# Nuclear Magnetic Resonance Determination of Molecular Species in Condensed Phosphoryl Chloride Mixtures at Equilibrium

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Modern ^{31}P nmr techniques have been employed on equilibrated mixtures of P_2O_5 in $POCl_3$ to show the presence of the straight-chain molecules ranging from the mono- through the pentapolyphosphoryl chloride, *i.e.*, $n = 1-5$ in $P_nO_{2n-1}Cl_{n+2}$. In addition there is evidence for three condensed phosphoryl chloride molecules involving branch groups and having the molecular skeletons
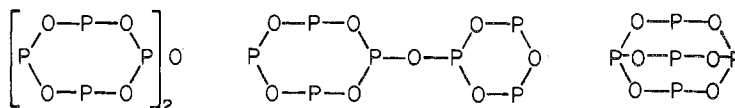
There also appear to be several simple-ring molecules, $P_nO_{3n}Cl_n$. Although all of the molecules present in these mixtures were not accounted for, it seemed fairly certain that there was very little or no isotetraphosphoryl chloride, $[Cl_2(O)PO]_3$-P(O). Intermolecular as well as building-unit equilibrium constants are reported for this system along with nmr chemical shifts and coupling constants for the molecules which were quantitatively determined. ^{31}P spin–lattice relaxation data are presented and interpreted in terms of a combination of nuclear dipole–dipole and spin–rotation interactions.

Introduction

The reaction products obtained from equilibrating mixtures of phosphorus pentoxide[1] with phosphoryl chloride were extensively investigated[2-5] by several groups about 15–25 years ago. In our work at that time,[5] we discounted the studies based on distillation or hydrolysis in aqueous media, on the experimentally demonstrated basis that molecular reorganization occurred during these processes. Our findings were later contested in a polemic.[6]

Unfortunately, the original ^{31}P nuclear magnetic resonance (nmr) studies[5] on this system were carried out during a period in which it was experimentally impossible to resolve the important fine structure of the spectra. Now, however, advances in nmr technology and considerable experience with the ^{31}P nmr of related compounds[7,8] have enabled us to do an accurate analysis of the nmr spectral fine structure in terms of some of the constituent molecular species. In 1966, we carried out another study[9] of this system but did not publish it, since the results obtained at that time, although considerably better than those[5] from 1959, only included quantitative data on the relative concentrations of the ortho-, pyro-, and triphosphoryl chloride molecules. We believe that the measurements reported herein, which were obtained in

1973, finally give a good measure of the more prominent molecular species in the reasonably fluid P_2O_5-$POCl_3$ reaction mixtures at equilibrium and that these data should resolve the prior variance of opinions concerning the molecular constitution of these interesting compositions.

Experimental Highlights

The nmr studies were carried out in the continuous-wave mode under classical slow-passage conditions, using a Varian XL-100-15 nmr spectrometer. Both homo- and heteronuclear (^{1}H) field stabilizations were employed, along with signal averaging and ^{31}P-^{31}P internuclear double resonance (INDOR). With ^{1}H field stabilization, the reference-locking sample consisted of a 5-mm sealed tube of water, which was coaxially mounted in the usual thin-walled 12-mm spinning sample tube.

Spin–lattice relaxation times, T_1 values, were obtained on a single equilibrated composition with a Transform Technology, Inc., TT-100 Fourier-transform system[10] connected to the Varian spectrometer. The inversion–recovery pulse method was used with a $180°$–τ–$90°$ pulsing sequence.[10] Because of the complexity of the nmr spectrum, it was necessary to resort to the observation of null points for obtaining the reported T_1 values. We believe that the standard deviation of these measurements is only *ca.* ±5% of each value, since about 10 τ values in the null-point region corresponding to each of the reported T_1 values were employed to locate precisely each position of zero signal intensity on the oscilloscope.

