Formation of 1-Phosphapropyne,† $CH_3C{\equiv}P$, by Pyrolysis of Dichloro(ethyl)phosphine: a He(I) Photoelectron Spectroscopic Study ‡

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The conditions for the isolation of 1-phosphapropyne, $CH_3C{\equiv}P$, recently detected by microwave spectroscopy in the products of the gas-phase pyrolysis of $PEtCl_2$, have been studied by photoelectron spectroscopy. Although $CH_3C{\equiv}P$ is not the major product it can be trapped and separated from other reaction products under controlled conditions and subsequently revaporised. The He(I) photoelectron spectrum of $CH_3C{\equiv}P$ has been assigned and compared with that of $FC{\equiv}P$ and $HC{\equiv}P$ and the related nitrogen analogues.

RECENT work has shown that low-pressure pyrolysis techniques are particularly useful for the production of unstable molecules containing phosphorus–carbon double and triple bonds such as $CF_2{=}PH$, $CH_2{=}PCl$, and $HC{\equiv}P$.[1] These methods were an extension of those previously used to obtain $CH_3CH{=}S$,[2] $CH_2{=}C{=}S$,[3] and more recently $ClB{=}S$ and $CH_3B{=}S$.[4] Prior to this work the only phospha-alkyne species containing a $C{\equiv}P$ triple bond which had been detected was $HC{\equiv}P$ produced by a carbon-arc discharge in phosphine.[5] The pyrolysis experiments [1] indicated that other new phospha-alkynes might be obtained from suitable precursors and subsequently $CH_3C{\equiv}P$ [6] and $FC{\equiv}P$ [7] have been detected. In the case of $FC{\equiv}P$ an alternative highly efficient room-temperature synthesis has been devised.[7]

Initially we used microwave techniques to characterise $CH_3C{\equiv}P$ among the pyrolysis products of dichloro(ethyl)phosphine, $PEtCl_2$. The microwave technique is extremely sensitive to species such as $CH_3C{\equiv}P$ and $FC{\equiv}P$ and it is doubtful if the photoelectron (p.e.) spectral measurements discussed here would have been successful had not $CH_3C{\equiv}P$ been positively identified by the initial microwave studies. On the other hand, microwave spectroscopy is much less sensitive for the detection of species having small effective dipole moments. Photoelectron spectroscopy has complementary qualities since the photoionisation cross-sections of molecules are roughly comparable and in this work we have exploited this ability to detect *all* the products of the pyrolysis of $PEtCl_2$ and to optimise the conditions for the isolation of pure $CH_3C{\equiv}P$.

EXPERIMENTAL

Dichloro(ethyl)phosphine (kindly provided by Professor R. Schmutzler) was purified by high-vacuum fractional condensation and allowed to flow slowly at low pressure (*ca.* 0.05 mmHg) § through a quartz tube (outside diameter 10 mm) heated at 900—950 °C along *ca.* 150 mm of its length. Two traps were used selectively to remove starting material and side products of the reaction under the conditions discussed in detail below. The reaction products were led directly into the ionisation chamber of a Perkin-Elmer PS16 photoelectron spectrometer. Spectra were calibrated using the known ionisation potentials (i.p.s) of C_2H_4, C_2H_2, and HCl which were side products of the reaction as well as those of CH_3I and Ar which were added when required.

RESULTS AND DISCUSSION

Figure 1(*a*) shows the p.e. spectrum of the starting $PEtCl_2$ which has not previously been reported, 1(*b*) the spectrum obtained when $PEtCl_2$ is pyrolysed at *ca.* 930 °C and the products are passed through a trap at −78 °C to remove starting material, 1(*c*) the spectrum of the products of pyrolysis after passage through traps at −78 °C (to retain $PEtCl_2$) and −126 °C (to retain PCl_3), and finally 1(*d*) indicates the spectrum of pure $CH_3C{\equiv}P$ obtained by warming the products whose spectra are shown in 1(*c*) from liquid-nitrogen temperature (see below). Figure 2 shows an expansion of the first two bands in the p.e. spectrum of $CH_3C{\equiv}P$ and the ionisation potentials are listed in the Table, together with appropriate assignments.

