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FC≡P, C-Fluorophosphaethyne: Preparation and Detection by Photoelectron and Microwave Spectroscopy

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Abstract: An original method of synthesizing compounds containing the C=P double bond (phosphaalkenes) and C≡P triple bond (phosphaalkynes) has been developed. This method has been used to produce the new reactive linear triatomic molecule FC≡P, C-fluorophosphaethyne, in very high yield. When trifluoromethylphosphine, CF₃PH₂, vapor is passed slowly over solid KOH at room temperature two HF units are eliminated to yield FC≡P. If the relative quantity of KOH is reduced or the flow rate increased the intermediate phosphaalkene resulting from the elimination of one HF fragment is detected. This species, CF₂=PH, had previously been characterized during pyrolysis experiments on CF₃PH₂. Both photoelectron and microwave measurements have been made on this system. There are three distinct ionization potentials which can be assigned to FC≡P, the first occurring at 10.57 ± 0.01 eV. The rotational constant B₀ has been determined from the J = 3 ← 2 transition as B₀ = 5257.78 ± 0.1 MHz.

Introduction

Until recently the only compound containing a C≡P triple bond was HC≡P, which was produced by a carbon arc discharge in phosphine by Gier in 1961.¹ Although several spectroscopic studies of this species have been reported,²⁻⁵ subsequently the chemistry of the interesting C≡P moiety (phosphaalkynes) appears to have been neglected. The absence of a satisfactory synthetic route has presumably been mainly responsible for this lack of development. As a consequence a series of experiments has been initiated to develop efficient synthetic routes to phosphaalkynes in general and also to the intermediate phosphaalkenes which contain the C=P double bond which had hitherto been unidentified. In this way it was hoped that new RC≡P species could be produced and also that the latent chemistry of these intriguing species could be explored. In this endeavor we have made full use of both microwave and photoelectron techniques to detect, characterize, and study these new molecules and in particular determine the optimum conditions for production.

Such techniques have already proven very successful in the study of various carbon-sulfur and carbon-selenium multiply bonded species such as CH₃CH=S,⁶ CH₂=C=S,⁷ and CH₃CH=Se.⁸ Multiply bonded species involving boron such as HB=S,⁹ NH₂=BF₂,¹⁰ CH₃NH=BF₂,¹¹ CH₃B=S, and ClB=S¹² have also been investigated by these methods. In

general the species have been produced in high-temperature flow reactions and the extension of these techniques to the production and study of the new class of compounds—the phosphaalkenes CF₂=PH, CH₂=PCl, and CH₂=PH—has recently been reported by us.¹³ These experiments also indicated that further elimination of HX (X ≡ halogen) from phosphaalkenes should lead to derivatives of HC≡P. In this way the first new derivative, CH₃C≡P, was made by pyrolysis of CH₃CH₂PCl₂.¹⁴

During microwave investigations of the pyrolysis products of CF₃PH₂ not only was CF₂=PH detected¹³ but also two new species, PH₂F and FC≡P. These two new molecules were produced in very low yields and it was during attempts to improve this situation that an original, simple, and effective room temperature synthesis of FC≡P was evolved which avoids the destructive conditions which obtain in high-temperature processes. The synthesis promises to have wide application and also to allow us to explore the chemistry of the phosphaalkynes (and phosphaalkenes), the avowed aim of these initial studies.

Experimental Section

During a microwave search for FC≡P among the pyrolysis products of CF₃PH₂^{13,15} a weak group of lines was detected whose Stark and vibrational satellite patterns were consistent with the J = 3 ← 2 transition of a linear molecule. The ground-state line frequency was 31 546.705 ± 0.01 MHz, which was within 450 MHz of the position predicted on the

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Table I. Experimental and Theoretical IPs for FC≡P

Assignment	IP, eV ^a	Vibrational structure, cm ⁻¹ ^c	Calculation, eV ^e
² Π	10.57	1725 760 ^d	10.53
² Σ ⁺	13.55	860	13.94
² Π	17.63 ^b		20.08
² Σ ⁺			22.31

^a ±0.01 eV, unless otherwise stated. ^b ±0.03 eV. ^c ±30 cm⁻¹, unless otherwise stated. ^d ±40 cm⁻¹. ^e Calculation performed to minimum energy assuming Koopman's theorem. $r(\text{C-F}) = 1.2995$, $r(\text{C}\equiv\text{P}) = 1.5365$ Å. Total energy = 12 988.748 eV.

basis of an estimated structure. This initial estimated structure had a C-F bond length of 1.262 Å and a C≡P bond length of 1.542 Å taken directly from FC≡N¹⁶ and HC≡P,² respectively. If semiquantitative account is taken of the bond length variations estimated from available data on related species then using $r(\text{C-F}) = 1.270$ and $r(\text{C}\equiv\text{P}) = 1.547$ Å one comes even closer: ca. 160 MHz. The weakness of the new spectrum indicates that the species represents but a small fraction of all the species present in the pyrolysis products. The major components are CF₂=PH and unpyrolyzed CF₃PH₂ so this process is clearly an unsatisfactory source of FC≡P.

