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Microwave Spectra and Structure of Six Isotopic Species of 1-Chlorophosphaethene, $CH_2=PCl$

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Six isotopic species of 1-chlorophosphaethene, $CH_2=PCl$, have been produced by pyrolysis of CH_3OPCl_2, methyldichlorophosphite, $^{13}CH_3OPCl_2$ and CD_3OPCl_2. Vapor-phase microwave spectra (26.5–39.7 GHz) of $CH_2=P^{35,37}Cl$, $^{13}CH_2=P^{35,37}Cl$ and $CD_2=P^{35,37}Cl$ have been recorded and analyzed in a rigid rotor approximation (ground-level rotational constants A_0, B_0, C_0 with inertial defects). Planar rigid models have been derived reproducing B_0, C_0 for all six species almost within the experimental errors. The acceptable models have C=P distances close to 1.655 Å, P–Cl distances close to 2.060 Å and an angle CPCl= 103.3°. The angles around carbon are as in ethylene to within a degree.

In a "flow" system described earlier[1] CH_3OPCl_2, methyldichlorophosphite, splits off CH_3Cl at *ca.* 50 mTorr on a hot (825 °C) quartz surface as seen by microwave (mw) detection. However, the so far unknown stoichiometric moiety, POCl, the phosphorous analogue of nitrosyl chloride, has not yet been identified by us in mw spectra of products of pyrolysis recorded for the 26.5–39.7 GHz region. Over a 750–850 °C range of temperature the immediate results were spectra of readily identified $HC\equiv P$(I)[2] and $CH_2=PCl$(II)[3a] together with a new spectral series, L, of equidistant (~1655 MHz) line-groups (width ~10–15 MHz). The molecule, M(L), giving rise to L was shown to be a symmetric top (linear Stark effect) not containing chlorine since no chlorine isotope effect was noticed. L was finally assigned to P_4O_7 by subsequently replacing CH_3OPCl_2 by CD_3OPCl_2 (99 % enriched) and $^{13}CH_3OPCl_2$ (90 %) in our pyrolyses. In both cases expected isotopic shifts for I and II were observed whereas L was simply repeated. Thus, M(L) contains at most P and O. Its final identification as P_4O_7 will be reported in a separate paper.[3b] Here, rotational constants of the title compounds (Table 1) will be used to derive an approximate structure of II based on fewer structural elements from other molecules than earlier.[3a] Our observed mw spectra still involve unassigned lines mainly occurring at lower temperature (POCl?). However, the present paper is a necessary prequisite in a search for mw absorption by further species.

PREPARATIONS

Small-scale preparations of $^{12}CH_3OPCl_2$, $^{13}CH_3OPCl_2$ and $^{12}CD_3OPCl_2$ were performed in accordance with Ref. 4 adjusted to vacuum-line operations. Vapors of 20 mmol of $CH_3OH-{}^{13}CH_3OH-CD_3OH$ were condensed into 20 mmol of freshly distilled and magnetically stirred PCl_3 at −78 °C. The temperature was raised slowly (16 h) under stirring. An evolution of HCl(gas) started at −25 °C indicating the beginning of the reaction $CH_3OH+PCl_3\rightarrow CH_3OPCl_2+HCl$, the final volume of HCl at 20 °C corresponding to 100 % conversion. The reaction vessel was again cooled to −78 °C and HCl removed by pumping. Vial-to-vial separation was performed at bath temperature 0 °C (stirring). The pertinent vapor pressures (v.p.) are 40 m Torr (PCl_3), 30 mTorr (CH_3OH) and 15 mTorr (CH_3OPCl_2), the v.p. of $(CH_3O)_2PCl$ being unknown. Sample fractions of v.p. between 17 and 5 mTorr were collected and redistilled. Quantities of 800 mg (~6 mmol) of constant boiling CH_3OPCl_2, $^{13}CH_3OPCl_2$ and $^{12}CD_3OPCl_2$ (v.p. 15–16 mTorr at 0 °C) were obtained. Ref. 4 has v.p. =15.5 mTorr. However, in pyrolyses the samples have to be kept at −50 °C (v.p.=0.5 mTorr) to produce a necessary pressure in front of the oven.

