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Kinetics of hydrolysis of PCl_5 *in situ* as evaluated from the partial hydrolysis products formed in [^{18}O]water

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The *in situ* hydrolysis products of PCl_5 **1**, namely $POCl_3$, HPO_2Cl_2, H_2PO_3Cl and H_3PO_4 **5**, were identified and their mol proportions measured at different extents of overall hydrolysis (from 7.0 to 93%). Partial hydrolysis in 95 atom % [^{18}O]H_2O, step 1, was followed by complete hydrolysis in non-enriched water, step 2. The phosphoric acid isotopomers obtained at step 2 were derived from mixtures that contained from 0 to 4 ^{18}O atoms per phosphate incorporated at step 1, depending upon the composition of the mixtures formed at step 1. The relative mol proportions of mixtures were deduced by regression analysis of the normalized peak intensities of the trimethyl phosphate isotopomer cluster at $m/z = 140, 142 \ldots 148$ (obtained by electron-impact GC analysis). The mixture compositions were used to evaluate kinetically a sequential, irreversible model for hydrolysis of PCl_5. The relative values obtained for apparent hydrolysis constants and the species to which they were attributed were: PCl_5, 1.0; $POCl_3$, 0.24; $PO_2Cl_2^-$, 0.02; with that for HPO_3Cl^- being too great to measure. These values accurately predicted the composition of mixtures in all but a narrow range of overall hydrolysis between 60 and 70% where the hitherto undetected monochloro acid accumulated in yields up to 30%. As the water content becomes small with respect to the acid components in this region, the equilibrium between the monoanion and undissociated forms of the acids is shifted in favour of the undissociated acids (the final end products as the mixture becomes anhydrous). The relative rate constants in this region were estimated to be 0.02 and 0.08 for HPO_2Cl_2 and H_2PO_3Cl, respectively, thereby accounting for accumulation of the monochloro acid in this range. It is proposed that under these conditions the rates of hydrolysis of the mono and dichloro components are comparable because both components are present largely in their free acid forms which undergo hydrolysis by an associative mechanism.

Introduction

Although the vast majority of chemical reactions occur *in situ* ('in place'), such conditions are generally not amenable to conventional thermodynamic or kinetic studies which usually are carried out in a diluent solvent under controlled conditions of temperature, pressure, pH, ionic strength, *etc*. That *in situ* reactions may differ markedly from their counterparts *in vitro* has been recognized since Berthollet's observations of the deposition of sodium carbonate by the action of salt on limestone deposits, which is the reverse of the commonly encountered double decomposition of $CaCl_2$ and $NaCO_3$ in dilute solution to yield NaCl and $CaCO_3$.

Analysis of *in situ* reactions is relevant to the study of natural phenomena and to chemical manufacturing processes. Van Wazer and Fluck[1] used NMR spectroscopy to measure the compositions of complex equilibrium mixtures obtained by the reorganization of phosphoryl chloride and phosphoric acid upon prolonged heating in sealed tubes. However, kinetic studies of the *hydrolysis* of phosphorus halides and oxohalides have been limited mostly to titrimetric or potentiometric measurements of proton or chloride release, using water or 1,4-dioxane as solvent in the presence of an excess of water, *i.e.* under pseudo-first-order conditions, which may not resemble the conditions that obtain when a limiting amount of water is added directly to PCl_5 or to $POCl_3$. Indeed, phosphorochloridic acid, H_2PO_3Cl, has never been detected as an intermediate of either PCl_5 or $POCl_3$ hydrolysis, because its rate of hydrolysis was much faster than its rate of formation from its precursor, phosphorodichloridic acid, HPO_2Cl_2.[2–4] From a practical standpoint, partial hydrolysis mixtures generated *in situ* from $POCl_3$ plus limiting amounts of water are commonly used as phosphorylating reagents.[5–7] The compositions of these mixtures have never been determined and the presence of one putative phosphorylating agent, 'pyrophosphoryl chloride', $(Cl_2PO)_2O$, has been a topic of controversy.[8]

This report describes a simple mass spectrometric procedure for measuring the compositions of partial hydrolysis mixtures of PCl_5, These compositions should be dependent on the amount of water added and (if kinetically determined) on the abilities of the various intermediates to compete for limiting water. The relative proportions of products therefore should contain information on the kinetics of *in situ* hydrolysis. Mechanistic implications governing the accumulation of H_2PO_3Cl are discussed briefly.