The samples were prepared as previously described[5] and all of them turned out to be clear water-white liquids containing a few tiny specks of black precipitate, which presumably arose from impurities in the phosphorus pentoxide. The methods used for obtaining a quantitative molecular assay from the ^{31}P nmr data on these samples have been previously described.[5,7,11]

Results and Conclusions

Interpretation of Nmr Spectra. The ^{31}P nmr patterns of the equilibrated P_2O_5-$POCl_3$ reaction were found to be remarkably similar to those which have been obtained[7,12] for the condensed phosphates. Thus, in addition to the neso peak at -3.5 ppm for the $POCl_3$ molecule, there was a clearly defined end-group spectral region (4.9–11.2 ppm), a middle-

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(1) Throughout this paper, phosphorus pentoxide [*i.e.*, phosphorus(V) oxide] is denoted by the generic formula P_2O_5, since the degree of polymerization of this compound is known to have no significance with respect to the equilibria described herein.

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(8) T. Glonek, T. Costello, T. C. Myers, and J. R. Van Wazer, *Appl. Spectrosc.*, in preparation.

(9) J. Riess and J. R. Van Wazer, unpublished results.

(10) W. E. Morgan and J. R. Van Wazer, submitted for publication in *J. Amer. Chem. Soc.*

(11) J. R. Van Wazer in "Analytical Chemistry of Phosphorus Compounds," M. Halmann, Ed., Wiley, New York, N. Y., 1972, p 163.

(12) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 5 (1967).

group region (25.4–33.4 ppm), and a branch-group region (47.9–54.2 ppm), as was previously noted.[5] Typical examples of the fine details now observed in these three spectral regions are shown in Figure 1. In complete analogy with the condensed phosphates, the pyrophosphoryl chloride, $P_2O_3Cl_4$, exhibits a single peak in the end-group region; the triphosphoryl chloride, $P_3O_5Cl_5$, shows a doublet in the end-group region and a triplet in the middle-group region; and the tetra- and pentaphosphoryl chlorides, $P_4O_7Cl_6$ and $P_5O_9Cl_7$, exhibit the same distinctive second-order multiplets in the end and middle regions of the spectrum as those observed[8,12] on the respective pure polyphosphate ions $P_4O_{13}{}^{6-}$ and $P_5O_{16}{}^{7-}$. The chemical shifts and spin–spin coupling constants for the condensed phosphoryl chloride molecules which were quantitatively determined in this study are presented in Table I along with similar data for the respective condensed phosphate anions. Proof that all of the resonances ascribed to a single molecule do indeed belong only to one species comes from (1) the fact that these resonances increase or decrease as a group with changing composition as well as from (2) INDOR studies,[13] which have been carried out for each appropriate phosphoryl chloride molecule listed in Table I.

Recent studies[7] have demonstrated the existence of several moderately sized condensed phosphate molecules based on conjoined or fused rings with POP linkages. Similar nmr patterns were observed in this study of the condensed phosphoryl chlorides and we hence ascribe them to the α, β, and γ
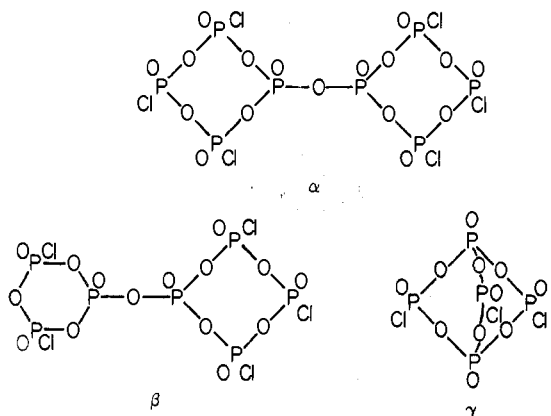
molecular structures. The nmr spectral data for these condensed phosphoryl chlorides are compared with their condensed phosphate analogs (values in parentheses) in Table I. After prolonged signal averaging, a close-lying group of resonances (see Figure 1) are found to show up around 33 ppm. One of these resonances is considerably more prominent than the others and could not be related to any other observed resonance(s). Because of this and its location in the middle-group region of the spectrum, we have assigned this resonance and each of its immediate neighbors to simple-ring metaphosphoryl chlorides $P_m O_{2m} Cl_m$. Although other authors[3,4,6] have proposed the presence of the trimetaphosphoryl chloride ($m = 3$), our guess is that this more prominent ring may be the tetrametaphosphoryl chloride ($m = 4$), as suggested by the chemical shift[12,14] which lies to the high-field side of the middle region.

