An Infrared Study of 1-Phosphapropyne

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The infrared spectra of gaseous and solid 1-phosphapropyne $(CH_3C \equiv P)$ have been obtained for the first time and all the fundamentals have been assigned. Gaseous $CH_3C \equiv P$ reacts with HCl to yield $C_2H_3PCl_2$ at room temperature but, without HCl, it can be stored for a few days under low pressure. The molecular force field of $CH_3C \equiv P$ resembles that of $CH_3C \equiv N$, in conformity with the structural resemblance. Comparison of the values of the $C \equiv P$ stretching force constant for a series of $HC \equiv P$, $FC \equiv P$, and $CH_3C \equiv P$ with those of the $C \equiv N$ stretching force constant for the nitrile analogues shows a good correlation between the two series.

Introduction

The first reactive intermediate compound containing a $C \equiv P$ bond, phosphaethyne (HC \equiv P), was found by Gier in 1961.¹ Since then several phosphaalkynes have been produced in general by flow pyrolysis and detected by microwave, photoelectron, and/or NMR techniques.² Despite their great importance as an experimental test of theoretical prediction, only the two compounds HC \equiv P³ and FC \equiv P⁴ have been characterized by infrared spectroscopy. We report in this paper the first vibrational analysis of an alkyl-substituted phosphaalkyne, 1-phosphapropyne (C-H₃C \equiv P), which is the phosphorus analogue of the well-characterized by the several phosphare of the several phosphare of the several phosphare of the several phosphare of the several phosphare.

terized compound acetonitrile CH₃C=N.

Experimental Section

The sample of 1-phosphapropyne was produced by low-pressure pyrolysis of ethyldichlorophosphine at 900–950 °C by the method of Kroto et al.⁵ Two traps were used to collect the reaction products; one cooled at -126 °C to retain C₂H₅PCl₂ and PCl₃ and the other cooled at -196 °C to retain lower boiling-point products including CH₃C=P. The products trapped at -196 °C were then distilled in vacuum and only materials having vapor pressures lower than ca. 3 torr⁶ at -112 °C were collected. The infrared spectra



Figure 1. Infrared spectra of the pyrolysis products and the precursor $C_2H_5PCl_2$: (a) mixture products obtained immediately after pyrolysis; (b) mixture products after ca. 20 h; and (c) the precursor $C_2H_5PCl_2$. The bands marked with arrows disappeared after 20 h. The bands indicated by numbers are assigned to (1) HCl, (2) CH_2 —CHCl, (3) C_2H_5Br and C_2H_5Cl , (4) CH_2 —CH2, and (5) HC=CH; the band marked with a star in Figure 1c is due to impurity.

⁽¹⁾ T. E. Gier, J. Am. Chem. Soc., 83, 1769 (1961).

C. T. R. Burckett-St. Laurent, H. W. Kroto, J. F. Nixon, and K.
Ohno, J. Mol. Spectrosc., 92, 158 (1982), and the references cited therein.
A. Cabana, Y. Doucet, J. M. Garneau, C. Pénin, and P. Puget, J. Mol.

⁽³⁾ A. Cabana, Y. Doucet, J. M. Garneau, C. Pépin, and P. Puget, J. Mol. Spectrosc., 96, 342 (1982), and the references cited therein.

⁽⁴⁾ K. Ohno, H. Matsuura, H. W. Kroto, and H. Murata, Chem. Lett., 981 (1982).

⁽⁵⁾ H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, J. Mol. Spectrosc., 77, 270 (1979).



Figure 2. Infrared spectrum of the mixture, in the gaseous state, mainly containing $CH_3C = P$. The bands due to $CH_3C = P$ are marked with arrows.



Figure 3. Infrared spectra of the mixtures, in the solid state, mainly containing $CH_3C = P$. The bands due to $CH_3C = P$ are marked with arrows. (a) and (b): mixtures with different $CH_3C = P$ contents.

were measured on a JEOL JIR-40X Fourier transform infrared spectrometer and a Perkin-Elmer 621 spectrometer. The sample pressure was ca. 40 torr in a 10-cm gas cell.