Methods

Rationale

Phosphorus pentachloride ($PCl_4^+PCl_6^-$ in the solid state, **1**) reacts violently with water to form sequentially phosphoryl chloride, $POCl_3$ **2**, phosphorodichloridic acid **3**, phosphorochloridic acid **4**, orthophosphoric acid, H_3PO_4 **5**, and possibly $(Cl_2PO)_2O$ (see ref. 9 for a review). Limited hydrolysis of PCl_5 in [^{18}O]H_2O should thus yield a mixture of compounds containing from 0 to 4 oxygen atoms derived from labelled water. The subsequent addition of an excess of non-enriched water should convert these compounds into a mixture of isotopomers of phosphoric acid, Scheme 1, that can be analysed by electron-impact mass spectroscopy after conversion into their trimethyl phosphate esters. The observed abundances for the ions at $m/z = 140, 142 \ldots 148$ should reflect the sum of the individual ^{18}O-labelled isotopomer contributions. Linear regression analysis of the composite spectrum of the above cluster should yield estimates of the mol proportions of the partial hydrolysis components present at step 1.

Step 1	PCl_5	$P^{18}OCl_3$	$HP^{18}O_2Cl_2$	$H_2P^{18}O_3Cl$	$H_3P^{18}O_4$
	↓	↓	↓	↓	↓
Step 2	$H_3P^{16}O_4$	$H_3P^{18}O^{16}O_3$	$H_3P^{18}O_2{}^{16}O_2$	$H_3P^{18}O_3{}^{16}O$	$H_3P^{18}O_4$
m/*z*	140	142	144	146	148

Scheme 1 Isotopomers of H_3PO_4 produced by partial hydrolysis of PCl_5 in $[^{18}O]H_2O$, step 1, followed by complete hydrolysis in normal enrichment water, step 2

Partial hydrolysis and mass spectral analysis

Phosphorus pentachloride (Aldrich) was obtained in a sealed container. Small aliquots of PCl_5 were stored in capped Wheaton vials in a desiccator over sulfuric acid. Amounts of it (8–16 mg) were added to tared Wheaton vials (0.3 cm^3) in a glove-bag and the vials were capped and reweighed. Subsequent additions of water were made to adjust the percentage of overall hydrolysis to the approximately desired level, based on the actual weight of PCl_5. Partial hydrolysis of PCl_5 in highly enriched $[^{18}O]H_2O$ (nominally 97–99 atom %, obtained from ICN) was carried out in Wheaton vials with conical wells, either by addition of water under N_2 in a glove-bag using a positive-displacement micropipette, or by injection of water through the cap septum using a Hamilton microsyringe. No diluent solvent or buffer was added, neither was the pH nor the temperature controlled. The vigorous reaction between water and PCl_5 appeared to provide adequate mixing. Data acquired from three separate runs carried out at different times with slight modifications of the procedure (*e.g.* the use either of capped vials and a microsyringe or of non-capped vials and a positive-displacement pipette) yielded consistent results. After the addition of $[^{18}O]H_2O$ the mixture was allowed to stand at room temperature for 10 min before the addition of an excess of non-enriched water, to convert any unreacted PCl_5 or partial hydrolysis products into H_3PO_4. The solution thus obtained was either taken to dryness under vacuum without heating or else the phosphate was purified through two precipitation steps before being converted into trimethyl phosphate using a diethyl ether–diazomethane distillate.[10] A JEOL model AX-505 GC mass spectrometer was used for electron-impact ionization analysis of the trimethyl phosphate isotopomers, using the intensities of the ions at *m/z* 140, 142 . . . 148. Were the hydrolysis to be carried out in 100 atom % $[^{18}O]H_2O$ then the relative peak intensities of the above ion cluster would directly represent the relative mol proportions of the components of a partial hydrolysis mixture. For water of lower enrichment these compositions must be calculated as below.

