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# Gas-Phase Infrared Spectra of the Unstable Phosphaalkenes $CF_2{=}PH$, $CF_2{=}PCF_3$, and $CH_2{=}PCl$: The $C{=}P$ Stretching Vibration and Force Constant

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**Abstract:** Gas-phase infrared spectra of the unstable phosphaalkenes $CF_2{=}PH$, $CF_2{=}PCF_3$, and $CH_2{=}PCl$ and their deuteriated species have been measured and vibrational assignments have been made. The $C{=}P$ stretching bands are observed at 1349.5, 1350.2, and 1365.3 $cm^{-1}$ for $CF_2{=}PH$, $CF_2{=}PD$, and $CF_2{=}PCF_3$, respectively, and at 979.7 and 847.9 $cm^{-1}$ for $CH_2{=}PCl$ and $CD_2{=}PCl$, respectively. Normal coordinates were treated for these molecules. For the fluorophosphaalkenes, the $C{=}P$ stretching mode is highly coupled with the $CF_2$ symmetric stretching mode; one of the coupled vibrations is shifted to higher wavenumber of about 1350 $cm^{-1}$ and the other to lower wavenumber of about 730 $cm^{-1}$. For $CH_2{=}PCl$, the $C{=}P$ stretching vibration of 979.7 $cm^{-1}$ is almost negligibly perturbed by other vibrational modes, so that it gives an almost intrinsic $C{=}P$ stretching wavenumber. For $CD_2{=}PCl$, the $C{=}P$ stretching mode is coupled largely with the $CD_2$ scissoring mode. The band intensities of the $C{=}P$ stretching vibration have also been discussed. The $C{=}P$ stretching force constant was determined to be 562-668 N $m^{-1}$. The values for the carbon-phosphorus force constants of the double and triple bonds are roughly two and three times, respectively, as large as the value for the single bond, and the values for the carbon-phosphorus bonds are about half the values for the corresponding carbon-nitrogen bonds.

In recent years, there has been a great interest in the multiple bonding that involves elements in the third and higher rows in the periodic table. A new class of transient molecules containing a $C{=}P$ bond was first reported by Kroto et al.[1] in 1976; these molecules were produced by thermal decomposition and were detected by microwave spectroscopy. At the same time, Becker[2] found by NMR spectroscopy some phosphaalkenes that were kinetically stabilized by bulky substituents. Since then many phosphaalkenes have been prepared by a large variety of methods.[3,4] However, owing to their instability, gas-phase infrared spectra of simple phosphaalkenes have been scarcely obtained, and therefore the $C{=}P$ stretching vibration has not been definitively assigned.

In the present paper, we report the gas-phase infrared spectra of several unstable phosphaalkenes, namely difluorophosphaethene ($CF_2{=}PH$ and $CF_2{=}PD$), perfluoro-2-phosphapropene ($CF_2{=}PCF_3$), and 1-chlorophosphaethene ($CH_2{=}PCl$ and $CD_2{=}PCl$). We have derived unambiguous wavenumbers for the $C{=}P$ stretching vibration and the force constant associated with this vibration.

Difluorophosphaethene $CF_2{=}PH$ was first detected in 1976[1] by microwave spectroscopy in the products of low-pressure flow pyrolysis of $CF_3PH_2$ and was later identified by photoelectron and NMR spectroscopy in the products of a reaction of $CF_3PH_2$ with KOH.[5] Recently we have obtained the infrared spectrum of $CF_2{=}PH$ in part in the course of the preparation of $FC{\equiv}P$.[6]

Perfluoro-2-phosphapropene $CF_2{=}PCF_3$ was first trapped in 1979 in base hydrolysis of $(CF_3)_2PH$ with KOH by Nixon et al.,[7] who identified it by NMR spectroscopy. Later Burg[8] reported the infrared spectrum of this molecule in a pyrolysis study of its cyclic dimer and trimer species. Very recently, Steger et al.[9] have determined the $r_a$ structure of $CF_2{=}PCF_3$ by using electron diffraction.

1-Chlorophosphaethene $CH_2{=}PCl$ was first characterized by microwave spectroscopy in 1976[1] through high-temperature pyrolysis of $CH_3PCl_2$ and later identified by NMR spectroscopy in 1980 through a reaction of $CH_3PCl_2$ with $N(C_2H_4)_3N$.[10] Among the several preparations reported,[1,10-13] an efficient route to $CH_2{=}PCl$ is to utilize pyrolysis of $(CH_3)_3SiCH_2PCl_2$ at about 680 °C. Recently, the $r_s$ structure of this molecule has been determined by Kroto et al.[11] and Bak et al.[13] by using a microwave technique.

## Experimental Section

The samples of $CF_2{=}PH$, $CF_2{=}PD$, and $CF_2{=}PCF_3$ were prepared by passing $CF_3PH_2$, $CF_3PD_2$, and $(CF_3)_2PH$ vapors, respectively, at room temperature and low pressure (ca. 20 Pa) through a glass tube, 1 cm i.d. and 70 cm long, filled with KOH pellets.[5-7] The products were passed through a trap cooled at −120 °C so that the generated water was condensed and were stored at −196 °C. No exchange reaction from $CF_2{=}PD$ to $CF_2{=}PH$ occurred in this preparation process. The precursors were prepared by reactions of the corresponding iodo compounds with $PH_3$ or $PD_3$.[5] $CH_2{=}PCl$ was prepared by pyrolysis of $(CH_3)_3SiCH_2PCl_2$ at about 680 °C,[11] and $CD_2{=}PCl$ was prepared, less efficiently than $CH_2{=}PCl$, by pyrolysis of $CD_3PCl_2$ at about 1000 °C.[1] The pyrolysis products were passed through two traps successively, one cooled at −120 °C and the other cooled at −196 °C. The greater part of the $CH_2{=}PCl$ or $CD_2{=}PCl$ product was, however, polymerized to yield white solid on a glass wall inside the second trap. Vacuum distillation was used to separate $CH_2{=}PCl$ or $CD_2{=}PCl$ from a large amount of byproducts.

The infrared spectra were recorded on a JEOL JIR-40X Fourier transform spectrometer at a resolution of 0.12 or 0.25 $cm^{-1}$ with a globar source and a TGS or an MCT detector. Mylar and KBr/Ge beam splitters were used for the measurements in the regions 50-500 and 400-4000 $cm^{-1}$, respectively. Dry nitrogen gas was continuously passed through the instrument during the measurement to get rid of water vapor. Sample pressures were 1-5 kPa in a 12-cm glass cell fitted with KBr or polyethylene windows. Wavenumbers of absorption peaks were calibrated against the standard lines of $CO_2$, $H_2O$, HCl, and DCl.[14]

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**Table I.** Rotational Constants and PR Separations of Band Envelopes for Phosphaalkenes

| | rotational constant (cm$^{-1}$) | | | PR separation (cm$^{-1}$) | | |
|---|---|---|---|---|---|---|
| | $A$ | $B$ | $C$ | A type | B type | C type |
| $CF_2{=}PH$[a] | 0.370 493 | 0.158 990 | 0.111 103 | 18.4 | 14.7 | 27.6 |
| $CF_2{=}PD$[a] | 0.356 114 | 0.155 868 | 0.108 282 | 18.1 | 14.5 | 27.2 |
| $CF_2{=}PCF_3$[b] | 0.113 43 | 0.034 84 | 0.030 90 | 9.0 | 7.4 | 13.5 |
| $CH_2{=}P^{35}Cl$[c] | 0.757 607 | 0.155 685 | 0.128 940 | 18.3 | 15.2 | 27.4 |
| $CD_2{=}P^{35}Cl$[c] | 0.655 267 | 0.144 181 | 0.118 003 | 17.5 | 14.6 | 26.3 |

[a] Microwave data.[3] [b] Calculated from the electron-diffraction data.[9] [c] Microwave data.[11]