The phosphorus lone-pair i.p. of 9.70 ± 0.05 eV § for $PEtCl_2$ compares closely with those of previously published data for $PMeCl_2$ [8,9] and PBu^tCl_2.[8] Pyrolysis at *ca.* 800 °C leads to the formation of HCl and small amounts of other compounds. At 930 °C the p.e. spectrum shown in Figure 1(*b*) exhibits an intense band at *ca.* 12.75 eV and a structured band with an onset at 16.25 eV, which are due to HCl.[10] Ethylene is also evident in the spectrum, giving rise to bands at *ca.* 10.5, 12.6 (hidden under HCl), and 15.8 eV,[10] and the presence of PCl_3 is shown by bands at *ca.* 11.8 and 14.3 eV.[11] A very weak band at 9.9 eV is ascribed to $CH_3C{\equiv}P$ discussed below.

Ionisation-potential data for $CH_3C{\equiv}P$

Ionisation potential (eV)	Vibrational band (cm^{-1})	Orbital assignment
9.89 ± 0.01	1 420 ± 50 [a]	e $\pi(C{\equiv}P)$
12.19 ± 0.01	1 230 ± 56 [b]	a_1 σ n.b.(P) [c]
14.7 ± 0.2		e (CH_3)
15.6 ± 0.1		a_1 (CH_3)

[a] $C{\equiv}P$ stretching frequency. [b] Probably CH_3 deformation. [c] n.b. = Non-bonding.

Previous work using microwave spectroscopy to analyse the products of the pyrolysis of $PEtCl_2$ had identified only $CH_3C{\equiv}P$ and so the process shown below

$$CH_3CH_2PCl_2 \xrightarrow[-HCl]{Heat} [CH_3CH{=}PCl] \xrightarrow[-HCl]{Heat} CH_3C{\equiv}P$$

was postulated as the major reaction mechanism. The present p.e. spectroscopic study indicates that this is not

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† Phosphinetriylethane or ethylidynephosphine.

‡ No reprints available.

§ Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 mmHg ≈ 13.6×9.8 Pa.