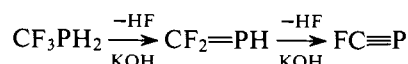
We are, however, now able to produce the species which gives rise to this transition in excellent yield by the simple expedient of passing CF₃PH₂ vapor at room temperature and low pressure (ca. 30 μmHg) through a spiral glass tube, 1 cm i.d. and 40 cm long, filled with broken KOH pellets. The products from the reactor flowed directly (via ca. 15 cm of glass tubing) into the cell of the microwave spectrometer or the ionization chamber of the photoelectron spectrometer. The new species is readily detected and the effectiveness of this method can be judged from Figure 1, where the photoelectron spectrum obtained when the products are flowed directly into the spectrometer ionization chamber is shown. The only strong peaks observed can be unambiguously assigned to FC≡P.

The photoelectron measurements were made using a Perkin-Elmer P.S.16 spectrometer operating at 584 Å. Under the experimental conditions resolution was ca. 30 meV. A Hewlett-Packard 8460A microwave spectrometer operating between 26.5 and 40 GHz was used for the measurements on the rotational spectra. In both cases the pressure of the flowing sample was maintained at ca. 30 μmHg. At these pressures we have also found that FC≡P can be isolated in the microwave spectrometer cell for several hours at room temperature.

The parent compound, CF₃PH₂, was made by reduction of CF₃PI₂ with PH₃.¹⁷ The theoretical calculation used to confirm the assignments of the photoelectron spectra was carried out using the GAUSSIAN 70 program with a STO 4-31G basis set (without d orbitals).¹⁸

Results

The photoelectron spectrum of FC≡P shown in Figure 1 consists of three distinct bands whose ionization potentials are listed in Table I together with details of the vibrational structure. These three bands can be unequivocally assigned to FC≡P and the absence of any other significant features serves to show just how close to completion the reaction



comes in the simple flow system. Although shorter lengths of the reactor, as well as faster flow rates, yield CF₂=PH, the experiments carried out so far have concentrated on optimizing the conditions under which FC≡P is produced.

The first band, for which the adiabatic and vertical IPs are

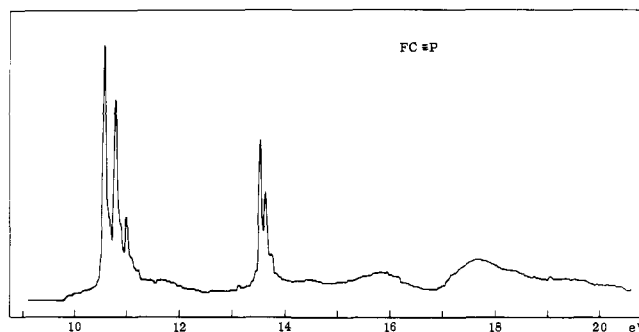


Figure 1. The photoelectron spectrum of FC≡P between 9 and 21 eV.

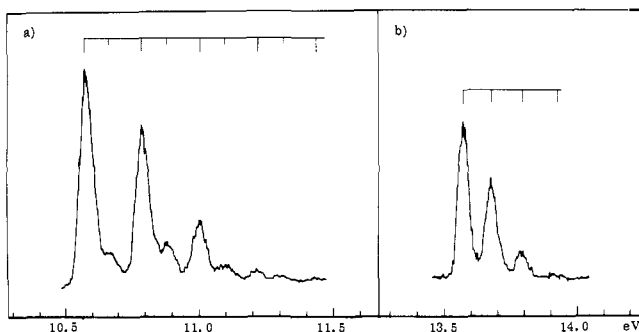


Figure 2. (a) High-resolution scan of the first band at 10.57 eV showing vibrational progression in 1725 and 760 cm⁻¹. (b) High-resolution scan of the second band at 13.55 eV showing a vibrational progression in ca. 860 cm⁻¹.

coincident at 10.57 ± 0.01 eV, shows a well-resolved progression consisting of at least four members with a frequency of 1725 ± 30 cm⁻¹ (Figure 2a). A shorter progression in 760 ± 40 cm⁻¹ can also be resolved. The second band, for which the adiabatic and vertical IPs are similarly coincident, in this case at 13.55 ± 0.01 eV, also shows a well-resolved progression of four members in a frequency of 860 ± 30 cm⁻¹ (Figure 2b). Although there are some very weak broad features, only the strongest band which has an adiabatic IP at 17.63 ± 0.03 eV is assigned to FC≡P.