Although the presence of the isotetraphosphoryl chloride, $[Cl_2(O)PO]_3PO$, has been reported[4,6] as an important con-
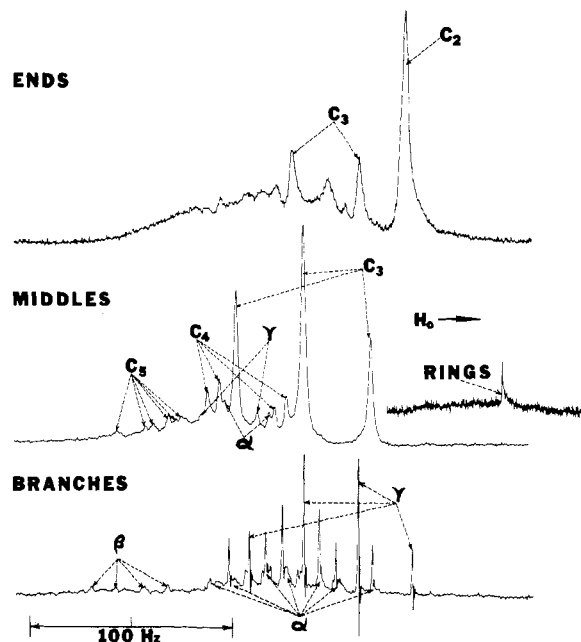
(13) *E.g.*, T. Glonek, T. C. Myers, P. Z. Han, and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **92**, 7214 (1970).

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Figure 1. Signal-averaged ^{31}P nmr spectra of the end-, middle-, and branch-group regions from an equilibrated condensed phosphoryl chloride mixture exhibiting an overall Cl:P mole ratio of 2.2. A 250-Hz scan is depicted for each region, wherein the prominent resonance signals ascribed to the molecules of Table I are denoted. The relative intensities of the spectra (including the "middles" insert labeled "rings") are not comparable, since the amplitude of each region was adjusted for illustrative clarity; however, within each spectrum the intensity ratios are comparable.

stituent of these mixtures, INDOR studies gave no evidence for coupling between branch- and end-group resonances, although they readily showed the expected coupling between end and middle-group resonances in the identified straight-chain polyphosphoryl chlorides. Furthermore, the anticipated end-group doublet and branch-group quartet, corresponding to the shifts and coupling constants suggested in Table I for this as yet unobserved molecule, did not stand out in the spectrum. Of course in these complicated spectra, small amounts of a particular species may not be detectable; however, we estimate that our lower limit of detection for the isotetraphosphoryl chloride was *ca.* 1% of the total phosphorus, assuming that it exhibits an A_3X multiplet pattern corresponding more or less to the parameters suggested in Table I.

Molecular Assay and Equilibrium Constants. The distribution of the total phosphorus in terms of the nine molecular species which were clearly identified and could be quantitatively determined is presented in Figure 2 as a function of the total composition in the P_2O_5–$POCl_3$ system of reaction products. The composition is given in terms of the overall mole ratio of chlorine to phosphorus. Note that the molecular species presented do not add up to the total phosphorus, since some uncharacterized molecules are present. The percentage of total phosphorus corresponding to end (e), middle (m), and branch (b) groups[5] occurring in these uncharacterized molecular species is shown by the respectively labeled dashed lines in Figure 2.