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Tables 1. Isotopic species (ISOTOPES), percent enrichment (PERCENT), number of observed transitions N, rotational constants A_o, B_o, C_o(MHz) and inertial defects I.D. (u.Å.^{2}) for ground level. ROTFIT data treatment.[a]

ISOTOPES	PERCENT	N^b	A_o	B_o	C_o	I.D.
$^{12}CH_2=P-{}^{35}Cl$	75	11	22704(20)[c]	4667.26(7)[c]	3865.448(68)[c]	0.20(2)
$^{12}CH_2=P-{}^{37}Cl$	25	7	22662(34)	4539.04(10)	3775.72(10)	0.21(4)
$^{13}CH_2=P-{}^{35}Cl$	68	12	22118(16)	4559.177(55)	3774.048(55)	0.21(2)
$^{13}CH_2=P-{}^{37}Cl$	22	8	22065(38)	4433.51(12)	3685.92(12)	0.22(4)
$CD_2=P-{}^{35}Cl$	75	12	19652(6)	4322.593(26)	3537,424(26)	0.23(1)
$CD_2=P-{}^{37}Cl$	25	8	19549(27)	4205.26(11)	3456.94(11)	0.16(4)

[a] Ref. 6. [b] Includes resolved quadrupole components. [c] Ref. 3a has $A_o=22711.17$, $B_o=4667.23$, $C_o=3865.45$ MHz. No experimental frequencies.

Prior to any pyrolyses PCl_3 was seen to be present in the samples (mw lines at 31407.0 and 36641.8 MHz at 1000 V/cm). This might be due to contamination in spite of the separations but more likely to equilibration such as $2CH_3OPCl_2$ (liq.) $\leftrightarrow (CH_3O)_2PCl+PCl_3$. Thus, the applied samples are more complicated than desirable. CH_3PCl_2 was absent. Table 1 summarizes the isotopic species studied, their abundance and, for sake of convenience, their final rotational constants and inertial defects.

MW SPECTRA. ROTATIONAL CONSTANTS

$K_{-1}=0$ and 1 μ_a-transitions were recorded at 1000 V/cm square-wave amplitude, $K_{-1}=2$ transitions at 300 V/cm (Table 2). The multiplet structure (when observed) due to the ^{35}Cl and ^{37}Cl quadrupoles was predictable and in fair agreement with experiment when based on quadrupole coupling constants for $NO^{35}Cl$ and $NO^{37}Cl$.[5] For unresolved patterns (^{37}Cl species; ^{35}Cl species with $K_{-1}=0$ and 1) positions of maximum intensity are reported in Table 2 both under F_A and ν_{RED}. This introduces errors of an estimated ± 0.5 MHz. The r.m.s. deviations of Table 2 are of this order or less. The fits, $\nu_{RED}-\nu_{CALC}$, and the rotational constants were obtained using ROTFIT[6] in a rigid rotor approximation. The calculated inertial defects are of the same order as for $CH_2=NCN$.[7]

STRUCTURE OF $CH_2=P-Cl$

Pioneering work on the production of $CH_2=PCl$ by pyrolysis of CH_3PCl_2 (as different from CH_3OPCl_2) has been published in 1976 by Kroto and collaborators[3a] with a preliminary rigid planar model (rotational constants B_M, C_M) obtained by fitting the C=P distance and the angle α (Fig. 1) to the observed B_o and C_o of $CH_2=P^{35}Cl$ with a view to guarantee correct identification of the new species. The fit had $|B_o-B_M| \sim |C_o-C_M| \leq 5$ MHz.[3a] Knowing B_o and C_o for 6 isotopic species we want to draw more material into a derived structure. No r_s-structure can, of course, be obtained since only $(|a|, |b|)=(1.252705, 0.147619)$ for chlorine and $(|a|, |b|)=(1.604012, 0.783055)$ for carbon can be calculated (nominal numbers in the inertial system of $CH_2=P^{35}Cl$ (Fig. 1)). The resulting C···Cl distance is 2.926 Å. It should be reproduced approximately in any suggested structure. The "M_5" structure of Table 3 has C···Cl = 2.924 Å. The

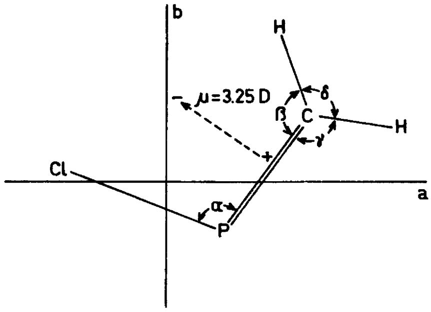

Fig. 1. 1-Chlorophosphaethene, $CH_2=PCl$, in the inertial system of $CH_2=P-{}^{35}Cl$. Bond angles α, β, γ, δ. Dipole moment $\mu=3.25$ Debye (D) from Ref. 15 with $\mu_a=2.68$ D and $\mu_b=1.84$ D. No experimental determination in this paper.

