CHROMATOGRAPHIC STUDIES ON THE HYDROLYSIS OF PHOSPHORUS COMPOUNDS

PART I. THE HYDROLYSIS OF TRIPHOSPHONITRILIC CHLORIDE

F. H. POLLARD, G. NICKLESS AND R. W. WARRENDER

Department of Chemistry, University of Bristol, Bristol (Great Britain)

The hydrolysis of triphosphonitrilic chloride $(PNCl_2)_3$ can be conveniently separated into two distinct stages:

(1) The hydrolysis of triphosphonitrilic chloride in neutral or alkaline solution to trimetaphosphimic acid $[PN(OH)_2]_3$[1-5].

(2) The hydrolysis of trimetaphosphimic acid in acid solution through a variety of phosphorus-nitrogen containing acids to orthophosphate and ammonia[6-8].

The reaction (1) is slow, and stepwise substitution of chlorine atoms by hydroxyl groups occurs. The partially substituted intermediates, of which five are theoretically possible, are called chlorohydrines. STOKES[9,10] prepared a mixture of chlorohydrines containing largely the dihydroxy-tetrachlorohydrine, but was unable to determine whether or not substitution occurred in pairs on the same phosphorus atoms. The solid triphosphonitrilic chloride is unreactive with water, and this lack of reactivity is probably due to their insolubility in water. By use of ethereal solutions of triphosphonitrilic chloride it can be brought into intimate contact with water.

A mixture of chlorohydrines was prepared by interrupting the hydrolysis of triphosphonitrilic chloride after a definite time. STOKES[9] reported the preparation of the tetrachlorohydrine $[P_3N_3Cl_4(OH)_2]$ by stopping the hydrolysis after 6–8 h, but was unable to separate it from small quantities of other chlorohydrines.

This communication is the first of a series of investigations concerning the hydrolysis of the phosphonitrilic halides. The aims of the research were:

(1) To study the hydrolysis of triphosphonitrilic chloride under neutral conditions, when trimetaphosphimic acid is the final product, and postulate the order in which the chlorine atoms are replaced by hydroxyl groups (Part I).

(2) To determine the course of the acid hydrolysis of the trimetaphosphimate ion, propose mechanisms for all stages, and determine the rates of the hydrolysis of the ring compounds (Part II).

(3) To study aspects of the hydrolysis of higher chlorides in view of the results obtained for the trimer (Parts III, IV, V).

EXPERIMENTAL

Preparation of intermediate chlorohydrines

Triphosphonitrilic chloride (30 g) was dissolved in diethyl ether (300 ml) and the

solution agitated with water (100 ml) for 6 h. The aqueous layer then contained hydrochloric acid and trimetaphosphimic acid, while the diethyl ether contained unchanged triphosphonitrilic chloride and a mixture of chlorohydrines.

The diethyl ether was separated and dried over calcium chloride, overnight. The greatest part of the diethyl ether was then distilled off on a water bath, and the final residues by blowing a current of hot dry air over the product. The unreacted phosphonitrilic chloride was removed by washing with a small volume of benzene in which the chlorohydrines are relatively insoluble, followed by a washing with carbon disulphide. The product which was obtained in about 5 % yield, due to continuous conversion of the chlorohydrine to the metaphosphimic acid, was dried over silica gel in a vacuum desiccator.

Preparation A. Found: N, 13.6; P, 29.8; Cl, 42.0. Calculated for $P_3N_3Cl_4(OH)_2$: N, 13.5; P, 29.9; Cl, 45.6.

A similar preparation was carried out but the hydrolysis was allowed to proceed for 50 h before isolation of the chlorohydrine.

Preparation B. Found: N, 14.6; P, 30.8; Cl, 30.4. Calculated for $P_3N_3Cl_2(OH)_4$: N, 15.3; P, 33.9; Cl, 25.9.

Both products were unstable in a moist atmosphere, first absorbing water and becoming sticky solids (releasing hydrogen chloride), and later hardening to brittle solids.

Preparation of sodium trimetaphosphimate[6]

Trimeric phosphonitrilic chloride (15 g) was dissolved in diethyl ether (75 ml), and this solution was shaken with a solution of sodium acetate (55 g) in water (100 ml) for 94 h.

Crystals of sodium trimetaphosphimate began to crystallise from the aqueous layer after about 15 h, but at least 80 h were required for complete decomposition of any chlorohydrines formed as intermediate products.