The equilibrium constants based on the total number of neso, end, middle, and branch groups are found to agree well with the values previously reported[5] and with the values obtained in 1966.[9] Thus, in this work we find that $K_1 = [e][b]/[m]^2 = 0.45 \pm 0.04$ as compared to the previously published value of 0.42 ± 0.03, with the $\pm$ value referring in every case to the respective standard deviation. For the

Table I. Nmr Shifts and Coupling Constants

Phosphate[a]	Shifts,[b] ppm			P-O-P coupling constants, Hz			
	Ends	Middles	Branches	em	mm	mb	bb
C_1	-3.5[c] (-0.1)[d]						
C_2	9.7 (9.8)						
C_3	8.8 (9.6)	28.9 (26.7)		33.3 (22.0)			
C_4	8.5 (10.2)	28.2 (25.5)		39.0 (19.8)	23.0 (17.2)		
C_5	8.2	26.9, emm 27.4, mmm		38.9	24.1		
R_4		32.9 (24.2)					
α		28.1, mmm 28.2, mmb (26.5, mmm) (26.6, mmb)	51.4 (37.0)		25.0[e] (31.5)	26.4 (27.3)	18.0 (---)[f]
β		28.0, mmm 28.1, mmb[g] (27.5, mmm) (27.7, mmb) (27.6, mmb)	49.4 (34.7) (35.0)		25.0[e] (31.1)	27.8 (27.1)	14.5 (---)[f]
γ		27.9 (27.3)	51.8 (39.0)			26.7 (25.3)	
$i\text{-}C_4$[h]	11.1		49.8	32.8[i]			

[a] C_x Corresponds to the straight-chain $P_xO_{2x-1}Cl_{x+2}$ molecule; R_y corresponds to the simple-ring $P_yO_{2y}Cl_y$ molecule; α, β, and γ correspond to the respective molecular structures depicted in the text. [b] Relative to 85% orthophosphoric acid. Positive chemical shifts are associated with increasing magnetic field strength. [c] The shift of the neso molecule, $POCl_3$, is listed incorrectly under ends to save space. [d] The values in parentheses are the shifts of the corresponding chlorine-free acids dissolved in a solvent consisting of N,N,N',N'-tetramethylurea–tri-n-butylamine, 1:1 by volume.[6,7] [e] Approximated. [f] Estimated to be <2 Hz. [g] The value given applies to both rings. In this case the chemical shift difference, which must exist between the two rings, is too small and the spectrum too complicated to allow for an accurate assessment of its value. [h] Predicted for the isotetraphosphoryl chloride molecule, $[Cl_2(O)PO]_3PO$. [i] End-to-branch coupling.
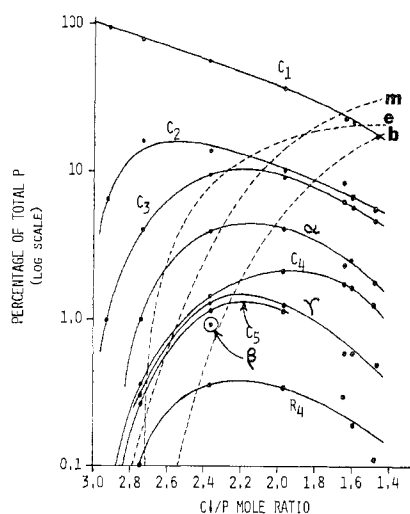

Figure 2. Molecular concentrations as a function of the overall Cl:P mole ratio. The concentrations are given as the percentage of total phosphorus present in a given molecule. The symbols referring to the individual molecules are described in the text and e, m, and b refer to amounts of end, middle, and branch groups, respectively which could not be ascribed to specific molecules.

equilibrium constant $K_2 = [n][m]/[e]^2$, the value observed in this study was 0.68 ± 0.08 as compared to the previously reported value of 0.64 ± 0.05.

According to the graph-theory analysis which we have developed,[15] these equilibrium constants ought not to include cyclic molecules nor cyclic molecular fragments, even for a reorganizational heat order[15] of unity. Therefore, the values of the building-unit equilibrium constants given above have been recalculated, omitting the middle and branch groups

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known to be directly involved in rings. Since the building units involved in cyclization could only be obtained for the characterized molecules, there is an unestablished error (in addition to that corresponding to the given standard deviation) in the following ring-free equilibrium constants: $K_1^* = 0.51 \pm 0.07$ and $K_2^* = 0.57 \pm 0.08$. This error is due to the possible inclusion of some branch and middle groups involved in cyclic portions of the uncharacterized molecules. Our supposition is that the correct value of K_1^* and K_2^* is *ca.* 0.55.