Regression analysis of spectral data

The two-step hydrolysis procedure yields a spectrum corresponding to phosphoric acid isotopomers containing from 0 to 4 ^{18}O atoms. The observed spectrum may be considered as a composite made up of the contributions of the individual components in the partial hydrolysis mixture. If the spectrum associated with each component (PCl_5, $POCl_3$, *etc.*) is known then the simultaneous equations can be solved to determine the relative amounts of the components present in the partial hydrolysis mixture. For example, if PCl_5 is hydrolysed to $POCl_3$ in 95 atom % $[^{18}O]H_2O$ then 95% of the oxygen in $POCl_3$ will contain ^{18}O and 5% ^{16}O. Following hydrolysis of this labelled $POCl_3$ in $[^{16}O]H_2O$, the expected spectrum of the resulting trimethyl phosphate would contain peaks at *m/z* 140 and 142 in proportion 0.05:0.95. Any unhydrolysed PCl_5 present in a mixture would produce only a peak at *m/z* 140, as the natural abundance of ^{18}O in non-enriched water (0.204 atom %) can be ignored in these calculations. The theoretical spectra of the other components were calculated using a binomial distribution equation.

For each partial hydrolysis mixture there are maximally five unknown components to be determined. These correspond to the components present in step 1, although in practice fewer than five were detected simultaneously as unhydrolysed PCl_5 did not coexist with the more extensively hydrolysed products (a further indication that complete mixing had occurred at step 1). In the regression equation (1) *a, b . . . e* represent the mol

$$^{\mathbf{obs}}P_i = a\,{}^aP_i + b\,{}^bP_i + c\,{}^cP_i + d\,{}^dP_i + e\,{}^eP_i \qquad (1)$$

proportions of PCl_5, $POCl_3$ . . . H_3PO_4 to be determined in a mixture. The observed peak intensities $^{\mathbf{obs}}P_i$ ($i = 0, 1 \ldots 4$) are the dependent variables. The binomially calculated peak intensities calculated for the individual components are the independent variables, *e.g.* ^aP_i ($i = 0, 1 \ldots 4$) would represent the spectrum calculated for the component present in mol proportion *a*. In addition the normalized peak intensities must sum to 1, providing a sixth equation (2). For example, a 1:1

$$\sum_{i=0}^{i=4} {}^{\mathbf{obs}}P_i = 1 = \sum_{i=0}^{i=4} (a\,{}^aP_i + b\,{}^bP_i + c\,{}^cP_i + d\,{}^dP_i + e\,{}^eP_i) \qquad (2)$$

mixture of non-enriched phosphate ($a = 0.5$, $^aP_0 = 1$, $^aP_4 = 0$) and fully ^{18}O-enriched phosphate ($e = 0.5$, $^eP_0 = 0$, $^eP_4 = 1$) would produce a normalized two-line spectrum, $^{\mathbf{obs}}P_0 = {}^{\mathbf{obs}}P_4 = 0.5$.

The initial reacting proportions of PCl_5 and H_2O cannot be estimated accurately from the small amounts of PCl_5 and water added to the vials. However, they can be calculated from the oxygen-18 content of the hydrolysis mixture after step 2. For example, an H_3PO_4 sample with an atom % oxygen-18 content equal to half that of 95 atom % $[^{18}O]H_2O$ must have undergone 50% overall hydrolysis at step 1, signifying that the initial reacting proportions of $H_2O:PCl_5$ were 2:1.

Estimation of relative second-order rate constants from mol proportions of partial hydrolysis products

The sequential hydrolysis reaction is minimally described by six differential equations (3)–(8) based on the assumptions that each

$$d(PCl_5)/dt = -k_1(PCl_5)(H_2O) \qquad (3)$$

$$d(POCl_3)/dt = k_1(PCl_5)(H_2O) - k_2(POCl_3)(H_2O) \qquad (4)$$

$$d(HPO_2Cl_2)/dt = k_2(POCl_3)(H_2O) - k_3(HPO_2Cl_2)(H_2O) \qquad (5)$$

$$d(H_2PO_3Cl)/dt = k_3(HPO_2Cl_2)(H_2O) - k_4(H_2PO_3Cl)(H_2O) \qquad (6)$$

$$d(H_3PO_4)/dt = k_4(H_2PO_3Cl)(H_2O) \qquad (7)$$

$$d(H_2O)/dt = -[k_1(PCl_5) + k_2(POCl_3) + k_3(HPO_2Cl_2) + k_4(H_2PO_3Cl)](H_2O) \qquad (8)$$