The sodium salt of the acid was filtered off in almost quantitative yield (the product being insoluble in the relatively concentrated sodium chloride solution), washed with 50 % v/v aqueous ethanol and finally with 96 % ethanol, followed by drying in a vacuum desiccator.

Found: N, 10.9; P, 24.6; H_2O, 19.6. Calculated for $Na_3P_3(NH)_3O_6 \cdot 4H_2O$: N, 11.0; P, 24.8; H_2O, 20.0.

Paper chromatography of the chlorohydrines

Paper chromatographic separations of the chlorohydrine reaction products were largely unsuccessful because of a large amount of tailing; probably resulting from the hydrolysis of the species during the elution of the chromatogram.

The technique used was descending elution, with BIBERACHER's basic solvent[11] for 13 h at 18° using Whatman No. 541 filter paper in the conventional all-glass apparatus[12].

The position of a particular species on a paper chromatogram is usually recorded by its R_F value, which is defined as the ratio of distance moved by the species to the distance moved by the solvent front. But in cases where the solvent is eluted off the lower edge of the chromatogram, we recorded the R_x value which we define as the ratio of the distance moved by the species to the distance moved by orthophosphate.

Under the normal standard conditions[13] of elution, the R_x values are subject to deviate from the values given below by $\pm$ 5 %. When large quantities of some cation or anion other than a phosphate species occur in a position close to a phosphate species, the spot is "pushed" from its original position and may have an R_x value outside the $\pm$ 5 % limit. This is easily recognised, however, since the spot usually assumes a crescent shape around the spot of the interfering ion.

BIBERACHER's basic solvent gave chromatograms of the chlorohydrines which showed three quite distinct spots with R_x values 2.45, 1.20 and 0.54. The spot at R_x 1.20 is due to trimetaphosphimate, but with no very pure samples of chlorohydrines available, the identity of the other spots can only be suggested.

Preparation A gave a large spot at R_x value 2.45 and a smaller spot at R_x 1.20 with tailing in between. The analysis shows the composition of the chlorohydrine to approximate to $P_3N_3Cl_4(OH)_2$ and this makes it highly probable that the spot with R_x value 2.45 is due to the tetrachlorohydrine.

Preparation B showed only a trace with R_x value 2.45, but spots at R_x values 1.20 and 0.54. By similar reasoning to the above, it was highly probable that the spot at R_x 0.54 was due to the dichlorohydrine $P_3N_3Cl_2(OH)_4$.

The trimetaphosphimate found in each case is formed by hydrolysis of the chlorohydrines, as it is unlikely to be obtained in preparations where the chlorohydrines are recovered from the ethereal layer. Sodium trimetaphosphimate is insoluble in diethyl ether.

Ion-exchange chromatography of the chlorohydrines

Further evidence to support the postulations as to the identity of the spots on the paper chromatograms, was added when preparations A and B were subjected to ion-exchange separations. Ion-exchange chromatographic separations of phosphate mixtures were effected by a modification of the gradient elution method of GRANDE AND BEUKENKAMP[14], and the technique will be described fully in Part II of this series[15].

The elution patterns for Preparation A and Preparation B are shown in Fig. 1.
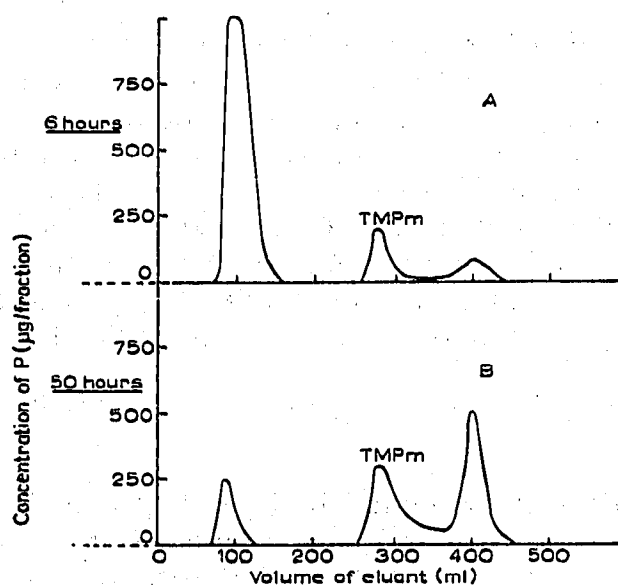

Fig. 1. Elution behaviour of the chlorohydrine preparations. (A) 6 h preparation; (B) 50 h preparation.