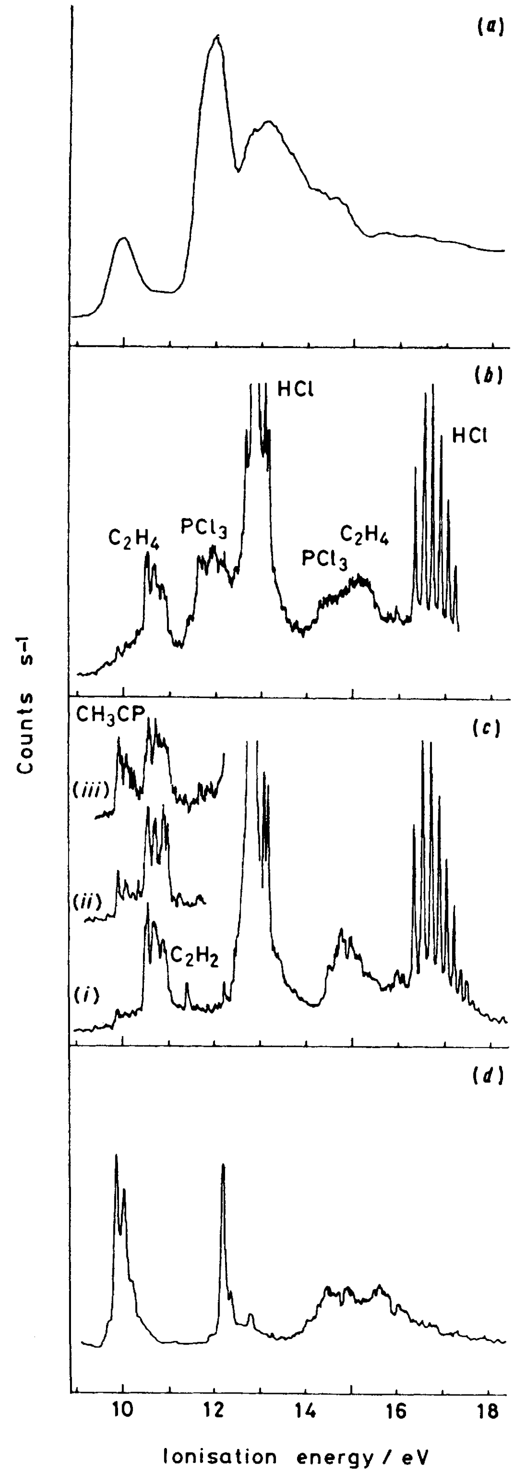

FIGURE 1 Photoelectron spectra of (*a*) parent $PEtCl_2$, (*b*) the pyrolysis products of $PEtCl_2$ at *ca.* 930 °C *after* passage through a trap at −78 °C, (*c*) pyrolysis products after passage through traps at −78 *and* −126 °C [As the pressure in the flow system is reduced the new feature at 9.89 eV assigned to $CH_3C{\equiv}P$ increases in intensity relative to the other features: (*i*) *ca.* 0.07, (*ii*) *ca.* 0.05, (*iii*) *ca.* 0.03 mmHg], and (*d*) $CH_3C{\equiv}P$ only

the only process occurring, nor indeed the main one. Yields of $CH_3C{\equiv}P$ are low (at best 10%) and then only under carefully controlled conditions. As indicated in Figures 1(*b*) and (*c*), the observation of HCl shows that one or both the above steps occur, but the detection of C_2H_4 and PCl_3 demonstrates the existence of other efficient decomposition and reaction pathways under these conditions, in particular cleavage of the P–C bond. Trapped material has not so far been analysed and the postulated intermediate $CH_3CH{=}PCl$ which is analogous to the known [1] phospha-alkene $CH_2{=}PCl$ has not yet been detected either by microwave or p.e. spectral studies. Subsequent experiments (see below) establish that small amounts of C_2H_6 and C_2H_2 are also formed in the pyrolysis reaction. Although from the standpoint of microwave spectroscopy these by-products are not troublesome, the pyrolysis procedure is not a very efficient route to $CH_3C{\equiv}P$ for a p.e. spectral study, and an alternative low-temperature synthesis similar to that devised [7] for $FC{\equiv}P$ offers more promise.

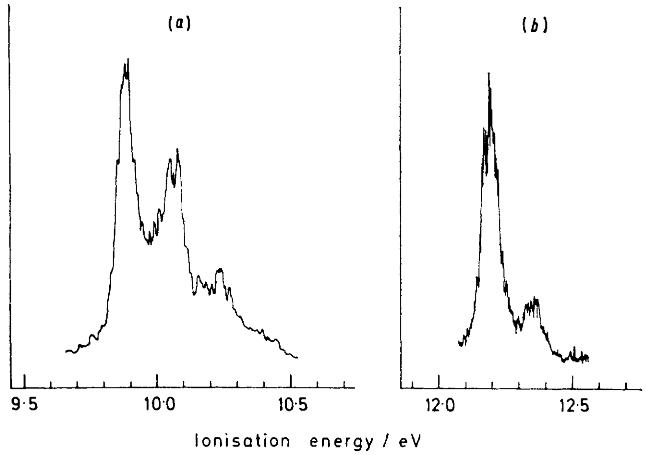

FIGURE 2 High resolution scans of (*a*) the first band of $CH_3C{\equiv}P$ at 9.89 eV, (*b*) the second band of $CH_3C{\equiv}P$ at 12.19 eV

Previous work [6] indicated that $CH_3C{\equiv}P$ could be condensed and revaporised from a trap at −120 °C, but under the more rapid flow conditions employed in the present study we note that $CH_3C{\equiv}P$ just passes through a trap at −126 °C. Trichlorophosphine is conveniently removed by this procedure, as indicated in Figure 1(*c*), where traces of C_2H_2 are also evident (peak at 11.4 eV), and we find that a reduction of the overall pressure of the flowing gases leads to an increase in the yield of $CH_3C{\equiv}P$. This is illustrated in the insets (*i*) and (*ii*) of Figure 1(*c*) where *decreasing* pressure increases the yield of $CH_3C{\equiv}P$ relative to C_2H_4 so that as shown in (*iii*) the bands in the p.e. spectrum of $CH_3C{\equiv}P$ and C_2H_4 corresponding to the first i.p.s have almost the same intensity. This represents the maximum yield of $CH_3C{\equiv}P$ that could be obtained by this method. The best method of removing both HCl and C_2H_4 involves passing the reaction products through a trap at −126 °C into a trap cooled to liquid-nitrogen temperature [Figure 1(*c*)] and subsequently warming the trap at −196 °C. By carefully controlling the conditions it is possible to monitor the side products as they appear in the order of their volatility.