Only one *J* transition lies within the range of the Sussex spectrometer and thus the derived B_0 value of 5257.78 ± 0.1 MHz has a slightly larger error than usual. This value will be refined when further transitions have been measured.

Discussion

The microwave spectrum of the new species shows that it is a small linear molecule with an observed rotational constant so close to that predicted on the basis of an estimated structure as to leave little doubt that the identity is FC≡P. The identity is further confirmed by the photoelectron spectrum, which is in good agreement with that expected for this species. These experiments have shown that the new synthetic procedure is a convenient and efficient source of an interesting species which is expected to have useful chemical properties. Modification of this system promises to yield a wide range of substituted phosphalkynes and phosphalkenes, considerably broadening the chemistry of these species.

FC≡P has 16 valence electrons and is expected to have the ground state electron configuration

$$(6\sigma)^2(7\sigma)^2(8\sigma)^2(2\pi)^4(9\sigma)^2(3\pi)^4$$

The first three IPs of FC≡P are quite distinct and are readily assigned with reference to those of HC≡P⁵ and FC≡N.¹⁹ The assignment is further confirmed using a theoretical calculation (Table I).

The first band, at 10.57 eV, is therefore assigned as arising

from the ionization of an electron from the 3π orbital. This assignment is consistent with its position, relative intensity, and the associated vibrational structure. No spin-orbit splitting was resolved nor is it expected to be resolved with the resolution available. The calculation indicates that the 3π orbital is localized mainly in the $C\equiv P$ group and thus the associated vibrational frequency of 1725 cm^{-1} must be assigned to the $C\equiv P$ stretching vibration in the ground electronic state of $FC\equiv P^+$. This value appears somewhat high when compared with the values observed in $HC\equiv P$ and $HC\equiv P^+$, which are 1276 and 1110 cm^{-1} , respectively; however, it is roughly in line with that expected when one considers the frequencies of $HC\equiv CH$, $HC\equiv CH^+$, $FC\equiv CH$ and $FC\equiv CH^+$, which are 1983 , 1830 , 2250 , and 2180 cm^{-1} , respectively.^{20,21} The 760-cm^{-1} frequency probably belongs to the C-F stretching frequency which in FCN^+ is 1077 cm^{-1} .²² These observations imply that the vibrational modes of the new species are not particularly localized in the bonds and/or that Fermi resonance effects are important.

The second band at 13.55 eV appears to have only a single vibrational progression of 860 cm^{-1} . This band is assigned to a $2\Sigma^+$ state produced by ionization of a σ electron localized mainly on the phosphorus atom. The corresponding band of HCP shows no C-H vibrational excitation and an extremely weak $C\equiv P$ stretch component⁵ in accord with the ionization of a P lone pair electron. In the case of $FC\equiv P$, however, rather more structural relaxation appears to occur and the observation of a frequency as low as 860 cm^{-1} implies that only the C-F bond length changes on ionization. This result implies that either there is some fluorine contribution to the σ molecular orbital from which excitation occurs or that reorganizational effects are rather important when this electron is ejected. A similar phenomenon occurs in methyl cyanide^{23,24} and the cyanogen halides^{23,25} when a N lone pair excitation occurs. Replacement of H by F in this species leaves the π orbital relatively unaffected (a slight destabilization of 0.22 eV is observed) whereas the σ orbital is stabilized by some 0.69 eV . This effect is in qualitative agreement with that observed in general on fluorine substitution,²⁶ though not as large as usual.

By comparison of the spectrum of FCP with that of FCN we see that, as expected, the first IP (2Π state) shifts down by ca. 3 eV whereas the second ($2\Sigma^+$ state) shifts down by ca. 1 eV . A parallel effect is observed for HCP and HCN, where the shifts are 2.82 and 1.14 eV for the first and second IPs, respectively.

The third band, which is broad and occurs at 17.63 eV , is assigned to the excitation of fluorine lone pair electrons. The corresponding band in FCN lies at 19.3 eV .

The calculations are in satisfactory agreement with experiment when account is taken of the discrepancies that occur

in general when highly electronegative groups are present. The calculation indicates that the π orbital has a small amount of C-F antibonding character, whereas the σ orbital is slightly C-F bonding, as expected, though it consists mainly of a phosphorus σ lone pair atomic orbital.

The charge distribution indicates that there is a large positive charge on the P atom ($+0.48$), a small negative charge at the C atom (-0.09), and a large negative charge at the F atom (-0.39). In HCP the charge distribution is P ($+0.08$), C (-0.31), and H ($+0.23$).²⁷ The large positive charge on P as compared to that on N in FCN ²⁸ indicates that FCP might act as an acceptor of electron density in chemical reactions.

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