step is irreversible and that the mol proportions of the reactants can be used in place of molar concentrations. These simultaneous equations were solved numerically by a fast Runge–Kutta algorithm for specified time intervals and starting conditions, using preliminary estimates of the four rate constants (MATHCAD, version 5.0, MathSoft Inc., Cambridge, MA). The amount of PCl_5 was set to 1 and estimates of the rate constants for compounds **2**–**4** were made relative to k_1, set to 1). Integration times were made long enough to permit the simulation to go nearly to completion as judged by the mol proportion of residual water (typically 10^{-3}).

Kinetically calculated final compositions were compared to the experimentally observed target compositions obtained by regression analysis, using a least-squares minimization calculation. When two rate constants had to be fitted simultaneously a pairwise combination of their values was used to construct a 3 by 3 minimization surface plot that served as a guide for further

Table 1 Observed and calculated (italics) relative peak intensities of isotopomers derived by partial hydrolysis of PCl_5 in $[^{18}O]H_2O$. Calculated values are based on the mol proportions of the components in mixtures as estimated by regression analysis of the observed peak intensities

Mol proportion	*m/z*				
$H_2O:PCl_5$	140	142	144	146	148
0.28:1	0.733	0.251	0.015	0.000	0.000
	0.734	*0.251*	*0.015*	*0.000*	*0.000*
1.18:1	0.122	0.647	0.210	0.019	0.001
	0.122	*0.648*	*0.210*	*0.019*	*0.000*
1.57:1	0.034	0.467	0.475	0.020	0.004
	0.034	*0.468*	*0.475*	*0.020*	*0*
1.57:1*	0.030	0.146	0.788	0.027	0.010
	0.032	*0.147*	*0.788*	*0.028*	*0*
1.84:1	0.021	0.280	0.641	0.045	0.012
	0.013	*0.282*	*0.642*	*0.046*	*0.013*
1.92:1	0.021	0.237	0.666	0.057	0.019
	0.010	*0.240*	*0.669*	*0.059*	*0*
2.40:1	0.018	0.127	0.484	0.281	0.091
	0.004	*0.129*	*0.486*	*0.283*	*0.093*
2.78:1	0.004	0.056	0.469	0.235	0.235
	0.001	*0.057*	*0.469*	*0.235*	*0.235*
3.26:1	0.002	0.030	0.322	0.126	0.520
	0.000	*0.028*	*0.325*	*0.110*	*0.527*
3.31:1	0.002	0.033	0.290	0.135	0.541
	0.000	*0.033*	*0.290*	*0.136*	*0.541*
3.72:1	0.002	0.012	0.121	0.138	0.727
	0.000	*0.010*	*0.120*	*0.151*	*0.723*

* This aliquot was treated with ethanol before step 2 to remove $POCl_3$ as triethyl phosphate before complete hydrolysis at step 2.

refinement. Overall success in fitting was judged by the ability to obtain a single self-consistent set of estimates for data sets derived from mixtures of widely differing composition.

Results and Discussion

The nature of the products formed by partial hydrolysis of $POCl_3$ is poorly defined; initial reaction mixtures have been considered to contain almost entirely the dichloro acid **3** and $(Cl_2PO)_2O$[4] although evidence that 'hydrated phosphorus oxychloride,' $H_2O:POCl_3 = 1:1$, contains polyphosphoryl chlorides has been shown to be highly questionable.[8] Addition of water to $POCl_3$ has been found to promote phosphorylation of nucleosides and ascorbate derivatives[5–7] although to what extent added water modifies the reactivity of the substrate as opposed to generating reactive hydrolytic products of $POCl_3$ is still uncertain. Pyrophosphoryl chloride and the dichloro acid have been considered as active reagents produced by partial hydrolysis of $POCl_3$; however, the former has not been established firmly as a hydrolytic intermediate[8] and the dichloro acid by itself was ineffective.[5]

Table 1 shows the observed and calculated spectral data (based on the compositions deduced by regression analysis) for 10 mixtures derived by partial hydrolysis of PCl_5 over a wide range of hydrolysis (7–93%). The bimodal frequency distributions at $m/z = 144$ and 148, derived from initial stoichiometries of $H_2O:PCl_5 = 3.26:1$ and $3.31:1$ (Table 1), are indicative of a binary mixture of the dichloro acid and H_3PO_4 with no detectable monochloro acid, in agreement with titrimetric studies on the hydrolysis of $POCl_3$ in an excess of water. In no case PCl_5 was found to coexist with more extensive hydrolysis products, which helped to exclude the possibility that mixing artifacts arise from incomplete contact of PCl_5 with enriched water during step 1.