**Table II.** Observed and Calculated Wavenumbers for $CF_2{=}PH$ and $CF_2{=}PD$

| | | $\nu$(obsd) (cm$^{-1}$) | int[a] | type | $\Delta\nu$(PR)[b] (cm$^{-1}$) | $\nu$(calcd) (cm$^{-1}$) | P.E.D.[c] (%) |
|---|---|---|---|---|---|---|---|
| | | | | | $CF_2{=}PH$ | | |
| a′ | $\nu_1$ | 2326.9 | m | ~B | 14 | 2340.0 | $s_1(100)$ |
| | $\nu_2$ | 1349.5 | vs | ~A | 18 | 1347.2 | $\underline{s_2(59)}$, $\underline{s_5(49)}$, $s_6(19)$ |
| | $\nu_3$ | 1228.5 | s | ~B | 16 | 1229.5 | $s_3(78)$, $s_7(18)$, $s_4(12)$ |
| | $\nu_4$ | 884.4 | m | AB | 15 | 890.4 | $s_4(86)$, $s_3(12)$ |
| | $\nu_5$ | 729.3 | m | AB | 18 | 729.4 | $\underline{s_5(55)}$, $\underline{s_2(26)}$, $s_6(5)$ |
| | $\nu_6$ | 485.5 | m | AB | 18 | 486.8 | $s_6(81)$, $s_2(15)$ |
| | $\nu_7$ | 418.3 | w | | | 414.6 | $s_7(83)$, $s_3(10)$ |
| a″ | $\nu_8$ | 1088.8 | w | C | | 1088.8 | $s_8(91)$, $s_9(2)$ |
| | $\nu_9$ | 568.0 | w | C | | 568.0 | $s_9(103)$, $s_8(14)$ |
| | | | | | $CF_2{=}PD$ | | |
| a′ | $\nu_1$ | 1690.6 | m | ~B | 14 | 1680.8 | $s_1(100)$ |
| | $\nu_2$ | 1350.2 | vs | ~A | 18 | 1347.2 | $\underline{s_2(59)}$, $\underline{s_5(49)}$, $s_6(19)$ |
| | $\nu_3$ | 1219.9 | s | ~B | 16 | 1216.9 | $s_3(85)$, $s_7(18)$, $s_4(5)$ |
| | $\nu_4$ | 736.6 | m | AB | 18 | 742.5 | $\underline{s_5(50)}$, $\underline{s_2(26)}$, $s_4(11)$, $s_6(3)$ |
| | $\nu_5$ | 661.5 | w | ~B | 14 | 655.3 | $s_4(77)$, $s_3(7)$, $s_6(6)$, $s_5(5)$ |
| | $\nu_6$ | 483.5 | m | AB | 18 | 482.8 | $s_6(77)$, $s_2(15)$, $s_4(2)$ |
| | $\nu_7$ | 401.2 | w | | | 403.5 | $s_7(80)$, $s_3(8)$, $s_4(5)$ |
| a″ | $\nu_8$ | | | | | 834.0 | $s_8(75)$, $s_9(12)$ |
| | $\nu_9$ | 544.7 | vw | C | | 544.7 | $s_9(94)$, $s_8(31)$ |

[a] int, intensity; s, strong; m, medium; w, weak; v, very; and sh, shoulder. [b] PR separation of band envelope. [c] P.E.D., potential-energy distribution. For the description of the symmetry coordinates $s_i$, see Table VIII. For the underlined P.E.D., see text.

**Table III.** Observed and Calculated Wavenumbers for $CF_2{=}PCF_3$

| | | this work | | Burg[a] | | | |
|---|---|---|---|---|---|---|---|
| | | $\nu$(obsd) (cm$^{-1}$) | int[b] | $\nu$(obsd) (cm$^{-1}$) | int | $\nu$(calcd) (cm$^{-1}$) | P.E.D.[c] (%) |
| a′ | $\nu_1$ | 1365.3 | vs | 1363 | 64 | 1363 | $\underline{s_2(61)}$, $\underline{s_5(50)}$, $s_6(13)$ |
| | $\nu_2$ | 1248.9 | s | 1248 | 33 | 1247 | $s_3(87)$, $s_7(17)$ |
| | $\nu_3$ | 1149.1 | vs | 1148 | 80 | 1145 | $s_9(99)$, $s_{11}(13)$ |
| | $\nu_4$ | 1095 | w | | | 1094 | $s_8(67)$, $s_1(42)$, $s_{10}(29)$ |
| | $\nu_5$ | 746 sh | vw | 742 | 2.3 | 763 | $\underline{s_5(51)}$, $\underline{s_2(24)}$ |
| | $\nu_6$ | 737 | w | 737 | 2.3 | 736 | $s_{10}(16)$, $s_8(35)$, $s_1(25)$ |
| | $\nu_7$ | 484 sh | vw | | | 488 | $s_7(28)$, $s_{11}(22)$, $s_{10}(20)$, $s_4(8)$ |
| | $\nu_8$ | 470 | w | 458 | 0.6 | 470 | $s_{11}(58)$, $s_7(15)$, $s_{10}(11)$ |
| | $\nu_9$ | 432 | vw | | | 424 | $s_6(82)$, $s_2(8)$ |
| | $\nu_{10}$ | | | | | 327 | $s_1(24)$, $s_7(33)$, $s_{10}(32)$ |
| | $\nu_{11}$ | | | | | 271 | $s_{12}(76)$, $s_6(9)$ |
| | $\nu_{12}$ | | | | | 97 | $s_4(83)$, $s_{12}(7)$ |
| a″ | $\nu_{13}$ | 1134.5 | m | 1132 | 86 | 1138 | $s_{14}(102)$, $s_{15}(14)$, $s_{16}(7)$ |
| | $\nu_{14}$ | 551 | vw | 541 | 0.5 | 551 | $s_{13}(97)$ |
| | $\nu_{15}$ | 475 | w | 458 | 0.6 | 472 | $s_{15}(87)$ |
| | $\nu_{16}$ | | | | | 296 | $s_{16}(89)$, $s_{15}(7)$ |
| | $\nu_{17}$ | | | | | 76 | $s_{17}(78)$, $s_{18}(19)$ |
| | $\nu_{18}$ | | | | | 55 | $s_{18}(79)$, $s_{17}(20)$ |

[a] Reference 8. [b] See footnote *a* of Table II. [c] P.E.D., potential-energy distribution. For the a′ species, $s_1$ = C–P str, $s_2$ = C═P str, $s_3$ = $CF_2$ a-str, $s_4$ = CPC def, $s_5$ = $CF_2$ s-str, $s_6$ = $CF_2$ sci, $s_7$ = $CF_2$ rock, $s_8$ = $CF_3$ s-str, $s_9$ = $CF_3$ a-str, $s_{10}$ = $CF_3$ s-def, $s_{11}$ = $CF_3$ a-def, and $s_{12}$ = $CF_3$ rock; and for the a″ species, $s_{13}$ = $CF_2$ wag, $s_{14}$ = $CF_3$ a-str, $s_{15}$ = $CF_3$ a-def, $s_{16}$ = $CF_3$ rock, $s_{17}$ = C═P tor, and $s_{18}$ = C—P tor.

## Results and Discussion

The planar molecules of $CF_2{=}PH$ and $CH_2{=}PCl$ have $C_s$ symmetry and nine fundamentals are divided into seven of the a′ species and two of the a″ species. The molecule of $CF_2{=}PCF_3$ also belongs to the $C_s$ point group. Of eighteen fundamentals, twelve are of the a′ species and six are of the a″ species. The a′ vibrations are expected to give AB-type bands, whereas the a″ vibrations are expected to give C-type bands. The rotational constants and the PR separations of the band envelopes calculated by the Seth-Paul formulas[15] are given in Table I. The observed infrared data for these molecules are given in Tables II–V.