Since eight different molecules were quantitatively identified in the various equilibrated mixtures studied and a ninth quantified molecule was characterized as an unbranched cyclic species, equilibria between these molecules may be calculated regardless of the fact that there are also some unidentified molecules. In treating these intermolecular equilibria, we have assumed that the ninth quantified molecule is the tetrametaphosphoryl chloride, $P_4O_8Cl_4$. Twenty-six different equilibrium constants were calculated; and, for those for which values corresponding to a number of different overall Cl:P mole ratios could be obtained, it was seen that the equilibrium constants based on concentrations exhibited no systematic change from one measurement to another so that the use of equilibrium constants based on molar concentrations appears to be a suitable representation for the system of neat condensed phosphoryl chlorides, within the experimental error of the nmr determination (*ca.* 2% of the total phosphorus).

In order to calculate the concentrations of nine different molecules, only seven independent equilibrium constants are required, since a normalization equation for the total phosphorus plus an equation relating the total Cl:P mole ratio to the molecular distribution gives nine equations in nine unknowns when added to the selected seven equilibrium constants. The seven equilibrium constants which we have

Table II. Molecular Equilibrium Constants for the POCl$_3$-P$_2$O$_5$ System

Constant^a	No. of values
$[C_2]^2/[C_1][C_3] = 0.34 \pm 0.13$	7
$[C_2][C_3]/[C_1][C_4] = 0.85 \pm 0.16$	6
$[C_2][C_4]/[C_1][C_5] = 0.19 \pm 0.19$	2
$[C_3]^3/[C_2]^2[R_4] = 1.21 \pm 0.86\ M^{-1}$	6
$[C_4]^3/[C_1]^4[\alpha] = (7.6 \pm 4.3) \times 10^{-5}\ M^{-2}$	5
$[C_5]^2/[C_1]^3[\beta] = 2.3 \times 10^{-3}\ M^{-2}$	1
$[C_4]^2/[C_1]^3[\gamma] = (8.0 \pm 6.6) \times 10^{-3}\ M^{-2}$	6

^{a} C_x corresponds to the straight-chain $P_xO_{2x-1}Cl_{x+2}$ molecule; R_y corresponds to the simple-ring $P_yO_{2y}Cl_y$ molecule; α, β, and γ correspond to the molecular structures depicted in the text.

chosen as the minimal set for representing the molecular equilibrium data obtained on this system are presented in Table II. Note that all but two of the seven constants listed in this table are based on five or more determinations so that the mean standard deviations shown for them have some statistical validity.

Spin–Lattice Relaxation. Spin–lattice relaxation measurements were carried out on a single equilibrated composition corresponding to a Cl:P mole ratio of 2.2, at temperatures for which the rate of molecular scrambling is extremely slow as compared to the relaxation time. The results obtained at two temperatures are presented in Table III. A previous spin–lattice relaxation study covering a wide temperature range has been reported[16] for the neso molecule, POCl$_3$, as the pure liquid; and the results of that study have been carefully reinterpreted.[17] In both of these papers,[16,17] the dominant relaxation mechanism for the POCl$_3$ molecule at room temperature and above is claimed to be the spin–rotation interaction. This conclusion was based on the fact that the inter- and intramolecular dipole–dipole relaxation rates estimated from the standard equations[16–18] made negligible contributions to the observed relaxation and that the effect of chemical shift anisotropy is completely inconsequential.[17] Furthermore, the observed relaxation time was found to diminish with increasing temperature, as would be expected for a spin–rotation relaxation mechanism.

