  ( $\circ$ ) and  $\text{PCl}_2^-$  ( $\bullet$ ), from electron impact on phosphoryl chloride, and for  $\text{Cl}^-$  ( $\Delta$ ) from electron impact on carbon tetrachloride.



be explained by simultaneous production of negative ions, the electron affinity of which decreases the energy requirements of the total process. Surprisingly, very strong ion-currents were observed for several of the negative ions from phosphoryl chloride. This prompted a reinvestigation of the mass spectrum of phosphorus trichloride, and, here also, negative ions were found in high abundance (see Figs. 1 and 2).

<sup>1</sup> Halmann, J., 1962, 3270, and Fischler and Halmann, J., 1964, 31, are to be considered as Parts I and II, respectively.

<sup>2</sup> Kusch, Hustrulid, and Tate, *Phys. Rev.*, 1937, **52**, 840.

<sup>3</sup> Sandoval, Moser, and Kiser, *J. Phys. Chem.*, 1963, **67**, 124.

## RESULTS AND DISCUSSION

The observed relative abundances of positive- and negative-ion fragments, as well as their appearance potentials, are given in Table 1, for phosphorus trichloride, and in Table 2,

TABLE 1.

Positive- and negative-ion fragments from electron impact on phosphorus trichloride. Only the isotopically most abundant ion of each species is listed. The relative abundances given are those for positive ions at 60 v and for negative ions at 30 v electron energies.

| <i>m/e</i> | Relative abundance | Ion species                   | <i>A</i> (ev)   |            | <i>A</i> (ev) Non-resonance |        |
|------------|--------------------|-------------------------------|-----------------|------------|-----------------------------|--------|
|            |                    |                               | Resonance peaks | This work  | Ref. 2                      | Ref. 3 |
| 138        | 37                 | PCl <sub>3</sub> <sup>+</sup> |                 | 10.6 ± 0.2 | 12.2                        | 10.75  |
| 101        | 100                | PCl <sub>2</sub> <sup>+</sup> |                 | 11.8 ± 0.5 | 12.5                        | 12.32  |
| 66         | 19                 | PCl <sup>+</sup>              |                 | 16.5 ± 0.5 | 17.5                        | 16.85  |
| 35         | 16                 | Cl <sup>+</sup>               |                 | 19.8 ± 0.4 | 22.1                        | 20.2   |
| 31         | 10                 | P <sup>+</sup>                |                 | 21.0 ± 0.5 |                             | 21.2   |
| 35         | 100                | Cl <sup>-</sup>               | 0.05 ± 0.05     | 12 ± 1     |                             |        |
| 101        | 4                  | PCl <sub>2</sub> <sup>-</sup> | 0.4 ± 0.4       | 14 ± 1     |                             |        |
| 66         | <0.01              | PCl <sup>-</sup>              |                 |            |                             |        |

TABLE 2.

Positive- and negative-ion fragments from electron impact on phosphoryl chloride. Only the isotopically most abundant ion of each species is listed.

| <i>m/e</i> | Relative abundance at 60 ev | Ion species                    | <i>A</i> (ev)   |                 | <i>A</i> (ev) Non-resonance |
|------------|-----------------------------|--------------------------------|-----------------|-----------------|-----------------------------|
|            |                             |                                | First resonance | Other resonance |                             |
| 154        | 42                          | POCl <sub>3</sub> <sup>+</sup> |                 |                 | 13.1 ± 0.2                  |
| 117        | 100                         | POCl <sub>2</sub> <sup>+</sup> |                 |                 | 13.3 ± 0.2                  |
| 138        | 3                           | PCl <sub>3</sub> <sup>+</sup>  |                 |                 | 12.3 ± 0.5                  |
| 101        | 8                           | PCl <sub>2</sub> <sup>+</sup>  |                 |                 | 13.3 ± 0.5                  |
| 47         | 38                          | PO <sup>+</sup>                |                 |                 | 14.5 ± 0.5                  |
| 66         | 11                          | PCl <sup>+</sup>               |                 |                 | 17 ± 1                      |
| 16         | 0.5                         | O <sup>+</sup>                 |                 |                 | 13 ± 2*                     |
| 35         | 16                          | Cl <sup>+</sup>                |                 |                 | 19 ± 1                      |
| 31         | 11                          | P <sup>+</sup>                 |                 |                 | 21.4                        |
| 35         | 20                          | Cl <sup>-</sup>                | 0.05 ± 0.05     | 8 ± 2           | 14 ± 1                      |
| 101        | 100                         | PCl <sub>2</sub> <sup>-</sup>  | 0.05 ± 0.05     | —               | 16 ± 1                      |
| 138        | *                           | PCl <sub>3</sub> <sup>-</sup>  | *               |                 |                             |
| 66         | *                           | PCl <sup>-</sup>               | *               |                 |                             |
| 117        | *                           | POCl <sub>2</sub> <sup>-</sup> | *               |                 |                             |
| 82         | *                           | POCl <sup>-</sup>              | *               |                 |                             |
| 16         | *                           | O <sup>-</sup>                 | *               |                 |                             |