A trace of C_2H_6 is observed first, followed by C_2H_4 and HCl and the pressure in the system drops. Further warming gives $CH_3C{\equiv}P$ alone enabling the spectrum shown in Figure 1(*d*) to be recorded. Thus $CH_3C{\equiv}P$ may be trapped and revaporised and thus separated from impurities.

The Photoelectron Spectrum of Phosphapropyne, $CH_3C{\equiv}P$.—The p.e. spectrum of $CH_3C{\equiv}P$ is shown in Figure 1(*d*) and expansions of the first two bands in Figure 2. The assignments are relatively straightforward by comparison with the spectra of $HC{\equiv}P$,[12] $CH_3C{\equiv}N$,[10,13,14] and $FC{\equiv}P$.[7]

The first band shown in Figure 2(*a*) has a coincident adiabatic and vertical i.p. at 9.89 ± 0.01 eV, and an associated vibrational progression of 1 420 ± 50 cm^{-1}. This band is assigned to the excitation of an electron from the $C{\equiv}P$ π molecular orbital and the vibration at 1 420 cm^{-1} probably corresponds to the $C{\equiv}P$ stretching frequency. The corresponding bands of $[HCP]^+$ (1 110 cm^{-1}) [9] and $[FCP]^+$ (1 725 cm^{-1}) [7] have similar Franck–Condon envelopes. In $CH_3C{\equiv}P$ the ionisation from the π orbital gives rise to two series, but a second series is not resolved here.

The second band shown in Figure 2(*b*) consists of an intense first peak at 12.19 ± 0.01 eV, together with a very weak second component, yielding a vibrational interval of 1 230 ± 50 cm^{-1}. This band corresponds to the removal of a non-bonding electron localised on the P atom (a_1) and is very similar to the corresponding band of $HC{\equiv}P$ at 12.86 eV.[12] The excitation of 1 230 cm^{-1} may not, however, correspond to the $C{\equiv}P$ stretching frequency, since the molecular orbital is non-bonding and the vibrational interval ought to be close to that of the neutral molecule, whereas the value here seems low compared to that of 1 420 cm^{-1} for the first band, which is itself probably lower than in the neutral molecule. Furthermore, the corresponding band of $CH_3C{\equiv}N$ shows an excitation of the symmetric deformation of the CH_3 group and the same situation probably obtains for $CH_3C{\equiv}P$.

Broad bands centred at 14.7 ± 0.2 and 15.6 ± 0.1 eV are assigned to higher i.p.s associated with the excitation of electrons localised mainly in the C–H and C–C bonds. Analogous bands of $CH_3C{\equiv}N$ occur at 15.5 and 17.4 eV.[10,13,14]

In all respects the p.e. spectrum of $CH_3C{\equiv}P$ closely resembles that of $HC{\equiv}P$, where replacement of H by CH_3 destabilises all the orbitals and a lowering of 0.90 and 0.67 eV is observed for the π and σ levels respectively. The corresponding shifts of the π and σ levels from $HC{\equiv}N$ to $CH_3C{\equiv}N$ are 1.4 and 0.86 eV respectively. Figure 3 illustrates the correspondence between the energy levels of the triply bonded phosphorus compounds, $CH_3C{\equiv}P$, $HC{\equiv}P$,[12] and $FC{\equiv}P$,[7] and the corresponding triply bonded nitrogen compounds, $CH_3C{\equiv}N$,[10,13,14] $HC{\equiv}N$,[10] and $FC{\equiv}N$.[15] Apart from the overall shift to lower i.p., as is expected for the less electronegative P atom, the interesting feature of Figure 3 is the increased separation between the π and σ levels compared to that of the N-containing molecules. In general, the π levels are destabilised by *ca.* 2—3 eV, whereas the σ levels show rather less destabilisation (*ca.* 1 eV). The large π shift may reflect the increased diffuseness of the carbon to phosphorus triple bond.

Conclusion.—We have shown that pyrolysis of $PEtCl_2$ at low pressure leads to the formation of $CH_3C{\equiv}P$ although the yields are rather low. The other main products of the reaction are HCl, PCl_3, and C_2H_4, with traces of C_2H_6 and C_2H_2. Pure $CH_3C{\equiv}P$ may be obtained by appropriate low-temperature trapping procedures, since it may be revaporised from the solid. We have yet to determine the efficiency of the reverse reaction involving addition of HCl to $CH_3C{\equiv}P$. The chemical and spectroscopic properties of this interesting molecule may now be studied in the absence of other species. The photoelectron results indicate that $CH_3C{\equiv}P$ is electronically similar to $CH_3C{\equiv}N$.

