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INFRARED SPECTRA OF C-FLUOROPHOSPHAETHYNE FC≡P AND C-DIFLUOROPHOSPHAETHENE CF_2=PH

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The infrared spectra of gaseous CF_3PH_2 treated with KOH have been measured in the 2500-400 cm^{-1} region by a Fourier transform spectrometer. Most of the bands newly observed on the KOH treatment have been assigned to the vibrations of unstable species, C-fluorophosphaethyne FC≡P and C-difluorophosphaethene CF_2=PH.

Recently, new classes of unstable molecules such as phosphaalkynes[1] and phosphaalkenes[2] have been detected by microwave spectroscopy and in some cases also by photoelectron and NMR spectroscopy. Among these molecules, the infrared spectrum of phosphaethyne HC≡P has been studied by Johns *et al.*[3] and more recently by Garneau and Cabana in detail.[4] The substituted analogues of phosphaethyne and phosphaethene, namely FC≡P and CF_2=PH, were first detected in pyrolysis of CF_3PH_2 by microwave spectroscopy[5] and later by photoelectron[6] and NMR[7] spectroscopy. The molecules of FC≡P and CF_2=PH have been prepared in excellent yield by passing CF_3PH_2 through a tube filled with KOH pellets and found to be stable for several hours at room temperature.[6,7] In the present work, the infrared spectra of FC≡P and CF_2=PH were studied in order to obtain more information on vibrations for these new classes of molecules.

Samples of FC≡P and CF_2=PH were prepared by passing CF_3PH_2 vapor at room temperature and low pressure (*ca.* 0.08 Torr[8]) through a glass tube, 1 cm i.d. and 70 cm long filled with KOH pellets. The purity of CF_3PH_2 was checked by infrared spectrum.[9] The infrared spectra were measured on a JEOL JIR-40X Fourier transform infrared spectrometer. The interferogram was accumulated by scanning 200-300 times. The sample pressure was about 10 Torr in a 10 cm glass cell fitted with KBr windows.

Figures 1a, 1b, and 1c show the infrared spectra of a precursor CF_3PH_2 and mixtures obtained by single passing and by double passing CF_3PH_2 vapor through the glass tube filled with KOH pellets, respectively. In the flow system, the reaction has been found to occur as follows: $CF_3PH_2 \xrightarrow[KOH]{-HF} CF_2{=}PH \xrightarrow[KOH]{-HF} FC{\equiv}P$.[5-7] The strongest bands of CF_3PH_2 at 1152.7 and 1186.8 cm^{-1} in Fig. 1a decrease their relative intensities as the reaction proceeds and finally disappear in Fig. 1c. Several new bands are observed in Figs. 1b and 1c and some of them increase their relative intensities in Fig. 1c. Therefore, the new bands whose intensities are enhanced in Fig. 1c are assigned to FC≡P and the remaining new bands to CF_2=PH on the basis