\* These ions show both resonance capture peaks and onset of ion-pair formation; owing to their very low abundance, no data can be given.

for phosphoryl chloride. Previously reported<sup>2,3</sup> appearance-potential data for positive ions from phosphorus trichloride (cols. 6 and 7, Table 1) are included for comparison; the agreement with the present results is within the experimental error.

The ion-currents obtained for the most abundant negative ions, Cl<sup>-</sup> and PCl<sub>2</sub><sup>-</sup>, were similar in magnitude to those of the most abundant positive-ion species. Owing to the different conditions of ion optics, a direct comparison of the abundances of positive and negative ions was not made.

Negative ions are usually observed with low intensity only. In the present study also, O<sup>-</sup>, from electron capture in carbon monoxide or oxygen (which were used to calibrate the electron-energy scale), gave very weak ion-currents. Probably, the highly efficient formation of Cl<sup>-</sup>, and of some phosphorus chlorides, is connected with the high electron affinity of chlorine.<sup>4-8</sup>

*Tentative Reaction-paths for the Formation of Ions by Electron Impact on Phosphorus Trichloride and on Phosphoryl Chloride.*—The ions will be discussed in the order of their increasing appearance potential.

*Phosphorus Trichloride.*  $\text{Cl}^-$ . The ionisation-efficiency curve for  $\text{Cl}^-$  (see Fig. 1) shows several sharp maxima, which must be due to resonance electron-capture processes,<sup>4</sup> as well as a threshold of increasing ion-current at higher electron energy, which must be due to a dissociation process from which an ion-pair is formed. The appearance potential of the first (lowest energy) resonance peak is, within experimental error, equal to that of  $\text{Cl}^-$  from carbon tetrachloride (the ion used for calibrating the energy scale; <sup>5</sup> it is included in Fig. 2), *i.e.*,  $0.05 \pm 0.05$  eV. For the process



the appearance potential should be given by  $A(\text{Cl}^-) \geq D(\text{Cl-PCl}_2) - E(\text{Cl})$ , where  $D(\text{Cl-PCl}_2)$  is the dissociation energy of the P-Cl bond and  $E(\text{Cl}) = 3.65 \pm 0.01$  eV is the electron affinity of chlorine.<sup>6</sup> Thus the energy of dissociation of the *first* P-Cl bond in phosphorus trichloride is  $D(\text{Cl-PCl}_2) \leq 0.05 + 3.65 = 3.7 \pm 0.3$ . This is an upper limit, since the contribution of kinetic or electronic excitation is as yet unknown. The *average* bond-dissociation energy,  $\bar{D}(\text{P-Cl})$ , in phosphorus trichloride is known<sup>7</sup> from thermochemical measurements to be 3.4 eV. The peaks of  $\text{Cl}^-$  above 3 eV may be due to formation of chlorine atoms, which then capture electrons.<sup>8,9</sup>

The onset of increasing ionisation efficiency for formation of  $\text{Cl}^-$  above  $12 \pm 1$  eV must be due to a dissociation producing also a positive ion. The obvious process is