**Difluorophosphaethene.** The preliminary infrared spectrum of difluorophosphaethene $CF_2{=}PH$ has been obtained in the course of the preparation of fluorophosphaethyne $FC{\equiv}P$ by treatment of $CF_3PH_2$ with KOH.[6] The reaction may be described as follows

$$CF_3PH_2 \xrightarrow[-KF,\ -H_2O]{KOH} CF_2{=}PH \xrightarrow[-KF,\ -H_2O]{KOH} FC{\equiv}P$$

As the KOH treatment proceeded, several new bands appeared in the infrared spectrum. These bands are assigned to the vibrations of $CF_2{=}PH$ or $FC{\equiv}P$ on the basis of the rate of the relative intensity change with the KOH contact time or elapse time; the bands due to the same species change with the same

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**Table IV.** Observed and Calculated Wavenumbers for $CH_2{=}PCl$ and $CD_2{=}PCl$

| | | $\nu$(obsd) ($cm^{-1}$) | int[a] | type | $\Delta\nu(PR)$[b] ($cm^{-1}$) | $\nu$(calcd) ($cm^{-1}$) | P.E.D.[c] (%) |
|---|---|---|---|---|---|---|---|
| | | | | $CH_2{=}PCl$ | | | |
| a′ | $\nu_1$ | 3095.6 | vw | AB | | 3087.0 | $s_3(100)$ |
| | $\nu_2$ | 2974.3 | vw | | | 2982.6 | $s_5(99)$ |
| | $\nu_3$ | 1372.3 | m | AB | 17 | 1373.0 | $s_6(95)$, $s_2(11)$, $s_5(1)$ |
| | $\nu_4$ | 979.7 | w | AB | 18 | 980.2 | $\underline{s_2(90)}$, $s_6(6)$, $s_4(1)$ |
| | $\nu_5$ | 792.4 | s | ~B | | 794.9 | $s_7(93)$, $s_4(6)$, $s_1(2)$ |
| | $\nu_6$ | 499.7 | vs | AB | 15 | 505.3 | $s_1(89)$, $s_4(12)$, $s_7(4)$ |
| | $\nu_7$ | 340.2 | w | | | 339.8 | $s_4(82)$, $s_1(10)$, $s_7(4)$ |
| a″ | $\nu_8$ | 804.7 | vs | C | | 806.2 | $s_9(101)$, $s_8(1)$ |
| | $\nu_9$ | 609.4 | vw | C | | 609.4 | $s_8(100)$ |
| | | | | $CD_2{=}PCl$ | | | |
| a′ | $\nu_1$ | | | | | 2301.0 | $s_3(100)$ |
| | $\nu_2$ | | | | | 2165.7 | $s_5(98)$, $s_2(2)$, $s_6(1)$ |
| | $\nu_3$ | 1120.8 | m | AB | 17 | 1120.1 | $\underline{s_6(52)}$, $\underline{s_2(55)}$, $s_5(2)$ |
| | $\nu_4$ | 847.9 | w | AB | | 847.6 | $\underline{s_2(44)}$, $\underline{s_6(48)}$, $s_4(1)$ |
| | $\nu_5$ | 642.9 | s | ~B | | 641.6 | $s_7(72)$, $s_4(18)$, $s_1(12)$ |
| | $\nu_6$ | 490.0 | vs | AB | 15 | 483.9 | $s_1(83)$, $s_7(17)$, $s_4(2)$ |
| | $\nu_7$ | | | | | 309.0 | $s_4(79)$, $s_7(12)$, $s_1(5)$ |
| a″ | $\nu_8$ | 634.5 | s | C | | 633.4 | $s_9(101)$, $s_8(1)$ |
| | $\nu_9$ | 431.6 | vw | C | | 438.7 | $s_8(100)$ |

[a,b,c] See footnotes *a*, *b*, *c* of Table II.

**Table V.** Combination and Overtone Bands Observed for $CF_2{=}PH$, $CF_2{=}PD$, $CH_2{=}PCl$, and $CD_2{=}PCl$

| $\nu$(obsd) ($cm^{-1}$) | int[a] | assignment | $\nu$(obsd) ($cm^{-1}$) | int[a] | assignment |
|---|---|---|---|---|---|
| | | $CF_2{=}PH$ | | | |
| 2699.1 | vw | $2\nu_2$ | 1370.1 | w | $\nu_4 + \nu_6$ |
| 2229.0 | vvw | $\nu_2 + \nu_4$ | 1347.8 sh | vs | $\nu_2 + \nu_7 - \nu_7$ |
| 2111.4 | vw | $\nu_3 + \nu_4$ | 1346.2 sh | vs | $\nu_2 + 2\nu_7 - 2\nu_7$ |
| 2104.8 | vw | $\nu_3 + \nu_4 + \nu_7 - \nu_7$ | 1211.3 sh | s | $\nu_5 + \nu_6$, Fermi |
| 2075.6 | w | $\nu_2 + \nu_5$ | 1132.4 | vw | $2\nu_9$ |
| 2069.6 | vw | $\nu_2 + \nu_5 + \nu_7 - \nu_7$ | 727.8 sh | w | $\nu_5 + \nu_7 - \nu_7$ |
| | | $CF_2{=}PD$ | | | |
| 2700.2 | vvw | $2\nu_2$ | 1878.9 | vvw | $\nu_3 + \nu_4$ |
| 2083.2 | w | $\nu_2 + \nu_5$ | 1348.5 sh | vs | $\nu_2 + \nu_7 - \nu_7$ |
| 2079.1 | vw | $\nu_2 + \nu_5 + \nu_7 - \nu_7$ | 1347.1 sh | vs | $\nu_2 + 2\nu_7 - 2\nu_7$ |
| 2008.4 | vw | $\nu_2 + \nu_4$ | 1215.8 sh | s | $\nu_5 + \nu_6$, Fermi |
| | | $CH_2{=}PCl$ | | | |
| 2744.2 | vvw | $2\nu_3$ | 1401.9 | vvw | $\nu_5 + \nu_9$ |
| 2160.0 | vvw | $\nu_3 + \nu_5$ | 996.7 | w | $2\nu_6$, Fermi |
| 1951.5 | vvw | $2\nu_4$ | 496.6 sh | vs | $\nu_6 + \nu_7 - \nu_7$ |
| 1618.4 | vw | $2\nu_8$ | 493.6 sh | vs | $\nu_6 + 2\nu_7 - 2\nu_7$ |
| 1597.7 | vvw | $\nu_5 + \nu_8$ | | | |
| | | $CD_2{=}PCl$ | | | |
| 1122.9 | w | $\nu_5 + \nu_6$, Fermi | 486.8 sh | vs | $\nu_6 + \nu_7 - \nu_7$ |

[a] See footnote *a* of Table II.