To verify that the component identified and quantified as $POCl_3$ by regression analysis of spectral data was indeed that compound, an aliquot from one sample ($H_2O:PCl_5 = 1.57:1$), Table 1, was removed after step 1 and an excess of absolute ethanol was added to convert any $POCl_3$ present into triethyl phosphate, *before* the addition of water at step 2. This volatile derivative was largely lost at subsequent evaporative stages prior to derivatization and mass spectrometric analysis, although a trace of a component ($m/z = 184$) found *only* in the ethanol-treated sample probably represented a small residual amount of triethyl phosphate. The ethanol-treated sample had a considerably higher oxygen-18 content (45.9 atom %) than its non-treated counterpart (37.3 atom %), demonstrating the selective loss of a volatile component with a lower enrichment.

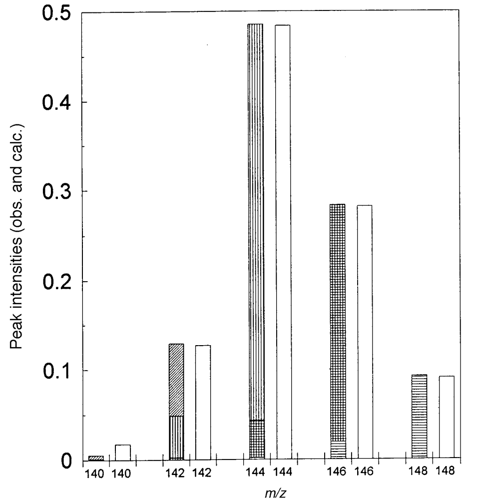


Fig. 1 Spectral evidence for the formation of phosphorochloridic acid in a partial hydrolysis mixture derived from $PCl_5:H_2O = 2.40:1$. Open bars show the observed normalized peak intensities. The hatched bars show the contributions from each component, based on the composition of mixtures determined by regression analysis of the observed peak intensities. Key: H_3PO_4, horizontal lines; H_2PO_3Cl, squares; HPO_2Cl_2, vertical lines; $POCl_3$, diagonal lines

These effects can be seen (Table 1, $H_2O:PCl_5 = 1.57:1$) by comparing the intensities of the peaks at $m/z = 142$ and 144 for the control (0.467, 0.475) and the ethanol-treated sample (0.146, 0.788). Regression analysis of the ethanol-treated mixture showed a decrease in $POCl_3$ by 0.37 mol proportion. The observed mol proportion of dichloro acid (0.87) in the ethanol-treated sample compared favourably with that predicted (0.83) if a 0.37 mol proportion of $POCl_3$ were to be selectively removed from the untreated sample. These observations lend credence to the identities and yields of the components deduced by mass spectral analysis. They also indicate that $POCl_3$ and phosphorodichloridic acid were not in rapid equilibrium, otherwise the dichloro acid would also be removed.

By contrast, the monochloro acid was obtained in good yield (about 30%) starting at $H_2O:PCl_5 = 2.40:1$ or $2.78:1$, *i.e.* with stoichiometric values consistent with expectations based on reacting proportions (Fig. 1). The observed spectra (open bars) and calculated spectra (hatched bars) are shown. The hatch marks show the individual contributions attributed to each component on the basis of regression analysis. The peaks at *m/z* 144 and 146 signify the major presence of the di- and monochloro-acid, respectively, at step 1. The formation of the monochloro acid in this region indicated that a mechanistic change in its hydrolysis relative to that of the dichloro acid must have occurred as water became limiting, *i.e.* that k_4 was no longer very much greater than k_3. The accumulation of phosphorochloridic acid, H_2PO_3Cl, a hitherto undetected hydrolytic intermediate, in moderately good yields in this region may be relevant to the use of $POCl_3$–water mixtures as phosphorylating agents.