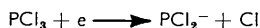
In fact, the appearance potential of  $\text{PCl}_2^+$  is  $11.8 \pm 0.4$  eV (see Table 1), in excellent agreement with that required by such a process. The ionisation potential,  $I(\text{PCl}_2)$ , should be equal to the difference between the appearance potential of  $\text{PCl}_2^+$  and the first resonance peak of  $\text{Cl}^-$ , *i.e.*,

$$I(\text{PCl}_2) = A(\text{PCl}_2^+) - A(\text{Cl}^-)_{\text{reson}} = 11.8 \pm 0.4 \text{ eV.}$$

This value is almost 3 eV higher than that previously deduced,<sup>3</sup> when it was assumed that  $\text{PCl}_2^+$  was formed only by the process

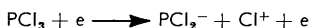


$\text{PCl}_2^-$ . The first resonance capture peak of  $\text{PCl}_2^-$  was of low intensity, and had an appearance potential of  $0.4 \pm 0.4$  eV (see Fig. 1). The most probable process is



which seems to occur even with essentially thermal electrons. Since  $A(\text{PCl}_2^-) \geq D(\text{Cl-PCl}_2) - E(\text{PCl}_2)$ , we find  $E(\text{PCl}_2) \geq 3.7 - 0.4 = 3.3$  eV.

The expected threshold for formation of an ion-pair according to the process



should be higher by  $I(\text{Cl}) = 13.01$  eV than the appearance potential of the resonance peak; *i.e.*, it should have a value of  $13.0 + 0.4 = 13.4$  eV. In fact (see Fig. 1) at  $14 \pm 1$  eV the ion-current of  $\text{PCl}_2^-$  increases sharply. It was not possible to detect ion-currents of  $\text{Cl}^+$  at this electron energy,  $A(\text{Cl}^+)$  being  $19.8 \pm 0.4$  eV. Possibly, these  $\text{Cl}^+$  ions are formed with kinetic energy, and are therefore collected with poor efficiency. It would be expected that the lighter  $\text{Cl}^+$  ions, rather than the  $\text{PCl}_2^-$  ions, would possess most of the kinetic energy.

<sup>4</sup> (a) Field and Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, 1957; (b) Schexnayder, jun., "Tabulated Values of Bond Dissociation Energies, Ionization Potentials and Electron Affinities," NASA, TN, D-1791, Washington, 1963.

<sup>5</sup> Fox and Curran, *J. Chem. Phys.*, 1961, **34**, 1995.

<sup>6</sup> Pritchard, *Chem. Rev.*, 1953, **52**, 529; Pritchard and Skinner, *ibid.*, 1955, **55**, 745; Berry, Stephen, Reimann, and Spokes, *J. Chem. Phys.*, 1961, **35**, 2237.

<sup>7</sup> Cottrell, "The Strengths of Chemical Bonds," 2nd edn., Butterworths, London, 1958, p. 283.

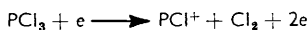
<sup>8</sup> Gutbier and Neuert, *Z. Naturforsch.*, 1954, **9a**, 335.

Halmann, *J.*, 1963, 2853; Humphries, Walsh, and Warsop, *Discuss. Faraday Soc.*, 1963, **35**, 148.

$\text{PCl}_3^+$ . The ionisation potential of phosphorus trichloride observed in the present work,  $10.6 \pm 0.2$  eV, is in agreement with that recently reported,<sup>3</sup>  $10.75 \pm 0.2$  eV.

$\text{PCl}_2^+$ . The threshold for this ion was shown above to be due mainly to ion-pair formation with  $\text{Cl}^-$ .

$\text{PCl}^+$ . It is difficult to decide whether the appearance of this ion at 16.5 eV is due to formation of neutral chlorine, as has been suggested,<sup>3</sup>

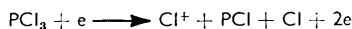


or to production of an ion-pair



Ion-pair formation would require an uprising break in the ionisation-efficiency curve of  $\text{Cl}^-$  at 16.5 eV. Since the electron beam in the ion-source used was not monoenergetic, such a break would be difficult to detect.