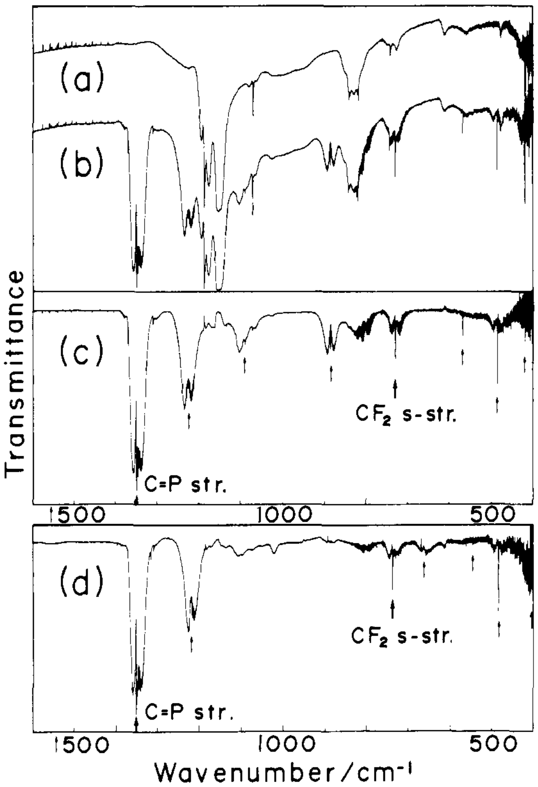

**Figure 1.** (a) Infrared spectrum of precursor $CF_3PH_2$; (b) spectrum of a mixture containing mainly $CF_3PH_2$ and $CF_2{=}PH$, prepared by passing $CF_3PH_2$ vapor through a glass tube filled with KOH pellets; (c) difference spectrum (spectrum b − spectrum a) of $CF_2{=}PH$; and (d) difference spectrum of $CF_2{=}PD$. The bands of $CF_2{=}PH/CF_2{=}PD$ are denoted by arrows.

intensity ratio. We have attempted to prepare a pure sample of $CF_2{=}PH$, but actually we obtained a mixture of $CF_2{=}PH$, $FC{\equiv}P$, and $CH_3PH_2$. The spectrum of the mixture containing mainly $CF_2{=}PH$ and $CF_3PH_2$ (Figure 1b) was obtained by a single passing of $CF_3PH_2$ vapor through a glass tube filled with KOH pellets. Thus, we had the spectrum of $CF_2{=}PH$ (Figure 1c) by subtracting the spectrum of the precursor $CF_3PH_2$ (Figure 1a) from the spectrum of Figure 1b; the bands of $CF_2{=}PH$ are denoted by arrows in the spectrum. Similarly, the spectrum of $CF_2{=}PD$ (Figure 1d) was obtained by the KOH treatment of $CF_3PD_2$. The observation of various combination bands is helpful for the spectral interpretation so that the bands which are pertinent to the component fundamentals of the combination are unequivocally assigned to the same molecular species. Table V lists the observed combination bands of $CF_2{=}PH$ and $CF_2{=}PD$, together with the overtone bands. The observed PR separations of the bands for $CF_2{=}PH$ and $CF_2{=}PD$ (Table II) are also in good agreement with the estimated values (Table I). Vibration–rotation analyses of the strong bands at about 1350 and 1220 $cm^{-1}$ for $CF_2{=}PH$ and $CF_2{=}PD$ gave reasonable values of the rotational constants in comparison with the reported microwave values (Table I), namely, the successive spacings of the bands are about 0.25 $cm^{-1}$ ($\simeq 2B$) for the A-type band and 0.46 $cm^{-1}$ ($\simeq 2[A - (B + C)/2]$) for the B-type band.[16]

The vibrational assignments were made on the basis of the wavenumber shift on deuteriation, band type, normal coordinate treatment, and spectral comparison with related molecules such as $CF_2{=}S$,[17] $CF_3PH_2$,[18] and $(CF_3)_2PH$.[19] The bands of $CF_2{=}PH$

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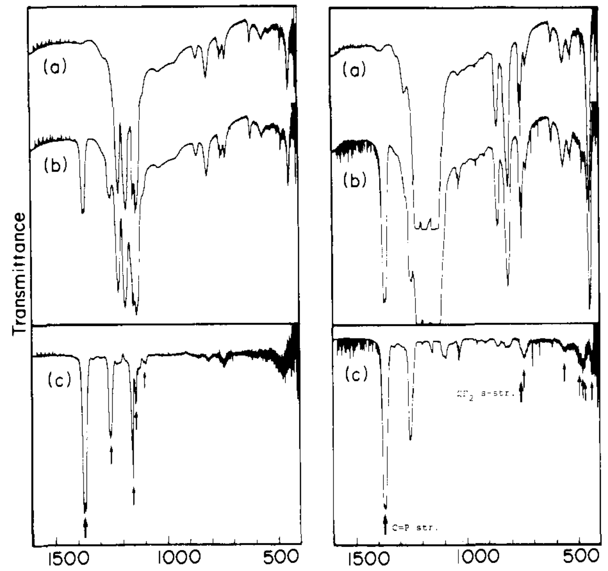

**Figure 2.** (a) Infrared spectrum of precursor $(CF_3)_2PH$; (b) spectrum of a mixture containing mainly $(CF_3)_2PH$ and $CF_2{=}PCF_3$, prepared by passing $(CF_3)_2PH$ vapor through a glass tube filled with KOH pellets; and (c) difference spectrum (spectrum b − spectrum a) of $CF_2{=}PCF_3$. The bands of $CF_2{=}PCF_3$ are denoted by arrows.

at 2326.9 (pseudo-B-type) and 884.4 cm$^{-1}$ (AB-type), which are shifted to a lower wavenumber region on deuteriation, are readily assigned to the P–H stretching and CPH in-plane deformation vibrations, respectively, and the weak Q branch at 1088.8 cm$^{-1}$, which is overlapped with unidentified bands, is assigned tentatively to the CPH out-of-plane deformation vibration. The pseudo-A-type band at 1349.5 cm$^{-1}$, the pseudo-B-type band at 1228.5 cm$^{-1}$, and the AB-type band at 729.3 cm$^{-1}$ are assigned respectively to the C=P stretching, $CF_2$ antisymmetric stretching, and $CF_2$ symmetric stretching vibrations. These bands are correlated well with the A-, B-, and A-type bands of $CF_2{=}S$ at 1368, 1189, and 787 cm$^{-1}$.[17] For $CF_2{=}S$, the $CF_2$ wagging, scissoring, and rocking vibrations have been assigned to the C-type band at 622 cm$^{-1}$, the A-type band at 526 cm$^{-1}$, and the B-type band at 417 cm$^{-1}$, respectively. Thus, for $CF_2{=}PH$, the C-type band at 568.0 cm$^{-1}$ and the AB-type band at 485.5 cm$^{-1}$ are safely assigned to the $CF_2$ wagging and scissoring vibrations, respectively, but the weak band at 418.3 cm$^{-1}$ is tentatively assigned to the $CF_2$ rocking vibration. The vibrational assignments of $CF_2{=}PH$ and $CF_2{=}PD$ are summarized in Table II, where some of the previous assignments for $CF_2{=}PH$[6] have been interchanged. The C=P stretching vibration is assigned to the very strong bands at 1349.5 and 1350.2 cm$^{-1}$ for $CF_2{=}PH$ and $CF_2{=}PD$, respectively, whose wavenumbers are, however, considerably higher than the C≡P stretching wavenumber (1278.3 cm$^{-1}$) for HC≡P.[20]

The P–H and P–D stretching modes are highly localized in the normal vibrations of 2326.9 and 1690.6 cm$^{-1}$, respectively, these wavenumbers being almost coincident with those for $PH_3$ (av. 2325.0 cm$^{-1}$)[21] and $PD_3$ (av. 1689.6 cm$^{-1}$).[22] If the relationship[23] between the bond length and the stretching wavenumber is assumed, the P–H bond length of $CF_2{=}PH$ is expected to be very close to 1.420 Å for $PH_3$.[24] The P–H bond length for $CH_2{=}PH$ has also been obtained to be 1.420 Å.[25] The CPH angle of $CF_2{=}PH$ may also be similar to the corresponding angle for $CH_2{=}PH$, because the changes of the bond angles from $NH_3$ (106.68°)[26] and $PX_3$ (X = H, 93.345°;[24] and X = Cl, 100.27°[27]) to $CH_2{=}NH$ (110.4°)[28] and $CH_2{=}PX$ (X = H, 97.4°;[25] and X = Cl, 103.0°[11]) have a good correlation with each other.