Results and Discussion

Since pyrolysis of C₂H₅PCl₂ gives various by-products in addition to CH₃C=P,⁵ identification of the infrared bands of $CH_3C \equiv P$ is essential in advance of detailed spectral analyses. Accordingly, the decomposition process of this compound was investigated by examining spectral changes with time. Figure 1a shows the infrared spectrum of the mixture products obtained immediately after the pyrolysis of C₂H₅PCl₂, Figure 1b the spectrum recorded after ca. 20 h, the gaseous materials having been retained in a gas cell, and Figure 1c the spectrum of the precursor $C_2H_5PCl_2$. The bands marked with arrows in Figure 1a disappeared in Figure 1b and the band at 674.7 cm^{-1} , which was assigned to HC=P,³ vanished ca. 30 min after pyrolysis. The intensity decrease of these bands along with that of the HCl band brought about the appearance of several new bands, which were readily assigned to $C_2H_5PCl_2$ by comparing with the spectrum in Figure 1c. Other bands equally observed in the spectra in Figure 1, a and b, did not show time dependence and were safely assigned to HC=CH, CH₂=CH₂, CH₂=CHCl, C₂H₅Cl, and C₂H₅Br,⁷ in light of the known spectral information about these materials.

The above spectral observations suggest that $CH_3C \equiv P$ reacts with HCl to yield $C_2H_3PCl_2$ at room temperature and that the bands at 1559 and 1437 cm⁻¹ which disappeared in Figure 1b are therefore assigned to $CH_3C \equiv P$. Without HCl, on the other hand, $CH_3C \equiv P$ can be stored for a few days at pressures below ca. 40 torr.

(7) The precursor of $C_2H_5PCl_2$ contains C_2H_5Br impurity.

Figure 2 shows a typical infrared spectrum of the mixture mainly containing gaseous CH₃C=P at a pressure of ca. 40 torr; small amounts of CH2=CHCl, C2H5Cl, and C2H5Br still remained in the sample. The bands marked with arrows are assigned to $CH_3C \equiv P$. The assignment was confirmed by examining the relative intensities of the bands observed for each of the distillation fractions. The bands of gaseous CH₃C=P clearly show parallel or perpendicular rotational structure. The observed intensity alternation of the ${}^{P}Q_{K}$ and ${}^{R}Q_{K}$ lines in the perpendicular bands is characteristic of a $C_{3\nu}$ symmetric rotor, supporting the band assignment to CH₃C=P. The solid-state infrared spectra were also measured at -196 °C (Figure 3) in order to confirm the vibrational assignment of gaseous CH₃C=P and to obtain the wavenumbers of the bands not observed in the gaseous state. The bands marked with arrows in Figure 3 are assigned to $CH_3C \equiv P$ on the basis of the relative absorption intensities observed for the mixture samples (a) and (b) which contain $CH_3C = P$ at different rates.

Table I gives the observed wavenumbers for gaseous and solid $CH_3C = P$. The wavenumber values for the CH_3 group vibrations of $CH_3C = P$ are smaller by 0.4-5.3% than those of $CH_3C = N.^8$ Table I also lists the results of normal coordinate treatment by using the force constants transferred directly from $CH_3C = N^8$ except for the C = P stretching constant. The calculated wavenumbers satisfactorily reproduced the observed ones, indicating that the force field of $CH_3C = P$ resembles that of $CH_3C = N$, in conformity with the structural resemblance.⁵

In refining the force field of $CH_3C = P$, only the C = P stretching force constant was adjusted so as to reproduce better the observed C = P stretching wavenumber. Table II lists the observed C = P

⁽⁸⁾ J. L. Duncan, D. C. McKean, M. W. Mackenzie, and J. Perez Peña, J. Mol. Spectrosc., 76, 55 (1979).

TABLE I: Observed and Calculated Wavenumbers of CH₃C≡P

		obsd wavenumbers/cm ⁻¹			calcd wavenumber/	
		gas	solid	harmn ^a	cm ⁻¹	PED^{b}
a 1	νı	2910.3	2923	3027	3049	CH ₃ sym str (100)
	ν,	1558.7	1543	1574	1574	$C \equiv P \text{ str } (58), C-C \text{ str } (42)$
	ν_{a}	1366.9	1377	1394	1405	CH_3 sym def (100)
	ν_{a}^{3}		750		747	$C-C \text{ str } (60), C \equiv P \text{ str } (38)$
e	ν_{s}	2966.0 ^c	2956	3085	3124	CH_3 deg str (100)
	ν	1437.5 ^c	1440	1446	1456	CH ₃ deg def (87), CH ₃ rock (11)
	v ,	988.4°	965	1008	1043	CH, rock (82), CH, deg def (13)
	ν'_8		316		295	CCP bend (91), CH_3 rock (9)