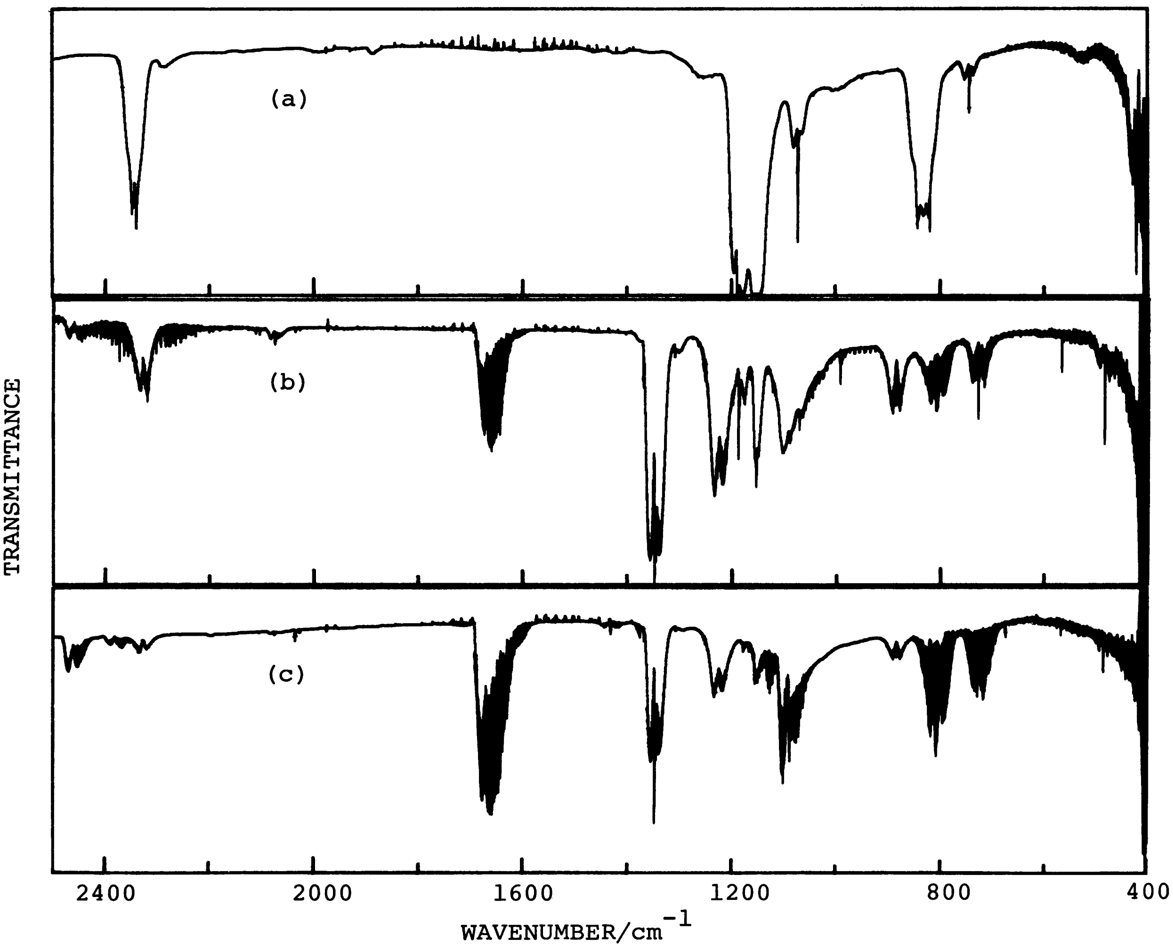

Fig. 1. Infrared spectra of (a) the precursor CF_3PH_2, (b) the mixture obtained by single passing CF_3PH_2 vapor through the glass tube filled with KOH pellets, and (c) the mixture obtained by double passing.

of the reaction scheme. The broad bands around 1100 cm^{-1} in Fig. 1b and the band at 1089.9 cm^{-1} in Fig. 1c are ascribed to decomposed compounds, because their relative intensities vary with no relation to the reaction process. Many absorption lines around 2300 and 990 cm^{-1} in Fig. 1b are due to PH_3 which is contained as impurities in the precursor. Table 1 summarizes the observed wavenumbers of the bands in Figs. 1a, 1b, and 1c, together with their assignments.

For FC≡P with $C_{\infty v}$ symmetry, the C≡P stretching (ν_1) and C-F stretching (ν_3) vibrations should give rise to parallel type bands, while the FCP bending vibration (ν_2) a perpendicular type band. The rotational constant of this molecule predicts the P-R separation to be about 17 cm^{-1}. The bands which have been assigned to FC≡P are of parallel type with the P-R separation of 17-19 cm^{-1} except the bands around 2030 cm^{-1}. On the other hand, the ν_2 and ν_3 wavenumbers have been estimated to be 390±10 and 790±60 cm^{-1}, respectively, from intensity measurements of the microwave spectra.[5)] Accordingly, the bands at 801.3 and 726.1 cm^{-1} are assigned to the ν_3 and $2\nu_2$ vibrations, respectively. The $2\nu_2$ vibration gives much stronger intensity than what has been expected for the overtone. This intensity enhancement is reasonably explained by the strong Fermi resonance with the ν_3 vibration as suggested by the microwave study.[5)] The band at 1670.8 cm^{-1}

is safely assigned to the ν_1 vibration, since the combination bands for this vibration with the ν_2 and ν_3 vibrations are observed at about 2030 and 2450 cm^{-1}.

For the planar molecule of $CF_2=PH$ with C_s symmetry, the nine fundamental vibrations are classified into seven in the a' species and two in the a" species. The a' vibrations are expected to give AB type bands and the a" vibrations C type bands. Since the C=P bond is nearly parallel to the a axis, the C=P stretching

Table 1. Observed wavenumbers for $FC\equiv P$, $CF_2=PH$, and CF_3PH_2 in the 2500-400 cm^{-1} region[a)]