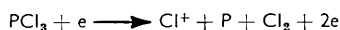
$\text{Cl}^+$ . It has been suggested<sup>3</sup> that the formation of  $\text{Cl}^+$  is due to the process



The required appearance potential, using average values<sup>7</sup> of  $\bar{D}(\text{P-Cl})$ , is

$$A(\text{Cl}^+) \geq I(\text{Cl}) + 2\bar{D}(\text{P-Cl}) = 13.0 + (2 \times 3.4) = 19.8 \text{ eV,}$$

in agreement with that observed,  $19.8 \pm 0.4$  eV. The alternative process suggested<sup>3</sup>



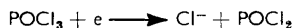
seems less likely because it involves formation of a neutral phosphorus atom, which has a lower ionisation potential (10.55 eV) than does chlorine (13.01 eV). As shown by Stevenson,<sup>10</sup> such reactions, if they occur at all, produce fragments with high electronic excitation energy, which undergo further dissociation. The ionisation-efficiency curve of Cl has a quite normal steep shape, and does not indicate considerable kinetic energy.

$\text{P}^+$ . The formation of  $\text{P}^+$  seems to be adequately explained by a process in which three chlorine atoms are formed,<sup>3</sup> and the calculated appearance potential,

$$A(\text{P}^+) \geq I(\text{P}) + 3\bar{D}(\text{P-Cl}) = 10.55 + (3 \times 3.39) = 20.7 \text{ eV,}$$

is in agreement with that observed,  $21.0 \pm 0.5$  eV.

*Phosphoryl chloride.*  $\text{Cl}^-$ . The ionisation-efficiency curve for  $\text{Cl}^-$  from phosphoryl chloride (see Fig. 2) shows several maxima which must be due to resonance capture processes, with  $A(\text{Cl}^-) = 0.05 \pm 0.05$  eV and  $8 \pm 2$  eV, as well as a threshold of increasing ion-current at  $14 \pm 1$  eV, probably due to ion-pair production. The curve is quite similar to that of  $\text{Cl}^-$  derived from phosphorus trichloride. The P-Cl bond-dissociation energy in phosphoryl chloride can be obtained for the process



from the sharp onset of the first peak, with

$$A(\text{Cl}^-) \geq D(\text{Cl-POCl}_2) - E(\text{Cl}^-)$$

Thus,  $D(\text{Cl-POCl}_2) \leq 0.05 + 3.65 = 3.7$  eV, as in phosphorus trichloride. The second resonance capture peak at 8 eV may be due to processes releasing further atoms such as oxygen or chlorine.

Ion-pair production by the process

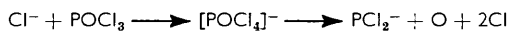


seems plausible, because  $A(\text{Cl}^-) = 14 \pm 1$  eV is similar to  $A(\text{POCl}_2^+) = 13.3 \pm 0.5$  eV.

<sup>10</sup> Stevenson, *Discuss. Faraday Soc.*, 1951, **10**, 35.

Therefore, the ionisation potential of the  $\text{POCl}_2$  radical must also be  $13.3 \pm 0.5$  ev, which is similar to that of the parent molecule [ $I(\text{POCl}_3) = 13.1$  ev].

$\text{PCl}_2^-$ . This highly abundant ion starts to be formed with a resonance capture appearance potential of only  $0.5 \pm 0.5$  ev. No simple primary dissociation process seems to account for such low energy-requirements. Possibly,  $\text{PCl}_2^-$  is formed by an ion-molecule reaction of  $\text{Cl}^-$  with the parent compound, *e.g.*,



The gas pressure in the ion-source of the apparatus used could not be varied sufficiently to test such a mechanism.

$\text{POCl}_2^-$ ,  $\text{PCl}_3^-$ , and  $\text{POCl}^-$ . These ions were observed only in very low abundance. Their ionisation-efficiency curves showed both resonance capture peaks and the onset of ion-pair formation.

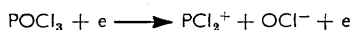
$\text{POCl}_2^+$ . This highly abundant ion has been shown above to be formed mainly together with  $\text{Cl}^-$ .