The relative values of the apparent second-order rate constants were determined to establish whether a simple sequential mechanism (Scheme 1) could adequately describe the observed distributions of hydrolysis products over a wide range of hydrolysis. Were the relative rate constants to be strongly

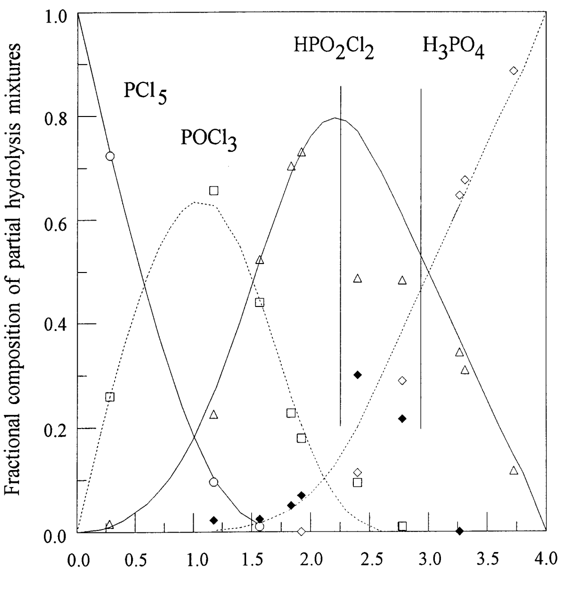
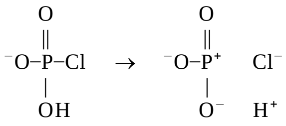


Fig. 2 Yields of products formed by partial hydrolysis of PCl_5. Compositions were calculated by linear regression analysis of the normalized peak intensities of trimethyl phosphate isotopomers as described in the text. The symbols represent observed yields of PCl_5 or its products. Key: PCl_5, ○; $POCl_3$, □; HPO_2Cl_2, △; H_2PO_3Cl, ◆; H_3PO_4, ◇. The labelled connecting lines show the kinetically predicted profiles of end products obtained by numerical integration of a set of differential equations describing a sequential hydrolytic process using relative second-order rate constants of $PCl_5:POCl_3:HPO_2Cl_2:H_2PO_3Cl = 1:0.24:0.02:2.0$. The accumulation of the monochloro acid in the region between the vertical lines is attributed to a change in its hydrolysis mechanism that occurs if water becomes limiting in this region, forcing the conversion of the monoanion forms of the chloro acids into their free acid forms

milieu-dependent then no single set of rate constants would satisfy all sets of hydrolytic data, and a separate set of values might be required for each mixture. Best-fitting values were determined for limited hydrolysis of PCl_5 to all of the relevant observed end products with the exclusion of two cases where significant amounts of the monochloro acid had formed. Using values of $k_1 = 1$ and $k_4 = 100k_3$, best fitting values for k_2 and k_3 were sought using the minimization procedure described. Values ranging from 0.2 to 0.3 were found for k_2 and from 0.01 to 0.04 for k_3 with average values of 0.24 and 0.02 respectively.

Fig. 2 shows the close correspondence between the observed compositions of the mixtures (symbols) and the predicted end-point compositions (connecting lines) computed for over 30 different values of $H_2O:PCl_5$ starting proportions, encompassing widely differing extents of overall hydrolysis, using the relative rate constant values of 1.0 (PCl_5), 0.24 ($POCl_3$), 0.02 (HPO_2Cl_2) and 2.0 (H_2PO_3Cl). At $H_2O:PCl_5 \geqslant 3.3:1$ the dichloro acid was converted into phosphoric acid with no detectable monochloro acid, in agreement with earlier studies performed with water in excess.[2–4] There was good agreement between observed and calculated compositions of partial hydrolysis mixtures for all cases except for two cases falling approximately between $H_2O:PCl_5 = 2:1$ and $3:1$ (Fig 2, vertical lines). These deviations can be attributed to the formation of the monochloro acid which was detected in small amounts at lower extents of hydrolysis but was only produced in relatively high yields within a narrow range of overall hydrolysis (Fig. 2, filled diamonds).