Table 2. Observed frequencies F_A (MHz) of μ_a-type transitions of 6 isotopic species of 1-chlorophosphaethene in the ground level. Frequencies corrected (see text) for chlorine quadrupole coupling effects ν_{RED}. Calculated frequencies ν_{CALC} based on a rigid rotor fit. ROTFIT r.m.s.[a]

	F_A				ν_{RED}	$\nu_{RED}-\nu_{CALC}$	r.m.s.
$^{12}CH_2=P^{35}Cl$							
$3_{13}\rightarrow4_{14}$	32476.25				32476.25	−0.241	0.1618
$3_{03}\rightarrow4_{04}$	33871.16				33871.16	0.086	
$3_{22}\rightarrow4_{23}$	34108.17	34109.75	34112.43	34113.72	34110.88	0.377	
$3_{21}\rightarrow4_{22}$	34367.68	34369.02	34371.78	34373.17	34370.28	0.019	
$3_{12}\rightarrow4_{13}$	35680.31				35680.31	−0.241	
$^{12}CH_2=P^{37}Cl$							
$3_{13}\rightarrow4_{14}$	31686.14				31686.14	−0.390	0.5621
$3_{03}\rightarrow4_{04}$	33024.50				33024.50	0.174	
$3_{22}\rightarrow4_{23}$	33239.23	33242.38			33241.23	0.543	
$3_{21}\rightarrow4_{22}$	33473.81	33476.42			33475.47	0.063	
$3_{12}\rightarrow4_{13}$	34736.70				34736.70	−0.389	
$^{13}CH_2=P^{35}Cl$							
$3_{13}\rightarrow4_{14}$	31712.53				31712.53	−0.174	0.2955
$3_{03}\rightarrow4_{04}$	33076.31	33077.44			33077.14	0.029	
$3_{22}\rightarrow4_{23}$	33310.58	33311.84	33314.72	33715.91	33313.21	0.336	
$3_{21}\rightarrow4_{22}$	33566.05	33567.46	33570.13	33571.49	33568.64	−0.017	
$3_{12}\rightarrow4_{13}$	34849.88				34849.88	−0.174	
$^{13}CH_2P^{37}Cl$							
$3_{13}\rightarrow4_{14}$	30937.17				30937.17	−0.136	0.6277
$3_{03}\rightarrow4_{04}$	32245.64	32246.23			32246.07	−0.250	
$3_{22}\rightarrow4_{23}$	32457.81	32461.84			32460.38	0.786	
$3_{21}\rightarrow4_{22}$	32688.72	32691.82			32690.69	−0.264	
$3_{12}\rightarrow4_{13}$	33924.80				33924.80	−0.136	
$CD_2=P^{35}Cl$							
$3_{13}\rightarrow4_{14}$	29813.03				29813.03	0.018	0.1309
$3_{03}\rightarrow4_{04}$	31148.44				31148.44	−0.151	
$3_{22}\rightarrow4_{23}$	31414.65	31416.48	31418.74	31419.48	31417.25	0.037	
$3_{21}\rightarrow4_{22}$	31705.89	31707.62	31710.14	31711.71	31708.59	−0.101	
$3_{12}\rightarrow4_{13}$	32949.58				32949.58	0.107	
$4_{14}\rightarrow5_{15}$	37215.74				37215.74	0.071	
$CD_2P^{37}Cl$							
$3_{13}\rightarrow4_{14}$	29100.05				29100.05	−0.388	0.4513
$3_{03}\rightarrow4_{04}$	30384.10				30384.10	0.401	
$3_{22}\rightarrow4_{23}$	30626.00	30629.50			30628.20	0.213	
$3_{21}\rightarrow4_{22}$	30891.81	30894.16			30893.30	0.254	
$3_{12}\rightarrow4_{13}$	32089.74				32089.74	−0.434	
$4_{14}\rightarrow5_{15}$	36329.35				36329.35	−0.037	

[a] Ref. 6.

Table 3. Geometric parameters GP of planar rigid models M_i of $CH_2=PCl$ isotopic species (ISOTOPES). Distances in Å, angles in degrees. Model rotational constants B_{Mi}, C_{Mi} (MHz), experimental rotational constants B_o, C_o (Table 1). Quality of fit measured by $Q \sim |B_o - B_{Mi}|_{max} \sim |C_o - C_{Mi}|_{max}$ (MHz).

