Detection of *C*-Chlorophosphaethyne, ClC≡P, by Microwave Spectroscopy

T. John Dennis, Steven Firth, Harold W. Kroto*, David R. M. Walton and Chup-Yew Mok

School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, UK

C-Chlorophosphaethyne, ClC≡P, is produced by flow thermolysis of trichloromethylphosphonous dichloride, Cl_3CPCl_2, over zinc metal at 530 °C, and is detected by microwave spectroscopy.

Although Gier originally detected HC≡P in 1961,[1] it was not until 1975 that a second member of the phosphaalkyne family, $CH_3C{\equiv}P$,[2] was synthesised. Subsequently, numerous other substituted phosphaalkynes, such as FC≡P,[3] $CH_2{=}CHC{\equiv}P$,[4] HC≡C–C≡P,[5] N≡C–C≡P[6] and $C_6H_5C{\equiv}P$[7] were made and studied by microwave spectroscopy and in some cases also by infrared and photoelectron techniques. Since then the chemistry of these molecules, particularly using $Me_3CC{\equiv}P$[8] as a synthon, has exploded, and this field has been comprehensively reviewed by Regitz.[9]

Table 1 Microwave transition frequencies and rotational constants of $^{35}Cl^{12}C\equiv{}^{31}P$[a]

$J + 1 \leftarrow J$	$F' \leftarrow F''$	Frequency/MHz	Obs. − calc./ MHz
$4 \leftarrow 3$	$2.5 \leftarrow 1.5$ $3.5 \leftarrow 2.5$	24 160.845	0.007
$4 \leftarrow 3$	$4.5 \leftarrow 3.5$ $5.5 \leftarrow 4.5$	24 162.937	−0.006
$5 \leftarrow 4$	$3.5 \leftarrow 2.5$ $4.5 \leftarrow 3.5$	30 202.044	−0.008
$5 \leftarrow 4$	$5.5 \leftarrow 4.5$ $6.5 \leftarrow 5.5$	30 203.301	0.005
$6 \leftarrow 5$	$4.5 \leftarrow 3.5$ $5.5 \leftarrow 4.5$	36 242.831	−0.007
$6 \leftarrow 5$	$6.5 \leftarrow 5.5$ $7.5 \leftarrow 6.5$	36 243.675	0.008

[a] $B_0 = 3020.31252(62)$ MHz; $D_0 = 0.419(10)$ kHz; $eQq = -72.57(16)$ MHz.

Although $FC\equiv P$ was made with relative ease,[3] $ClC\equiv P$, *C*-chlorophosphaethyne, has remained more elusive. This compound was finally prepared by thermolysis of $ClCH_2PCl_2$, Cl_2CHPCl_2 and Cl_3CPCl_2, the latter giving the highest yield, and identified by IR spectroscopy.[10] The molecule has also been prepared by Hermesdorf in the Regitz group.[11]

This molecule was expected to have a small dipole moment (*ca.* 0.2 Debye), and hence a very weak microwave spectrum. This fact, along with the splittings expected due to the chlorine nuclear quadrupole moment, was responsible for the lack of previous success in detecting this species by microwave spectroscopy. Using the rotational and centrifugal distortion constants from a high resolution FTIR study of the 1475 cm^{-1} band of $ClC\equiv P$[12] we have been able to detect some very weak microwave transitions of $^{35}ClC\equiv P$.

The general method of production of these molecules for spectroscopic study has been by thermolysis of a parent species leading to the elimination of fragments such as hydrogen halides to give the required phosphaalkyne.[13] The method of production of *C*-chlorophosphaethyne used in this study is similar in that trichloromethylphosphonous dichloride, Cl_3CPCl_2[14] was passed through an 8 mm ID-tube loosely packed with granulated zinc for *ca.* 15 cm of its length and heated to 530 °C. The presence of the zinc facilitates the elimination of chlorine from the precursor. The resulting vapour was passed through a U-tube immersed in a −94 °C bath (acetone–liquid nitrogen slush) to remove the unreacted precursor and other side products and collected at liquid nitrogen temperature to give a relatively pure sample of $ClC\equiv P$. The progress of the reaction and purity of the resulting sample were monitored by FTIR spectroscopy. Thermolysis of the precursor alone at *ca.* 1000 °C results in the formation of $ClC\equiv P$, along with further reaction products such as $COCl_2$ and ClCCH, as determined by IR spectroscopy.[10] The $ClC\equiv P$ samples produced in this way could be stored for several days at liquid nitrogen temperatures with no apparent decomposition or polymerisation. Spectra were recorded by warming the sample to *ca.* −120 °C to give a vapour pressure of 20 μmHg, and flowing the sample directly through the cell of a Hewlett Packard Stark modulated spectrometer using a Hewlett Packard 63 640A synthesized sweeper as a microwave source.