$\text{PCl}_3^+$ . The very low appearance potential of this ion,  $12.3 \pm 0.5$  ev, suggests that it is formed together with a negative ion



The ion-current of  $\text{O}^-$ , although observable, was of too low an abundance to enable its appearance potential to be measured. Taking  $I(\text{PCl}_3) = 10.6 \pm 0.2$  ev (Table 1) and  $E(\text{O}) = 1.465$  ev,<sup>11</sup> the required appearance potential should be given by  $A(\text{PCl}_3^+) \geq I(\text{PCl}_3) + D(\text{O-PCl}_3) - E(\text{O})$ , which gives  $D(\text{O-PCl}_3) \leq 12.3 - 10.6 + 1.5 = 3.2 \pm 0.5$  ev. This value is much lower than that (5.26 ev) obtained from the heat of hydrolysis of phosphoryl chloride.<sup>7</sup>

$\text{PCl}_2^+$ . Its onset at  $13.3 \pm 0.5$  ev may be due to the process



Taking  $I(\text{PCl}_2) = 11.8$  ev, from the above data on the decomposition of phosphorus trichloride, and  $E(\text{OCl}) = 2.90$  ev,<sup>5</sup> the expected appearance potential is given by

$$A(\text{PCl}_2^+) \geq I(\text{PCl}_2) + D(\text{O-PCl}_3) + D(\text{Cl-PCl}_2) - D(\text{Cl-O}) - E(\text{OCl})$$

This gives another value for the O-P bond-dissociation energy,

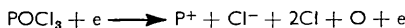
$$D(\text{O-PCl}_3) \leq 13.3 + 2.90 + 2.73 - 11.8 - 4.0 = 3.1 \text{ ev.}$$

The ion  $\text{OCl}^-$  was not, however, found in the mass spectrum of phosphoryl chloride.

$\text{PCl}^+$ . Formation of this ion may be due to various processes. Since it appears at only  $17 \pm 1$  ev, it must be formed together with some negative ion. There is insufficient data to suggest a probable process of formation.

$\text{Cl}^+$ . Part of the observed ion-current of  $\text{Cl}^+$ , appearing at  $19 \pm 1$  ev, may be due to formation of the ion-pair ( $\text{Cl}^+ + \text{POCl}_2^-$ ) mentioned above.

$\text{P}^+$ . The appearance potential of this ion derived from phosphoryl chloride, 21.4 ev, is closely similar to that of the same ion derived from phosphorus trichloride, 21.0 ev. Since, in the former, a P-O bond must be broken, part of the activation energy of the overall process must have been supplied by negative-ion formation, *e.g.*,



which would require that

$$A(\text{P}^+) \geq I(\text{P}) + D(\text{O-PCl}_3) + \overline{3D}(\text{P-Cl}) - E(\text{Cl}).$$

Taking  $I(\text{P}) = 10.55$ ,  $D(\text{O-PCl}_3) = 3.6$ ,  $\overline{D}(\text{P-Cl}) = 3.4$ , and  $E(\text{Cl}) = 3.65$  ev, we obtain  $A(\text{P}^+) = 20.7$  ev.

<sup>11</sup> Branscomb, Burch, Smith, and Geltman, *Phys. Rev.*, 1958, **111**, 504.

$\text{PO}^+$ . The low appearance potential of this ion,  $14.5 \pm 0.5$  eV, suggests that it is formed together with a negative ion, e.g.



Therefore,

$$A(\text{PO}^+) \geq I(\text{PO}) + 3\bar{D}(\text{P-Cl}) - E(\text{Cl}) - D(\text{Cl-Cl}).$$

The ionisation potential of the PO radical is unknown; assuming  $I(\text{PO}) = I(\text{NO}) = 9.25$  eV,<sup>4b</sup> we obtain  $A(\text{PO}^+) = 9.25 + (3 \times 3.39) - 3.65 - 2.48 = 13.3$  eV.

*Heats of Formation of Phosphorus Compounds.*—For several of the ion or radical fragments from phosphorus trichloride and phosphoryl chloride, reasonable processes of formation have been suggested. These permit calculation of the heats of formation of the fragments;<sup>4a</sup> the results are presented in Table 3. The heats of formation change sign (from positive to negative) on passing from positive ions to radicals, and become more negative for the negative ions. The value for  $\text{PCl}_2^+$  suggested here ( $\Delta H_f = 258$  kcal. mole<sup>-1</sup>) is much higher than those quoted in the literature;<sup>2,3</sup> this is a result of assuming  $\text{PCl}_2^+$  to be formed together with  $\text{Cl}^-$ , as shown above.