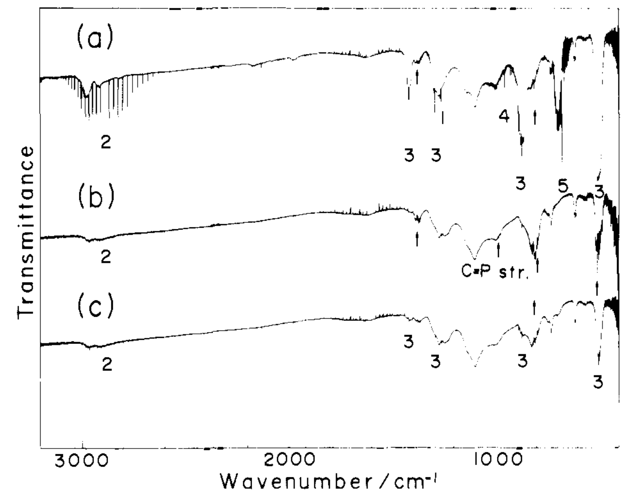

**Figure 3.** Infrared spectra for pyrolysis products of $(CH_3)_3SiCH_2PCl_2$: (a) immediately after the pyrolysis; (b) after elimination of HCl, HC≡P, and $CH_2{=}CH_2$ from the products; and (c) 12 h after spectrum b. The bands of $CH_2{=}PCl$ are denoted by arrows. Other bands are identified as $(CH_3)_3SiCl$ (1), HCl (2), $CH_3PCl_2$ (3), $CH_2{=}CH_2$ (4), and HC≡P (5).

**Perfluoro-2-phosphapropene.** Burg[8] has obtained the infrared spectrum of perfluoro-2-phosphapropene $CF_2{=}PCF_3$ by low-pressure pyrolysis of its cyclic dimer and trimer species. We have independently investigated the infrared spectrum of $CF_2{=}PCF_3$ by a base reaction of $(CF_3)_2PH$ with KOH. In this reaction, a trace of water played an important role in promoting the formation of $CF_2{=}PCF_3$. In the absence of water, only the precursor was recovered, whereas in the presence of a considerable amount of water, most of the low-boiling products were $CF_3H$ and $CF_2H_2$. Spectra a and b of Figure 2 are the infrared spectra of the precursor $(CF_3)_2PH$ and the mixture containing mainly $CF_2{=}PCF_3$ and $(CF_3)_2PH$. The difference spectrum (Figure 2, spectrum b–spectrum a) is shown in Figure 2c, where the bands of $CF_2{=}PCF_3$ are denoted by arrows. The observed wavenumbers for $CF_2{=}PCF_3$ are listed in Table III, together with Burg's results.[8] The strong bands observed above 700 cm$^{-1}$ are in good agreement with Burg's observation. The PR separations of 8 cm$^{-1}$ for the 1365.3-cm$^{-1}$ band and 7 cm$^{-1}$ for the 1248.9-cm$^{-1}$ band compare well with the expected values given in Table I. The weak bands in the region below 700 cm$^{-1}$, whose wavenumbers are somewhat different from Burg's results, have been assigned tentatively. The band assignable to the C=P stretching vibration is observed at 1365.3 cm$^{-1}$; this assignment is reasonable in comparison with the assignment for $CF_2{=}PH$ and $CF_2{=}PD$.

**1-Chlorophosphaethene.** $CH_2{=}PCl$ was prepared by the pyrolysis of $(CH_3)_3SiCH_2PCl_2$ at about 680 °C under a pressure of 5–8 Pa. The pyrolysis products were passed through two traps cooled at −120 and −196 °C. The gas-phase infrared spectra of the mixture collected in the second trap are shown in Figure 3, where the bands assignable to $CH_2{=}PCl$ are denoted by arrows and other bands are identified as those of $(CH_3)_3SiCl$, HCl, $CH_3PCl_2$, $CH_2{=}CH_2$, and HC≡P. Spectra b and c of Figure 3 indicate that the bands due to $CH_2{=}PCl$ decrease in intensity in the presence of HCl, while the bands due to $CH_3PCl_2$ gradually increase. The spectral observation in Figure 3 suggests the following reaction process

$$(CH_3)_3SiCH_2PCl_2 \xrightarrow[-(CH_3)_3SiCl]{\Delta(680\ ^\circ C)} CH_2{=}PCl \xrightarrow[-HCl]{\Delta} HC{\equiv}P$$

Byproducts such as $CH_2{=}CH_2$ and HC≡CH may be formed

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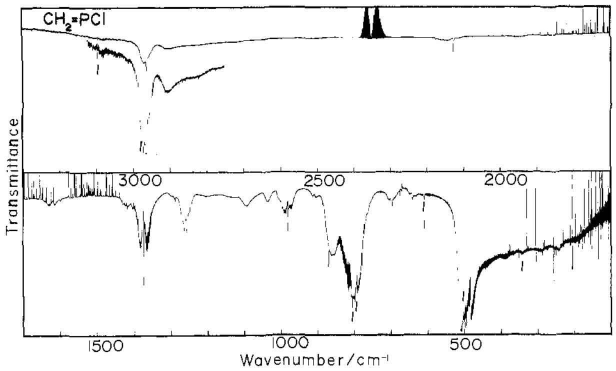

**Figure 4.** Infrared spectrum for pyrolysis products of $(CH_3)_3SiCH_2PCl_2$ containing mainly $CH_2$=PCl. Fundamentals of $CH_2$=PCl are denoted by arrows.

through a C–P bond cleavage which occurs more easily at higher temperatures. The sample of $CH_2$=PCl readily reacts with HCl to yield $CH_3PCl_2$ in an infrared cell at room temperature. The identification of $CH_2$=PCl is also supported by the observation of the relevant combination bands (Table V) and the PR separations of the bands assignable to $CH_2$=PCl (Tables I and IV). The vibration–rotation analysis of the AB-type band at 1372.3 $cm^{-1}$ has also identified $CH_2$=PCl.[16]

Figure 4 shows a typical spectrum of the products containing mainly $CH_2$=PCl. The weak Q branch at 3095.6 $cm^{-1}$ is reasonably assigned to the vinylic $CH_2$ antisymmetric stretching vibration, and the very weak band at 2974.3 $cm^{-1}$ is assigned tentatively to the $CH_2$ symmetric stretching vibration. The AB-type bands at 1372.3 and 979.7 $cm^{-1}$ may be attributed to the $CH_2$ scissoring and C=P stretching vibrations, respectively. The band contours around 800 $cm^{-1}$ are interpreted to be composites of the C-type band centered at 804.7 $cm^{-1}$ ($CH_2$ wagging) and the pseudo-B-type band centered at 792.4 $cm^{-1}$ ($CH_2$ rocking). The weak C-type band at 609.4 $cm^{-1}$ is assigned to the $CH_2$ twisting vibration, the strong band at 499.7 $cm^{-1}$ to the P–Cl stretching vibration, and the very weak band at 340.2 $cm^{-1}$ to the CPCl bending vibration. In this way, all of the fundamentals of $CH_2$=PCl have been detected. The $CH_2$ scissoring, rocking, and wagging wavenumbers of $CH_2$=PCl (1372.3, 792.4, and 804.7 $cm^{-1}$, respectively) are similar to those of $CH_2$=$SiH_2$ (1350, 741, and 817 $cm^{-1}$),[29] but they are considerably smaller than the wavenumbers for the corresponding vibrations of $CH_2$=S (1447.0, 991.0, and 990.2 $cm^{-1}$).[30] Similar wavenumber differences have been noted for the $CF_2$ vibrations between $CF_2$=PH and $CF_2$=S.[17] The C=P stretching wavenumber of $CH_2$=PCl, 979.7 $cm^{-1}$, differs significantly from the wavenumbers of fluorophosphaalkenes (ca. 1350 $cm^{-1}$).