The T_1 values we obtained for POCl$_3$ (*i.e.*, the C$_1$ molecule) at two temperatures agree well with the mean reported values[15] read from a graph (reported $T_1 = 5.5$ sec at 94° and 8.5 sec at 31° as compared to our measured values of 5.8 and 8.4 sec, respectively). According to the bond distances and angles reported[19] for P–O–P linkages in various condensed phosphates, the distance between nearest-neighbor phosphorus atoms in the condensed phosphoryl chlorides is probably close to 2.90 Å, while the P–Cl distance is taken to be 1.99 Å. These numbers were used to obtain the appropriate values of A in the standard relationship for the intramolecular dipole–dipole contribution to the relaxation rate, *i.e.*, $(1/T_1)_{\text{intra}}^{\text{DD}} = A\tau_c$, where τ_c is a correlation time which may be approximated by the Debye equation[18] $\tau_c = 4\pi\eta a^3/3kT$. An estimation of the radius, a, of the effigy spherical molecule turning in a continuum having a viscosity of η may be obtained from the density of the neat substance, assuming open packing of such spheres. The effective molecular

Table III. Spin–Lattice Relaxation in the POCl$_3$-P$_2$O$_5$ System

Building unit	Obsd T_1, sec	
	At 93.8°	At 31.0°
C$_1$^{a} (POCl$_3$ molecule)	5.8	8.4
C$_2$ ends	9.5	13.8
C$_3$ ends	10.4	13.6
C$_3$ middle	11.3	14.1
C$_4$ ends		13.4
C$_4$ middles		12.7
C$_n$^{b} ends (6.3–9.1 ppm)	9.5	12.3–12.9
C$_n$ middles next to ends (26.4–27.4 ppm)	7.5	7.1–7.3
C$_n$ middles (27.0–28.3 ppm)		10.7–10.9
Middles next to branches (28.0–28.2 ppm)	4.4^c	7.4^c
All branches (46.3–51.2 ppm)	3.8^c	4.0^c

^{a} C_x corresponds to the straight-chain $P_xO_{2x-1}Cl_{x+2}$ molecule. ^{b} $n \geqslant 5$. ^{c} Lower than normal accuracy of *ca.* ±10–15%.

radius, a, of the POCl$_3$ molecule (C$_1$) calculated from its density at room temperature is found to be 2.67 Å, as compared to a radius of 3.06 Å for P$_2$O$_3$Cl$_4$, the pyro or C$_2$ molecule. For the (fully branched) P$_4$O$_{10}$ cage molecule, the effective molecular radius is only 2.79 Å; and, from these data, we think that a value of $4 \leqslant a \leqslant 5$ Å would be appropriate for the α molecule.

Use of the standard simple equations[18] for intra- and intermolecular dipole–dipole relaxations indicates that for POCl$_3$ *ca.* 90% of the spin–lattice relaxation rate [*i.e.*, $(1/T_1)_{\text{obsd}}$] is due to the spin–rotation interaction and that this drops to *ca.* 70% for P$_2$O$_3$Cl$_4$. Depending on the choice of the Debye effective radius, the spin–rotation mechanism contributes from *ca.* 45% (for $a = 5$ Å) to *ca.* 70% (for $a = 4$ Å) of the total relaxation of the branch group in the α molecule. These estimations are in accord with the observed diminution in T_1 value with increasing temperature observed for the end and middle groups as well as for the POCl$_3$ molecule. Since for the branch groups there is no real difference in T_1 when going from 31 to 94°, it would seem that the dipole–dipole and spin–rotation mechanisms contribute about equally to the spin–lattice relaxation in this temperature range, assuming no other significant relaxation mechanisms. This conclusion is in reasonably good agreement with the above estimation that 45–70% of the relaxation of the branch groups is attributable to the spin–rotation interaction.

The most interesting feature of the data of Table III is that the smaller spin–lattice relaxation rates (*i.e.*, $1/T_1$) are associated with the phosphorus atoms in the medium-sized oligomers (*e.g.*, C$_2$–C$_4$ chains). This seems to result from a combination of (a) the increase in intramolecular dipole-dipole relaxation rate with substitution of a chlorine atom by a bridging oxygen plus (b) a concomitant decrease in volume per building unit, as well as (c) substitution of segmental writhing for molecular tumbling as the molecular size increases.

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(17) K. T. Gillen, *J. Chem. Phys.*, **56**, 1573 (1972).

(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 202–203; also see A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, pp 176–197.

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