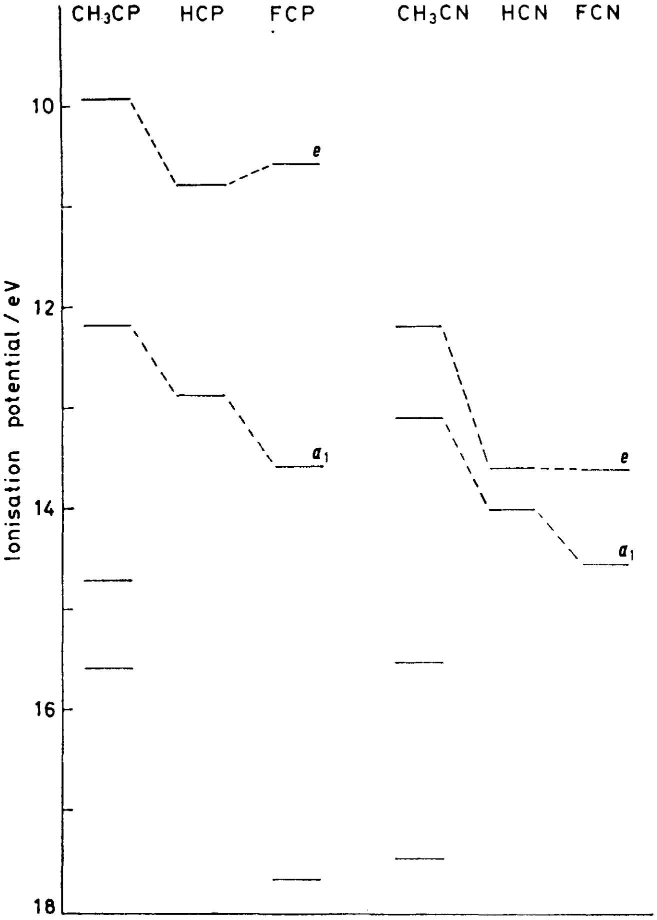

FIGURE 3 Comparison of the observed ionisation potentials of $CH_3C{\equiv}P$, $HC{\equiv}P$, and $FC{\equiv}P$ compared with those of the analogous nitrogen species $CH_3C{\equiv}N$, $HC{\equiv}N$, and $FC{\equiv}N$

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REFERENCES

[1] M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J.C.S. Chem. Comm.*, 1976, 513.

[2] H. W. Kroto and B. M. Landsberg, *J. Mol. Spectroscopy*, 1976, **62**, 346.

[3] K. Georgiou, H. W. Kroto, and B. M. Landsberg, *J.C.S. Chem. Comm.*, 1974, 739.

[4] C. Kirby and H. W. Kroto, *J.C.S. Chem. Comm.*, 1978, 19.

[5] T. E. Gier, *J. Amer. Chem. Soc.*, 1961, **83**, 1769.

[6] M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *Chem. Phys. Letters*, 1976, **42**, 460.

[7] H. W. Kroto, J. F. Nixon, N. P. C. Simmons, and N. P. C. Westwood, *J. Amer. Chem. Soc.*, 1978, **100**, 446.

[8] M. F. Lappert, J. B. Pedley, B. T. Wilkins, O. Stelzer, and E. Unger, *J.C.S. Dalton*, 1975, 1207.

[9] S. Elbel and H. Tom Dieck, *Z. Naturforsch.*, 1976, **B31**, 178.

[10] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley–Interscience, London, 1970.

[11] A. W. Potts and W. C. Price, *Phil. Trans.*, 1970, **A268**, 59.

[12] D. C. Frost, S. T. Lee, and C. A. McDowell, *Chem. Phys. Letters*, 1973, **23**, 472.

[13] D. C. Frost, F. G. Herring, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Letters*, 1970, **4**, 533.

[14] R. F. Lake and H. W. Thompson, *Proc. Roy. Soc.*, 1970, **A317** 187.

[15] G. Bieri, *Chem. Phys. Letters*, 1977, **46**, 107.