The initial proportions of H_2O to PCl_5 are critical for achieving substantial phosphorochloridic acid formation; the amount of water must be sufficient to drive the formation and the incomplete hydrolysis of the dichloro acid, but insufficient to subject the monochloro acid to a sufficiently aqueous environment that would favour its rapid hydrolysis. Fig. 2 also shows that the substantial accumulation of the monochloro acid cannot be attributed to the ability of PCl_5 or $POCl_3$ to compete for limiting water, as these components are largely absent in this region. Thus the data indicate that under *in situ* conditions the rates of hydrolysis of the dichloro and monochloro acids can become roughly comparable, in sharp distinction to conditions where water is in excess.



$$^{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}{-}Cl \rightarrow {}^{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O^{-}}{|}}{P^{+}}} \quad Cl^{-} \quad H^{+}$$

Scheme 2

There is strong evidence that in aqueous solution the chloro acids exist in their respective monoanion form and that the monochloro monoanion undergoes hydrolysis much faster than its dichloro monoanion counterpart.[4] In a less aqueous environment it is likely that the acids are forced largely into their undissociated (free acid) forms, thus negating the kinetic advantage of the monochloro over the dichloro component.

The water content in relation to the dissociable hydrogen content was evaluated in the region where the monochloro acid accumulated, by solving the differential equations using initial and final conditions corresponding to the mixtures obtained at $H_2O:PCl_5 = 2.40:1$ and $2.78:1$, respectively. The initial reacting proportions (see Fig. 2) corresponded to $POCl_3:HPO_2Cl_2:H_2PO_3Cl:H_3PO_4:H_2O = 0.1:0.49:0.30:0.11:0.38$, *i.e.* there was only sufficient initial water (0.38) to solvate about half of the protons of the mono-, di- and tri-basic acids and form the corresponding monoanion species and H_3O^+. Thus, it seems likely that under these conditions the undissociated rather than the anionic forms of the chloro acids were the predominant species in this region.

The value for k_4 that best described the reaction in this region was found by seeking the values for the hydrolysis constants that best described how the initial reacting proportions given above (generated from the starting proportions, $H_2O:PCl_5 = 2.40:1$) could give rise to the observed products (generated from the starting proportions, $H_2O:PCl_5 = 2.78:1$), as a result of the uptake of 0.38 mol fraction of water. The values obtained were 0.08 for the monochloro acid and 0.02 for the dichloro acid. These values are in marked contrast to those obtained in a more aqueous solution where the hydrolysis constant for the monochloro monoanion was $\geqslant 0.02$. These kinetic data suggest that in this region of low water content, the undissociated monochloro and dichloro acids are hydrolysed by a common mechanism, with roughly comparable rate constants, in contrast to their monoanion counterparts in a more aqueous medium.

In an excess of water the rapid hydrolysis of the monochloro monoanion (HPO_3Cl^-) with respect to the dichloro monoanion ($PO_2Cl_2^-$) has been attributed to the former's ability to undergo hydrolysis by a dissociative mechanism involving a metaphosphate-like (PO_3^-) transition state.[4,11] Loss of Cl^- and H^+ generates a species with two negatively charged oxygens (a resonance form of metaphosphate), thus reducing the developing negative charge on the Cl^- leaving group and the positive charge on the phosphorus atom, thereby facilitating expulsion of Cl^-. Reaction of PO_3^- with water would give $H_2PO_4^-$. A comparable metaphosphate-like transition state cannot be formed from the dichloro monoanion, which by contrast undergoes hydrolysis by a slower associative mechanism, namely an in-line displacement involving a five-co-ordinate structure analogous to an S_N2 reaction. As the *undissociated* monochloro acid (H_2PO_3Cl) likewise cannot form the metaphosphate type of structure depicted in Scheme 2, it is plausible to suggest that it too undergoes hydrolysis by a slower associative process.