^a Harmonic wavenumbers. The gaseous values are corrected by Dennison's rule, by using the anharmonic constants; 0.04 for CH stretching, 0.02 for CH bending, and 0.01 for C=P stretching vibrations. ^b Potential energy distributions. ^c The value is obtained by using the quadratic expression in K for the ^{P,R}Q_K lines.

stretching wavenumber and the force constant for $CH_3C \equiv P$, together with the values for $HC \equiv P$, FC $\equiv P$, and the nitrile analogues.^{10,11} The C=P stretching force constant has values ranging from 800 to 920 N m⁻¹, although the observed C=P stretching wavenumbers are spread over in the region between 1270 and 1680 cm⁻¹. The normal coordinate treatment reveals that a strong vibrational coupling of the C=P and C–C stretches shifts up the wavenumber for $CH_3C \equiv P$, similar to $FC \equiv P^9$ for which the coupling of the C=P and C-F stretches is responsible. On the contrary, for HC=P, the vibrational coupling is negligibly small, giving rise to an almost intrinsic C=P stretching wavenumber. The values of the C=P stretching force constant obtained for HC==P and CH₃C==P are not much different from each other, but the value derived for FC=P is somewhat smaller than these in spite of an apparently larger C = P stretching wavenumber.

TABLE II: Observed Wavenumbers and Force Constants for C≡P and C≡N Stretches

compd	wavenumber/ cm ⁻¹	force constant/ N m ⁻¹
HC≡P ^a	1278.3	918.4
FC≡P ^a	1670.8	807.1
$CH_{3}C \equiv P$	1558.7	887.2
$HC \equiv N^{b}$	2132.0 ^e	1877
FC≡N ^c	2348.0 ^e	1696
$CH_3C \equiv N^d$	2293.6 ^e	1838

^a Reference 9. ^b Reference 10. ^c Reference 11. ^d Reference 8. ^e Harmonic wavenumber.

Quite a similar correlation between the wavenumbers and force constants is found for the C=N stretching vibrations of the nitrile analogues, as seen in Table II.

Detailed vibration-rotation analysis of the observed spectra of $CH_3C = P$ and $CD_3C = P$ is now in progress and the results will be reported elsewhere.

Registry No. CH2=P, 34627-31-1; HCl, 7647-01-0; C2H5PCl2, 1498-40-4.

Estimation of Equilibrium Structure by Use of Isotopic Differences in the r_z Structure: Modification of the Mass Dependence Method and Application to H₂O, H₂CO, and H₂CS

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A general formulation is presented for estimation of the equilibrium (r_e) structure from isotopic differences in the average (r_z) structure by modification of Waton's mass dependence method. The method is so designed to eliminate systematic errors originating from the isotopic mass dependence of the moments of inertia. A correct estimate of the $r_{\rm e}$ structure of H₂O is obtained. The r_e (H...H) distances in H₂CO and H₂CS are estimated to be 1.871 (3) and 1.840 (8) Å, respectively.

Introduction

According to the mass dependence method of Watson,^{1,2} the equilibrium (r_e) structure of a molecule can be estimated if the zero-point moments of inertia, I_0 , for a sufficient number of isotopic species are known. He applied this method to diatomic and XY_2 molecules and showed that the derived structure, so-called $r_{\rm m}$, was a good approximation of $r_{\rm e}$. One of the limitations of this method is that the r_m parameters derived for very light atoms, particularly

hydrogen, are not very accurate, because this method is based on the first-order expansion of I_0 in terms of atomic mass. As pointed out recently,³ the systematic error from this origin can be removed with sufficient accuracy if the r_m parameters for a proper set of two isotopic species, so-called a complementary set, are averaged. This modified $r_{\rm m}$ structure, called the $r_{\rm c}$ structure, is expected to be very nearly equal to the r_e structure even for a molecule containing hydrogen atoms. However, the applicability of this

⁽⁹⁾ K. Ohno, H. Matsuura, H. Murata, and H. W. Kroto, J. Mol. Spectrosc., 100, 403 (1983).

⁽¹⁰⁾ I. Suzuki, M. A. Pariseau, and J. Overend, J. Chem. Phys., 44, 3561 (1966). (11) V. K. Wang and J. Overend, Spectrochim. Acta, Part A, 29, 1623

^{(1973).}

J. K. G. Watson, J. Mol. Spectrosc., 48, 479 (1973).
J. G. Smith and J. K. G. Watson, J. Mol. Spectrosc., 69, 47 (1978).

⁽³⁾ M. Nakata, M. Sugie, H. Takeo, C. Matsumura, T. Fukuyama, and K. Kuchitsu, J. Mol. Spectrosc., 86, 241 (1981).