In order to confirm the band assignments of $CH_2$=PCl mentioned above, the deuteriated derivative $CD_2$=PCl was prepared by the pyrolysis of $CD_3PCl_2$. The spectra of the pyrolysis products are shown in Figure 5; Figure 5a is the spectrum of the products immediately after the pyrolysis, Figure 5b is the spectrum of the products kept in an infrared cell for 15 h, and Figure 5c is the difference spectrum (spectrum a–spectrum b). More enhanced bands in Figure 5b than in Figure 5a are due to $CD_3PCl_2$ and $CD_2HPCl_2$. Thus, the following reaction process is suggested to occur

$$CD_2{=}PCl \xrightarrow[+DCl,\ +HCl]{} CD_3PCl_2 + CD_2HPCl_2$$

The spectral pattern in the region 500–1500 $cm^{-1}$ of $CD_2$=PCl (Figure 5c) resembles very much that of $CH_2$=PCl (Figure 4); on deuteriation, the bands of $CH_2$=PCl at 1372.3, 979.7, 792.4, and 804.7 $cm^{-1}$ are shifted to 1120.8 (AB-type), 847.9 (AB-type), 642.9 (pseudo-B-type), and 634.5 $cm^{-1}$ (C-type), respectively. The Q branch at 490.0 $cm^{-1}$, which is heavily overlapped with the absorptions of $CD_3PCl_2$ and $CD_2HPCl_2$, is assigned to the P–Cl stretching vibration, and the very weak Q branch at 431.6 $cm^{-1}$ is assigned tentatively to the $CD_2$ twisting vibration. The large wavenumber shift of the 1372.3-$cm^{-1}$ band ($CH_2$ scissoring) of $CH_2$=PCl to 1120.8 $cm^{-1}$ on deuteriation establishes the assignment of the fairly weak bands at 979.7 $cm^{-1}$ for $CH_2$=PCl and 847.9 $cm^{-1}$ for $CD_2$=PCl to the C=P stretching vibration. The weak intensities of these bands are in contrast with the strong intensities of the C=P stretching bands at about 1350 $cm^{-1}$ for fluorophosphaalkenes. Other fundamentals of $CD_2$=PCl were not detected in the present study due possibly to their weak intensities. The observed wavenumbers and assignments of the infrared bands of $CH_2$=PCl and $CD_2$=PCl are listed in Table IV. The weak C-type bands at 754.8 and 747.9 $cm^{-1}$ in Figure 5c are assigned to the CPH out-of-plane deformation of the CHD=PCl species with the cis and trans dispositions, respectively, of the H and Cl atoms.

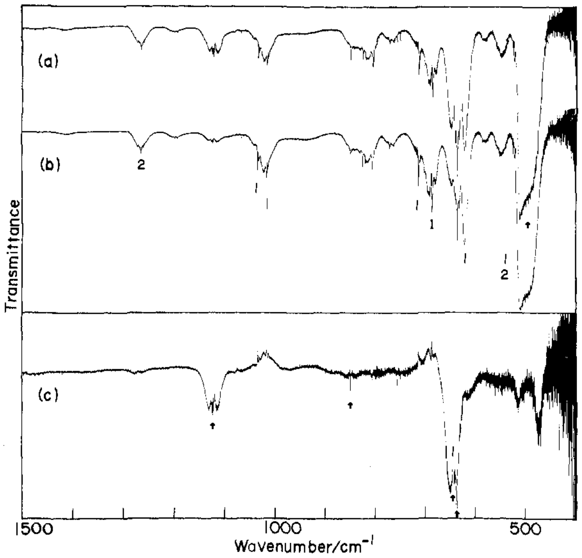

**Figure 5.** Infrared spectra for pyrolysis products of $CD_3PCl_2$: (a) immediately after the pyrolysis; (b) after 15 h of pyrolysis; and (c) after subtracting spectrum b from spectrum a. The bands of $CD_2$=PCl are denoted by arrows. Other bands are identified as $CD_3PCl_2$ (1) and $CD_2HPCl_2$ (2).

**Normal Coordinate Treatment.** Normal coordinates were treated for $CF_2$=PH, $CF_2$=$PCF_3$, and $CH_2$=PCl and their deuteriated species in order to elucidate the large difference in the C=P stretching wavenumber between $CF_2$=PH (1349.5 $cm^{-1}$) and $CH_2$=PCl (979.7 $cm^{-1}$) and to derive the force constant associated with this vibration. The molecular structures of $CF_2$=PH and $CH_2$=PCl were taken from the microwave results,[1,11] and those of $CF_2$=$PCF_3$ were transferred from the results of $CF_2$=PH[1] and $CF_3PH_2$.[18] The Urey–Bradley force field with moderate constraints was employed for the normal coordinate treatment, since only the limited vibrational data were available in the present study. At first, the Urey–Bradley force constants were determined for $CF_3PH_2$ and $(CF_3)_2PH$ on the basis of Bürger's vibrational assignments.[18,19] Secondly, the force constants for $CF_2$=S,[17] $CF_3PH_2$, and $(CF_3)_2PH$ were transferred to $CF_2$=PH as initial values. The force constants, except for the repulsion constants, *F*(FCF) and *F*(CPH), were then adjusted to fit the observed wavenumbers for $CF_2$=PH and $CF_2$=PD. Finally, the force constants for $CF_2$=PH and $(CF_3)_2PH$ were transferred to $CF_2$=$PCF_3$, and some of the force constants were adjusted. A similar procedure was utilized for the normal coordinate treatment of $CH_2$=PCl. Namely, the Urey–Bradley force constants were first determined for $CH_2$=S,[30] $CH_3PCl_2$,[31]

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**Table VI.** Urey–Bradley Force Constants for $CF_2=PH$, $CF_2=PCF_3$, and $CH_2=PCl$[a]

| force constant | value | force constant | value |
|---|---|---|---|
| | $CF_2=PH$ | | |
| $K$(P—H) | 3.081 | $H$(CPH) | 0.322 |
| $K$(C=P) | 5.565 | $F$(FCF) | 1.103[b] |
| $K$(C—F) | 4.527 | $F$(FCP) | 0.461 |
| $H$(FCF) | 0.291 | $F$(CPH) | 0.149[b] |
| $H$(FCP) | 0.337 | | |
| | $CH_2=PCl$ | | |
| $K$(P—Cl) | 2.331 | $H$(CPCl) | 0.447 |
| $K$(C=P) | 5.068 | $F$(HCH) | 0.0[b] |
| $K$(C—H) | 4.879 | $F$(HCP) | 0.285 |
| $H$(HCH) | 0.348 | $F$(CPCl) | 0.162[b] |
| $H$(HCP) | 0.102 | | |
| | $CF_2=PCF_3$[c] | | |
| $K$(C=P) | 5.895 | $H$(CPC) | 0.198 |
| $K$(C—P) | 3.078 | $F$(FCP), $CF_3$ | 0.207[b] |
| $K$(C—F), $CF_2$ | 4.885 | $F$(CPC) | 0.041[b] |
| $K$(C—F), $CF_3$ | 4.130 | $F(CH_2$ wag) | 0.548 |
| $H$(FCF), $CF_3$ | 0.202[b] | $\kappa(CF_3)$ | 0.023 |
| $H$(FCP), $CF_3$ | 0.242[b] | $\tau$(CP) | 0.100[b] |

[a] Units of the force constants are $10^2$ N m$^{-1}$ for stretching, $K$; bending, $H$; and repulsion, $F$; and $10^{-18}$ N m for intramolecular tension, $\kappa$; torsion, $\tau$; and $F(CH_2$ wag). [b] Values fixed in the least-squares fit. [c] Other constants than those listed here are transferred from $CF_2=PH$.

and $(CH_3)_2PCl$[32] and were then transferred to $CH_2=PCl$. The force constants, except for $F$(HCH) and $F$(CPCl), were varied to reproduce the observed wavenumbers of $CH_2=PCl$ and $CD_2=PCl$. The observed and calculated wavenumbers for $CF_2=PH$ and $CF_2=PD$ are given in Table II, those for $CF_2=PCF_3$ in Table III, and those for $CH_2=PCl$ and $CD_2=PCl$ in Table IV, where the calculated potential-energy distributions are also included. These results indicate that the vibrational coupling among the symmetry coordinates is appreciable in most of the normal vibrations. Accordingly, the most dominant mode in the potential-energy distribution is adopted, in general, for describing the vibrational assignment. The Urey–Bradley force constants obtained are listed in Table VI.