ISOTOPES	B_o, C_o	B_o, C_o	B_o, C_o	B_o, C_o	B_{M5}	C_{M5}
$CH_2=P^{35}Cl$	Engaged	Engaged	Engaged	Engaged	4667.3880	3865.5317
$CH_2=P^{37}Cl$	"	"	"	"	4539.0330	3775.5814
$^{13}CH_2=P^{35}Cl$	"	"	"	"	4559.2519	3774.1451
$^{13}CH_2=P^{37}Cl$	"	"	"	"	4433.3029	3685.8612
$CD_2=P^{35}Cl$	Not engaged	"	"	"	4322.6082	3537.5159
$CD_2=P^{37}Cl$	"	"	"	"	4205.2156	3456.8434

GP Fig. 1	M_1	M_2	M_3	M_4	M_5
C=P	1.6543	1.6616	1.6548	1.6556	1.6548
P–Cl	2.0609	2.0552	2.0600	2.0600	2.0600
C–H, D(cis)	1.090 (ass.)	1.085 (ass.)	1.085 (ass.)	1.13	1.085
C–H, D(trans)	1.090 (ass.)	1.085 (ass.)	1.085 (ass.)	1.14	1.085
α	103.3	103.5	103.3	103.3	103.3
β	120 (ass.)	120 (ass.)	121.9	115.8	121.9 (ass.)
γ	123 (ass.)	123 (ass.)	121.6	121.8	121.6(ass.)
δ	117 (ass.)	117 (ass.)	116.5	122.4	116.5
Q	0.2	1.0	0.4	0.6	0.2

structures derived (Table 3) aimed at a least square fit[8] to the observed B_o and C_o values (Table 1). Details are available on request. M_1 involves only data for species with almost equal zero-point energies. In M_2, data for the structurally different deuterated species get involved. This is compensated for by very slight changes in C=P, P–Cl and α, the dominating structural parameters (GP), and a slightly inferior "fit parameter" $Q=1$ MHz. In M_3 the angles β and γ (Fig. 1) have been included among the variables. The fit parameter Q is improved ($Q=0.4$ MHz), the distribution of angles in the methylene group being close to the distributions in related molecules (Table 4). An attempt to include all 7 GP was less successful (M_4). Finally, supposing $\beta=121.9°$ and $\gamma=121.6°$, varying C=P, C–Cl, α and C–H(D), *cis* and *trans*, resulted in M_5. We consider M_5 our ultimate model, its main merit being that its rotational constants B_{M5}, C_{M5} (Table 3) with A_{M5}'s taken as 22702, 22659, 22119, 22072, 19651 and 19545 respectively, from top to bottom of Table 3, reproduce observed frequencies of 6 isotopic species fairly accurately ($I_a(M_i)=I_c(M_i)-I_b(M_i)-$I.D.).

DISCUSSION. SUGGESTED EXPERIMENTS.

The geometric parameters (GP) of, for example, model M_5 can now be discussed in terms of GP from other molecules. The angles β, γ and δ have already been put on a satisfactory comparative basis (Table 4). Table 5 documents that the P=C distance is, indeed, in good agreement with other data. This is more problematic to illustrate for the P–Cl distance. It is noted, though, that the C–Cl distance of

Table 4. Value of angles β, γ and δ (Fig. 1) for ethylene, vinyl chloride and 1-chlorophosphaethene.

	$CH_2=CH_2$[16]	$CH_2=CHCl$[13]	$CH_2=PCl$[a]
β(cis)	121.08	119.53	121.9
γ(trans)	121.08	121.07	121.6
δ	117.83	119.53	116.5

[a] This paper, M_5. See text.

Table 5. Comparison of C,N and C,P bond lengths (Å) horizontally Δ_h ($C-N/C=N/C\equiv N$ and $C-P/C=P/C\equiv P$) and vertically Δ_V ($C-N/C-P$, $C=N/C=P$ and $C\equiv N/C\equiv P$).

		Δ_h		Δ_h	
	CH_3NH_2[9]		$CH_2=NH$[10]		$HC\equiv N$[11]
	1.471	0.198	1.273	0.116	1.156
Δ_V	0.392		0.387		0.386
	CH_3PH_2[12]		$CH_2=PCl$[a]		$HC\equiv P$[2]
	1.863	0.203	1.660	0.118	1.542

[a] This paper.

$CH_2=CHCl$[13] is 1.726 Å. Since the covalent radii of carbon and nitrogen differ by *ca.* 0.055 Å[14] the $N-Cl$ distance in hypothetical $CH_2=N-Cl$ would be 1.671 Å. Adding $\Delta_v=0.387$ from Table 5, a $P-Cl$ distance of 2.058 Å is predicted in (almost too) good agreement with the experiment.

By an *ab initio* geometry optimization of $CH_2=PCl$ on a STO-3G basis Thomson[15] calculated a $P=C$ length of 1.65 Å, a $P-Cl$ length of 2.11 Å and $\alpha=99.2°$. His estimate of the height of the barrier to in-plane inversion was *ca.* 5 kcal/mol. The predicted dipole moment was 3.25 Debye. Its predicted orientation could be seen from the indicated relative charge distribution,[15] the result being shown as the dotted vector of Fig. 1. This suggests that it might be worth-while to search for μ_b-transitions in the mw spectrum. Work in the infrared is also suggested since vibrational frequencies would help correcting our mw data for the effect of zero-point energy.

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