The observed spectrum consists of three weak R-branch (*J* 3, 4 and 5) transitions split by chlorine nuclear quadrupole coupling into $\Delta F = +1$ doublets. The observed frequencies and resulting constants are given in Table 1. The weakness of the observed transitions is consistent with the expected small dipole moment of $ClC\equiv P$. The derived B_0 value is within 0.1 MHz of that determined for $^{35}ClC\equiv P$ from the FTIR spectrum[12] and is consistent with a bond length of $r(Cl\text{–}C) = 1.646$ Å assuming a $C\equiv P$ bond length of 1.544 Å as found in $MeC\equiv P$.[2]

From the magnitude of the quadrupole coupling constant, the degree of π-bonding between the chlorine and carbon atoms can be estimated.[15] Using values of 3.0 and 2.5 for the electronegativities of chlorine and carbon respectively, a value for the σ-bond ionic character $i_\sigma = 0.25$ can be calculated. Using a value of $eQq_{n10} = 109.74$ MHz for ^{35}Cl results in a π-bond character $\pi_c = 0.177$ and a resulting ionic character $i_c = 0.073$. These values can be compared to those of the isoelectronic ClBS.[16] For this molecule, π_c has the value 0.225. This indicates that a π-bonded ionic structure of the form $Cl^+{=}B{-}S^-$ contributes more to ClBS than the analogous $Cl^-{=}C{=}P^-$ contributes to ClCP. This is most likely due to the somewhat greater electronegativity of sulphur than phosphorus, 2.5 compared with 2.1.[15]

We thank Don McNaughton for giving us his results prior to publication, Professor M. Regitz for sending us a copy of Dr. Hermesdorf's thesis, Dr. P. Botschwina for alerting us to these studies and Hewlett Packard for the loan of the synthesized sweeper used in this study.

Received, 12th July 1990; Com. 0/03142I

References

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

2 M. J. Hopkins, H. W. Kroto, J. F. Nixon and N. P. C. Simmons, *Chem. Phys. Lett.*, 1976, **42**, 460.

3 H. W. Kroto, J. F. Nixon, N. P. C. Simmons and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1978, **100**, 446.

4 K. Ohno, H. W. Kroto and J. F. Nixon, *J. Mol. Spectrosc.*, 1981, **90**, 507.

5 H. W. Kroto, J. F. Nixon and K. Ohno, *J. Mol. Spectrosc.*, 1981, **90**, 512.

6 T. A. Cooper, H. W. Kroto, J. F. Nixon and O. Ohashi, *J. Chem. Soc., Chem. Comm.*, 1980, 333.

7 J. C. T. R. Burckett-St. Laurent, H. W. Kroto, J. F. Nixon and K. Ohno, *J. Mol. Spectrosc.*, 1982, **92**, 158.

8 G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch Teil B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.*, 1981, **36**, 16.

9 M. Regitz, *Chem. Rev.*, 1990, **90**, 191.

10 M. C. Durrant, G. Y. Matti, D. McNaughton and H. W. Kroto, to be published; G. Y. Matti, D.Phil. Thesis, University of Sussex 1989.

11 M. Hermesdorf, Ph.D. Dissertation, University of Kaiserslautern 1989.

12 D. McNaughton, preliminary results.

13 H. W. Kroto, *Chem. Soc. Rev.*, 1982, **11**, 435.

14 L. D. Quinn and C. H. Rolston, *J. Org. Chem.*, 1985, **23**, 1693.

15 W. Gordy and R. L. Cook, *Microwave Molecular Spectra*, Wiley, New York, 1984.

16 C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 130.