$\tilde{\nu}/cm^{-1}$			P-R[b)]	Assignment		
Spectrum a	Spectrum b	Spectrum c		$FC\equiv P$[c)]	$CF_2=PH$[d)]	Others
	2459.2 w	2459.2 m	18	$\nu_1+\nu_3$		
		2380.7 w	19	$\nu_1+2\nu_2$		
2344.8 s						CF_3PH_2
2343.1 s						
2336.7 s, Q						
	2326.9 m, Q	2326.9 w, Q	14		ν_1	
	2111.4 vw, Q				$\nu_3+\nu_5$	
	2104.8 vw, Q				$\nu_3+\nu_5+\nu_7-\nu_7$	
	2075.6 w, Q	2075.6 vw, Q	19		$\nu_2+\nu_9$	
	2036.4 vw, Q	2036.4 w, Q		$\nu_1+\nu_2$		
		2026.8 vw, Q		$\nu_1+2\nu_2-\nu_2$		
		2017.8 vvw, Q		$\nu_1+3\nu_2-2\nu_2$		
	1670.8 ms	1670.8 vs	17	ν_1		
		1435.4 w, Q	26			
	1370.1 w, Q	1370.1 w, Q			$\nu_5+\nu_7$	
	1349.5 vs, Q	1349.5 s, Q	18		ν_2	
	1346.2 vs, Q	1346.2 s, Q			$\nu_2+\nu_7-\nu_7$	
	1309.2 w, Q	1309.2 vw, Q			$\nu_6+\nu_9$	
	1228.5 s, Q	1228.5 ms, Q	16		ν_3	
	1211.3 s, Q	1211.3 ms, Q			$\nu_7+\nu_9$	
1186.8 vs, Q	1186.8 m, Q		17			CF_3PH_2
		1177.9 w, Q				
		1156 m, b				
1152.7 vvs, Q	1152.7 s, Q					CF_3PH_2
	1102 s, b [e)]					
	1089 s, b [e)]	1089.9 s, Q [e)]	28			
1070.8 m, Q			16			CF_3PH_2
	991.9 w, Q					PH_3
	884.4 m, Q	884.4 w, Q	15		ν_5	
841.5 s, Q			20			CF_3PH_2
818.4 s, Q			18			
	801.3 m	801.3 ms	18	ν_3		
742.9 w, Q			17			CF_3PH_2
	729.3 m, Q	729.3 vw, Q			ν_9	
	727.8 w, Q				$\nu_9+\nu_7-\nu_7$	
	726.1 m	726.1 ms	18	$2\nu_2$		
		674.1 vw, Q				$HC\equiv P$
	568.0 w, Q	568.0 vw, Q			ν_6	
	564.6 vw, Q				$\nu_6+\nu_7-\nu_7$	
	485.5 w, Q	485.5 w, Q	19		ν_7	
418.7 ms, Q						CF_3PH_2

a) Spectrum a: the precursor CF_3PH_2, Spectrum b: the mixture mainly of CF_3PH_2, $CF_2=PH$, and $FC\equiv P$, and Spectrum c: the mixture mainly of $CF_2=PH$ and $FC\equiv P$.
s: strong, m: medium, w: weak, v: very, b: broad, and Q: Q branch. b) P-R separation in cm^{-1}. c) ν_1: $C\equiv P$ stretching, ν_2: FCP bending, and ν_3: C-F stretching. d) ν_1: P-H stretching, ν_2: C=P stretching, ν_3: CF_2 antisymmetric stretching, ν_4: P-H in-plane bending, ν_5: CF_2 symmetric stretching, ν_6: CF_2 scissoring, and ν_7: CF_2 rocking in the a' species, and ν_8: P-H out-of-plane bending, and ν_9: CF_2 wagging in the a" species. e) Decomposed compounds.

(ν_2), the P-H in-plane bending (ν_4), the CF_2 symmetric stretching (ν_5), and the CF_2 scissoring (ν_6) vibrations may give preferentially the A type, whereas the P-H stretching (ν_1), the CF_2 antisymmetric stretching (ν_3), and the CF_2 rocking (ν_7) vibrations the B type. The P-R separations expected from the Seth-Paul formulas[10)] are 18, 15, and 28 cm^{-1} for the A, B, and C types, respectively. Among the bands assigned to CF_2=PH, the one at 1349.5 cm^{-1} gives the pseudo-A type, the ones at 2326.9 and 1228.5 cm^{-1} give the pseudo-B type, and the one at 729.3 cm^{-1}, which is superimposed on the 726.1 cm^{-1} band, gives the C type. These bands have been easily assigned by comparing the spectrum of CF_2=PH with that of CF_2=S,[11)] as indicated in Table 1. The assignments are also supported by the observation of the combination bands. The observed wavenumbers and their band types for CF_2=PH are listed in Table 2, together with those for the related compound CF_2=S. The table shows a good correlation of the wavenumbers between the two compounds. Detailed vibration-rotation analyses on FC≡P are now in progress.

Table 2. Observed wavenumbers and band types for CF_2=PH and CF_2=S

		CF_2=PH		CF_2=S[11)]		Assignment
		$\tilde{\nu}/cm^{-1}$	Type	$\tilde{\nu}/cm^{-1}$	Type	
a'	ν_1	2326.9	pseudo-B	-	-	P-H str.
	ν_2	1349.5	pseudo-A	1368	A	C=X str. (X=P or S)
	ν_3	1228.5	pseudo-B	1189	B	CF_2 antisym. str.
	ν_4			-	-	P-H in-plane bend.
	ν_5	884.4	AB	787	A	CF_2 sym. str.
	ν_6	568.0		526	A	CF_2 scissor.
	ν_7	485.5	AB	417	B	CF_2 rock.
a"	ν_8			-	-	P-H out-of-plane bend.
	ν_9	729.3	C	622	C	CF_2 wag.

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