*The Radiolysis of Phosphorus Trichloride and Phosphoryl Chloride.*—The considerable ease of capture of even essentially thermal electrons in phosphorus trichloride, to form  $\text{Cl}^-$ , and in phosphoryl chloride, to form  $\text{PCl}_2^-$  and  $\text{Cl}^-$ , suggests that such ionic reactions should be considered when discussing the effects of radiolysis on these compounds. For example, the irradiation, by high-energy electrons, of mixtures of hydrocarbons with either of these compounds yielded mainly organic phosphorus dichlorides and dichlorophosphine oxides, so that the intermediate formation of hot chlorine and hydrogen atoms was postulated.<sup>12</sup> However, such products could conceivably also be formed by ionic mechanisms in which intermediates such as  $\text{Cl}^-$ ,  $\text{PCl}_2^+$ , or  $\text{POCl}_2^+$  are involved.

TABLE 3.  
Heats of formation of ion or radical fragments.

| Fragment          | Process used for calculation  | $\Delta H_f$ (kcal. mole <sup>-1</sup> ) |                    |
|-------------------|---|--|--------------------|
|                   |   | This work                                | Lit. (ref.)        |
| $\text{PCl}_3^+$  | $\text{PCl}_3 + e \longrightarrow \text{PCl}_3^+ + 2e$                | 171                                      | 175 (3)            |
| $\text{PCl}_3$    |   |  | -73.22 (4a)        |
| $\text{PCl}_3^-$  | $\text{POCl}_3 + e \longrightarrow \text{PCl}_3^- + \text{O}^+ + e$   | -216                                     |                    |
| $\text{PCl}_2^+$  | $\text{PCl}_3 + e \longrightarrow \text{PCl}_2^+ + \text{Cl}^- + e$   | 258                                      | 182 (3)<br>189 (2) |
| $\text{PCl}_2$    | $\text{PCl}_3 + e \longrightarrow \text{PCl}_2 + \text{Cl}^-$         | -13.0                                    | -25 (3)            |
| $\text{PCl}_2^-$  | $\text{PCl}_3 + e \longrightarrow \text{PCl}_2^- + \text{Cl}$         | -91                                      |                    |
| $\text{POCl}_3^+$ | $\text{POCl}_3 + e \longrightarrow \text{POCl}_3^+ + 2e$              | 160                                      |                    |
| $\text{POCl}_3$   |   |  | -141.5 (4a)        |
| $\text{POCl}_2^+$ | $\text{POCl}_3 + e \longrightarrow \text{POCl}_2^+ + \text{Cl}^- + e$ | 224                                      |                    |
| $\text{POCl}_2$   | $\text{POCl}_3 + e \longrightarrow \text{POCl}_2 + \text{Cl}^-$       | -81                                      |                    |

### EXPERIMENTAL

The mass spectrometer used was constructed at the Philips Research Laboratories, Eindhoven, Holland.<sup>13</sup> It was modified in two ways, to enable measurements at low electron energies to be made: (a) by careful adjustment of the small magnet collimating the electron beam; and (b) by connecting a 500  $\mu\text{F}$  condenser between the ion-chamber block and the filament; this provided a stable potential to the block and prevented this potential from being affected by changes in ion-current.

The energy scale for positive ions was calibrated by using argon or krypton as a reference gas.

For the observation of negative ions, a separate power supply was used, providing 1800 v

<sup>12</sup> Henglein, *Internat. J. Appl. Radiation Isotopes*, 1960, **8**, 156.

<sup>13</sup> Pelchowitch, Ph.D. Thesis, University of Amsterdam, 1953.

to the block of the ionisation chamber. For calibration of the energy scale for negative ions, the resonance peak appearance potential of either  $\text{SF}_5^-$  (0.03 eV, the same as that of  $\text{SF}_6^-$ ) from sulphur hexafluoride,  $\text{Cl}^-$  (0.05 eV<sup>5</sup>) from carbon tetrachloride, or  $\text{O}^-$  (9.6 eV<sup>4a</sup>) from carbon monoxide was used.

Phosphorus trichloride and phosphoryl chloride (Fluka, A.G.) were distilled in a vacuum system. Fractions having constant vapour pressure were expanded into evacuated 1-l. flasks which were connected to the inlet system of the mass spectrometer.

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