The force constants for $CF_2=PH$ and $CH_2=PCl$ in terms of the symmetry coordinates are given in Table VII. The C=P stretching force constant $F$(C=P str), as a diagonal element of the $\mathbf{F}_s$ matrix, is 642 N m$^{-1}$ for $CF_2=PH$ and $CF_2=PD$, 668 N m$^{-1}$ for $CF_2=PCF_3$, and 562 N m$^{-1}$ for $CH_2=PCl$ and $CD_2=PCl$; these values may be compared with those for the C=S stretching force constant, 764 N m$^{-1}$ for $CF_2=S$ and 655 N m$^{-1}$ for $CH_2=S$. The C—P stretching force constant $F$(C—P str) was determined to be 328 N m$^{-1}$ for $CF_3PH_2$, 329/324 N m$^{-1}$ for $(CF_3)_2PH$, 295 N m$^{-1}$ for $CH_3PCl_2$, and 267/262 N m$^{-1}$ for $(CH_3)_2PCl$.[16] These values are compared with 258, 302/250, and 308 N m$^{-1}$ reported previously for $CF_3PH_2$,[18] $(CF_3)_2PH$,[19] and $CH_3PCl_2$,[31] respectively.

**Band Intensity of the C=P Stretching Vibration.** Although the $\nu_2$ band of $CF_2=PH$ (1349.5 cm$^{-1}$) and the $\nu_4$ band of $CH_2=PCl$ (979.7 cm$^{-1}$) are assigned to the C=P stretching vibration, their intensities are remarkably different from one another (see Figures 1c and 4). This difference in intensity may be qualitatively explained as follows. The band intensity $\Gamma_i$ is expressed as[33]

$$\Gamma_i = (N_A \pi d_i / 3c^2 \omega_i)\,(\partial P/\partial Q_i)^2$$

where $(\partial P/\partial Q_i)$ is the derivative of the dipole moment $P$ with respect to the $i$th normal coordinate $Q_i$ and $d_i$ is the degeneracy of the $i$th normal mode with wavenumber $\omega_i$. $N_A$ is Avogadro's number and $c$ is the velocity of light. The quantity $(\partial P/\partial Q_i)$ may be transformed as

$$(\partial P/\partial Q_i) = \sum_j l_{ji}\,(\partial P/\partial s_j)$$

**Table VII.** Force Constants in Terms of the Symmetry Coordinates for $CF_2=PH$ and $CH_2=PCl$[a]

| | $CF_2=PH$ | | | $CH_2=PCl$ | |
|---|---|---|---|---|---|
| | force constant | value | | force constant | value |
| a′ | $F_{11}$(P—H str) | 3.151 | a′ | $F_{11}$(P—Cl str) | 2.439 |
| | $F_{12}$ | 0.093 | | $F_{12}$ | 0.104 |
| | $F_{14}$ | 0.092 | | $F_{14}$ | 0.143 |
| | $F_{22}$(C=P str) | 6.420 | | $F_{22}$(C=P str) | 5.620 |
| | $F_{23}$ | 0.0 | | $F_{23}$ | −0.012 |
| | $F_{24}$ | 0.110 | | $F_{24}$ | 0.115 |
| | $F_{25}$ | 0.530 | | $F_{25}$ | 0.307 |
| | $F_{26}$ | −0.211 | | $F_{26}$ | −0.130 |
| | $F_{27}$ | 0.0 | | $F_{27}$ | 0.011 |
| | $F_{33}(CF_2$ a-str) | 4.781 | | $F_{33}(CH_2$ a-str) | 5.052 |
| | $F_{35}$ | 0.0 | | $F_{35}$ | −0.014 |
| | $F_{36}$ | 0.0 | | $F_{36}$ | −0.001 |
| | $F_{37}$ | 0.228 | | $F_{37}$ | 0.121 |
| | $F_{44}$(CPH def) | 0.928 | | $F_{44}$(CPCl def) | 1.772 |
| | $F_{55}(CF_2$ s-str) | 6.285 | | $F_{55}(CH_2$ s-str) | 5.052 |
| | $F_{56}$ | 0.589 | | $F_{56}$ | −0.070 |
| | $F_{57}$ | 0.0 | | $F_{57}$ | 0.002 |
| | $F_{66}(CF_2$ sci) | 1.208 | | $F_{66}(CH_2$ sci) | 0.386 |
| | $F_{67}$ | 0.0 | | $F_{67}$ | −0.006 |
| | $F_{77}(CF_2$ rock) | 1.022 | | $F_{77}(CH_2$ rock) | 0.341 |
| a″ | $F_{88}$(CPH def) | 1.199 | a″ | $F_{88}(CH_2$ twist) | 0.368 |
| | $F_{89}$ | −0.204 | | $F_{89}$ | 0.028 |
| | $F_{99}(CF_2$ wag) | 0.666 | | $F_{99}(CH_2$ wag) | 0.237 |

[a] Units of the force constants are $10^2$ N m$^{-1}$ for str–str, $10^{-8}$ N for str–bend, and $10^{-18}$ N m for bend–bend.

where $s_j$ is the $j$th symmetry coordinate and $l_{ji}$ is the element of the **L** matrix. The **L** matrix elements calculated for $CF_2=PH$ and $CH_2=PCl$ are given in Table VIII. For $CF_2=PH$, the C=P stretching ($s_2$), $CF_2$ symmetric stretching ($s_5$), and $CF_2$ scissoring modes ($s_6$) contribute for the most part to the normal vibration $\nu_2$.

If the derivatives of the dipole moment for $CF_2=PH$ are assumed to be equal to those for $CF_2=S$, namely $(\partial P/\partial s_2) = -3.07$ D Å$^{-1}$, $(\partial P/\partial s_5) = 4.83$ D Å$^{-1}$, and $(\partial P/\partial s_6) = -1.81$ D rad$^{-1}$,[17] then the intensity $\Gamma_2$ is estimated to be much larger than $\Gamma_5$, being consistent with the experimental observation as shown in Figure 1c. For $CH_2=PCl$, the calculated **L** matrix suggests that the normal vibration $\nu_4$ is associated primarily with the C=P stretching ($s_2$) and $CH_2$ scissoring modes ($s_6$), whereas the potential-energy distribution defined by

$$(\mathrm{P.E.D.})_{ji} = (l_{ji}^2 F_{jj}/\lambda_i)100$$

shows that the C=P stretching mode ($s_2$) contributes almost exclusively to $\nu_4$. The coupling between vibrational modes, as evaluated through the potential-energy distribution, is reflected by the band shift from their intrinsic wavenumbers. These considerations indicate that the observed intensity of the $\nu_4$ band of $CH_2=PCl$ does not necessarily represent the intrinsic C=P stretching intensity, although this vibration gives the intrinsic C=P stretching wavenumber. The values of $(\partial P/\partial s_2)$ and $(\partial P/\partial s_6)$ are likely to be of the same sign, as suggested by the facts that the $\nu_3$ band is stronger than the $\nu_4$ band (Figures 4 and 5c) and that the **L** matrix elements associated with $s_2$ and $s_6$ are of the same sign for $\nu_3$.