The *in situ* kinetic analysis reported here differs from pre-

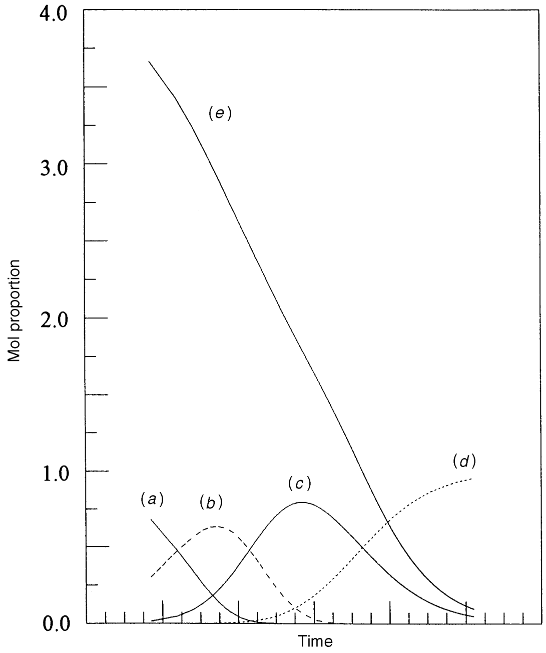


Fig. 3 Simulated course of PCl_5 hydrolysis with starting mol fractions $H_2O:PCl_5 = 4:1$. The reaction progress was calculated by numerical integration of the differential equations describing a sequential hydrolysis model, using the relative rate contants given in the legend to Fig. 2. The figure shows the predicted compositions of mixtures at different time points. The time intervals between successive points on the *x* axis are indeterminate (see text). Key: PCl_5 (*a*), $POCl_3$ (*b*), $PO_2Cl_2^-$ (*c*), $H_2PO_4^-$ (*d*) and H_2O (*e*)

vious kinetic studies in an aqueous environment in several ways. Water was not present in excess and the hydrolysis was not performed under conditions of pseudo-first-order kinetics. Mol proportions rather than molar concentrations were used in the rate equations and, more unusually, time was not measured as an independent variable. Instead the relative rates of hydrolysis of various components were reconstructed from the composition of partial hydrolysis mixtures, on the assumption that these end compositions were kinetically determined by competition between components for limiting amounts of water. The assumption that the end products were kinetically rather than thermodynamically determined (equilibrium conditions) is supported by several lines of evidence. (1) At high extents of overall hydrolysis the mixtures contained the dichloro acid and phosphoric acid but little or no monochloro acid. This effect has been well documented to be kinetically determined when water is in excess.[2–4] (2) The addition of ethanol to a hydrolysis mixture containing largely $POCl_3$ and the dichloro acid selectively removed the former, leaving the dichloro acid. If the two components were in rapid equilibrium then both should have been removed. (3) Hydrolysis of PCl_5 was accompanied by release of HCl which escapes (even through the septum of a capped vial) into the atmosphere, making reversal of hydrolysis unlikely. (4) The reaction can be modelled successfully as a series of irreversible, sequential reactions (Fig. 2). Indeed the assigned values of four relative rate constants are sufficient to accurately compute most of the observed spectral data shown in Table 1.

This competitive type of kinetic analysis provides *comparative* values for competing reactions. If changes in water content shift the chloro acids being compared from their anionic to their undissociated forms it is possible that no *relative* change in rate constants would be observed, even though the absolute rates of hydrolysis might be quite different for the dissociated and undissociated species. However, if one acid but not the other underwent a mechanistic change upon conversion from the anionic form into the free acid, then its apparent rate constant relative to its companion acid could change. This behaviour would explain the accumulation of monochloro acid in the region of 60–70% overall hydrolysis of PCl_5 but its conspicuous absence beyond 80% overall hydrolysis.

The strengths and limitations of this type of analysis are illustrated in Fig. 3, which depicts the course of hydrolysis ($H_2O:PCl_5 = 4:1$) calculated using the rate constants employed for Fig. 2. The constants are assigned to the monoanion forms of the chloro acids because of the high water content in the region of chloro acid formation. The relative proportions of hydrolysis products can be read for any particular time point although the intervals between time points are indeterminate because the computation was based on relative rather than absolute values for the rate constants as discussed above.

In summary, partial hydrolysis in $[^{18}O]H_2O$ offers a comparatively simple procedure for identifying the hydrolysis products of PCl_5 and for assessing their relative rates of reaction with water under *in situ* conditions. The procedure may be applicable to $POCl_3$–water mixtures, commonly used as phosphorylating agents, and perhaps to the hydrolysis of other phosphorus halides or oxohalides.

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