**The C=P Stretching Wavenumber and Force Constant.** The calculated potential-energy distributions for $CF_2=PH$, $CF_2=PD$, and $CF_2=PCF_3$ (Tables II and III) indicate that the C=P stretching mode ($s_2$) is highly coupled with the $CF_2$ symmetric stretching mode ($s_5$). This vibrational perturbation makes one of the coupled vibrations shift to higher wavenumber of about 1350 cm$^{-1}$ and makes the other shift to lower wavenumber of about 730 cm$^{-1}$. For $CH_2=PCl$ (Table IV), on the other hand, the C=P stretching vibration of 979.7 cm$^{-1}$ is almost negligibly perturbed by other vibrational modes, so that it gives an almost intrinsic C=P stretching wavenumber. This wavenumber compares well with the C=S stretching wavenumber 1059.2 cm$^{-1}$ for $CH_2=S$[17] and the C=Si stretching wavenumbers 985 and 984 cm$^{-1}$ for $CH_2=SiH_2$ and $CH_2=SiHCl$, respectively.[29] For $CD_2=PCl$,

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**Table VIII.** **L** Matrix Elements for $CF_2{=}PH$ and $CH_2{=}PCl$[a]

$CF_2{=}PH$

| | $Q_1$ | $Q_2$ | $Q_3$ | $Q_4$ | $Q_5$ | $Q_6$ | $Q_7$ |
|---|---|---|---|---|---|---|---|
| $s_1$(P—H str) | 1.0120 | −0.0076 | −0.0073 | 0.0177 | −0.0038 | −0.0012 | 0.0034 |
| $s_2$(C=P str) | −0.0032 | $\underline{0.3142}$ | −0.0039 | 0.0272 | $\underline{0.1132}$ | 0.0577 | −0.0031 |
| $s_3$($CF_2$ a-str) | −0.0009 | 0.0005 | −0.3819 | −0.1106 | 0.0108 | 0.0052 | 0.0460 |
| $s_4$(CPH def) | −0.0047 | −0.0382 | 0.3375 | −0.6580 | 0.0682 | 0.0172 | −0.0307 |
| $s_5$($CF_2$ s-str) | −0.0021 | $\underline{-0.2883}$ | −0.0049 | 0.0318 | $\underline{0.1650}$ | 0.0157 | −0.0015 |
| $s_6$($CF_2$ sci) | 0.0035 | $\underline{0.4127}$ | 0.0062 | −0.0172 | $\underline{0.1176}$ | −0.3058 | 0.0125 |
| $s_7$($CF_2$ rock) | −0.0255 | −0.0006 | 0.3905 | 0.0452 | 0.0025 | 0.0170 | 0.2866 |

| | $Q_8$ | $Q_9$ |
|---|---|---|
| $s_8$(CPH def) | 0.7286 | 0.1509 |
| $s_9$($CF_2$ wag) | −0.1549 | 0.5426 |

$CH_2{=}PCl$

| | $Q_1$ | $Q_2$ | $Q_3$ | $Q_4$ | $Q_5$ | $Q_6$ | $Q_7$ |
|---|---|---|---|---|---|---|---|
| $s_1$(P—Cl str) | −0.0002 | 0.0000 | −0.0034 | −0.0235 | −0.0545 | 0.2337 | 0.0524 |
| $s_2$(C=P str) | 0.0096 | −0.0628 | $\underline{0.1449}$ | $\underline{0.3008}$ | 0.0057 | 0.0011 | 0.0064 |
| $s_3$($CH_2$ a-str) | 1.0554 | 0.0392 | 0.0002 | −0.0020 | −0.0137 | −0.0037 | 0.0048 |
| $s_4$(CPCl def) | −0.0573 | −0.0048 | −0.0060 | −0.0526 | 0.1148 | −0.0994 | 0.1771 |
| $s_5$($CH_2$ s-str) | −0.0377 | 1.0159 | 0.0442 | −0.0070 | 0.0004 | 0.0001 | 0.0003 |
| $s_6$($CH_2$ sci) | 0.0071 | −0.1884 | $\underline{1.6506}$ | $\underline{-0.2973}$ | 0.0189 | 0.0009 | −0.0107 |
| $s_7$($CH_2$ rock) | −0.1313 | −0.0076 | −0.0211 | −0.0196 | 1.0074 | 0.1370 | −0.0858 |

| | $Q_8$ | $Q_9$ |
|---|---|---|
| $s_8$($CH_2$ twist) | −0.0787 | 0.7721 |
| $s_9$($CH_2$ wag) | 1.2754 | −0.0173 |

[a] Definition of the symmetry coordinates $s_i$ is the same as that of $CH_2{=}NH$[35] except for the coordinates $s_3$, $s_5$, and $s_7$; $s_3 = (\Delta r_3 - \Delta r_2)/\sqrt{2}$, $s_5 = (\Delta r_3 + \Delta r_2)/\sqrt{2}$, and $s_7 = (\Delta\beta_3 - \Delta\beta_2)/\sqrt{2}$. For the underlined **L** matrix elements, see text.

**Table IX.** Stretching Force Constants of Carbon–Phosphorus and Carbon–Nitrogen Bonds

| force constant | value[a] | force constant | value[a] |
|---|---|---|---|
| $F$(C—P) | 2.5–3.3 | $F$(C—N) | 5.1–7.2[c] |
| $F$(C=P) | 5.6–6.7 | $F$(C=N) | 13.4–14.3[c] |
| $F$(C≡P) | 8.0–9.2[b] | $F$(C≡N) | 16.9–18.8[b] |

[a] In units of $10^2$ N $m^{-1}$. [b] Reference 36. [c] Reference 37.

however, large vibrational coupling occurs between the C=P stretching ($s_2$) and $CD_2$ scissoring modes ($s_6$) with their intrinsic vibrational energies almost coincident with one another, resulting in large shifts of their vibrational levels. Thus, the observed wavenumbers of these vibrations are shifted by about 130 $cm^{-1}$ to higher and lower wavenumbers from the unperturbed wavenumber of approximately 980 $cm^{-1}$. This is the same situation as observed for fluorophosphaalkenes.

The C=P stretching force constant $F$(C=P str) was determined to be 562–668 N $m^{-1}$ for $CF_2{=}PH$, $CF_2{=}PCF_3$, and $CH_2{=}PCl$. Similar force constant values, 635.7 and 560–577 N $m^{-1}$, have been reported respectively for the C=S stretching vibration (1059.2 $cm^{-1}$) of $CH_2{=}S$[30] and the C=Si stretching vibration (1003.5 $cm^{-1}$) of $CH_2{=}Si(CH_3)_2$.[34]

The stretching force constants of the carbon–phosphorus multiple bonds are summarized in Table IX, where the force constants of the carbon–nitrogen multiple bonds are also included. It is interesting to note that the values for the double and triple bonds are roughly two and three times, respectively, as large as the value for the single bond and that the values for the carbon–phosphorus bonds are about half the values for the corresponding carbon–nitrogen bonds.

## Conclusions

The present infrared study of fluorophosphaalkenes and 1-chlorophosphaethene has given useful information for the C=P stretching vibration. The C=P stretching bands are observed in a wide range of 840–1370 $cm^{-1}$, in contrast with the characteristic C=N stretching bands that are observed at 1600–1700 $cm^{-1}$ well outside the fingerprint region. On the other hand, the determined values of the C=P stretching force constant are in a narrow range of 562–668 N $m^{-1}$ and are roughly two times as large as the value of the C–P stretching force constant. Thus, the observed C=P stretching wavenumbers are greatly dependent not only on the value of the C=P stretching force constant, which gives an intrinsic wavenumber of approximately 980 $cm^{-1}$, but also on the magnitude of the coupling with nearby vibrations of the same symmetry. The intensity of the C=P stretching vibration also varies with the magnitude of the vibrational coupling. The effect of the coupling on the intensity is different from that on the band shift from the intrinsic wavenumber. The isoelectronic C=Si, C=P, and C=S bonds have been shown to have similar values for the stretching force constants and accordingly similar intrinsic stretching wavenumbers.

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