For Preparation A, about 85 % of the total phosphorus occurred in the species whose peak was fraction 9, and was assigned to the tetrachlorohydrine $P_3N_3Cl_4(OH)_2$. The small peak with maximum at fraction 27 was the trimetaphosphimate peak, whilst the very small peak at fraction 40 was assigned to the dichlorohydrine.

Preparation B also gave 3 peaks, but the concentration of phosphorus in the peak at fraction 9 was very much smaller amounting to only about 10 % of the total phosphorus. The size of the fractions with peaks at fractions 27 and 40 had increased, and contained about 30 % and 60 % of the total phosphorus respectively. Notice also the tail forward of the species with peak at fraction 40 towards the trimetaphospimate peak. Fraction 40 was assigned to the dichlorohydrine.

No absolute proof as to the identities of the peaks at fractions 9 and 40 was obtained since all attempted methods of isolation yielded products contaminated with large amounts of trimetaphosphimate. From the difference in elution patterns of Preparations A and B coupled with the analysis figures for the products, and for the tendency of hydroxyl groups to substitution in pairs (similarly for ammonia and fluorine), we are confident that the peaks have been correctly assigned.

The patterns are definitely not due to any condensed phosphate or imidophosphate species, as paper chromatography in a number of solvents has shown such species to be absent and they are not formed from chlorohydrines under the conditions of elution (see Part II).

Infra-red spectra of the chlorohydrines

The infra-red spectra of the two preparations were recorded (in potassium bromide discs) and whilst showing certain differences, they were not diagnostic. They are listed in Table I, together with those of triphosphonitrilic chloride and sodium trimetaphosphimate tetrahydrate. The position of the peak is given by the frequency in cm^{-1}, and the intensity of the absorption is indicated by s $=$ strong, m $=$ medium, w $=$ weak, while the shape of the peak is indicated by b $=$ broad, n $=$ narrow, sh $=$ shoulder. Spurious peaks, due to moisture absorbed by potassium bromide are indicated by an asterisk.

The P–Cl vibrations in the region 400–700 cm^{-1} did not give any well-defined narrow peaks, but the absorption in decreasing intensity was $(PNCl_2)_3$, Preparation A, Preparation B. This can be seen in the 550 cm^{-1} line for $(PNCl_2)_3$ which was strong, until it disappeared completely in sodium trimetaphosphimate. A showed strongest absorption at 1232 cm^{-1}, rather close to the P–N stretching vibration of the parent chloride at 1256 and 1222 cm^{-1}, whilst B showed only medium absorption in the region 1210–1240 cm^{-1}. The other noticeable trend is the much larger peak at 1410 cm^{-1} in B than in A, its complete absence in $(PNCl_2)_3$, and its appearance at 1360 cm^{-1} in sodium trimetaphosphimate, and these may be the asymmetric stretching frequency of:

$$\text{>P}\!\!<^{\text{O}^-}_{\text{O}}$$
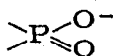
whilst the 950 cm^{-1} peak in A, 960 cm^{-1} in B, and 935 cm^{-1} in sodium trimetaphosphimate may be the symmetrical stretching frequency of the above grouping.

A paper chromatographic study of the hydrolysis

Triphosphonitrilic chloride (2 g) was dissolved in diethyl ether (20 ml) and the solution

TABLE I

INFRA-RED ABSORPTION FREQUENCIES OF THE CHLOROHYDRINES

Triphosphonitrilic chloride	Preparation A	Sodium trimetaphosphimate	Preparation B
*3450 m	*3440 s	*3420 s	*3420 s
2960 w	2950 wsh	3180 msh	3220 ssh
2370 vw	—	—	2350 w
2110 vw	—	—	—
*2030 wn	—	—	—
1973 vw	—	—	—
1876 vw	—	—	—
1745 vwsh	—	1690 msh	—
*1631 vb	*1640 mb	*1642 mb	*1640 mb
1372 wsh	1410 w	1360 m	1410 m
1317 msh	1287 ssh	1330 m	—
—	—	1286 m	—
1256 ssh	1232 s	—	1242 m
1222 vsb	—	1200 s	1210 m
1000 wsh	950 mb	1121 m	1018 mb
—	—	965 s	960 mb
—	—	935 s	—
875 mn	870 vw	860 w	—
—	—	820 m	—
786 vw	—	805 m	—
—	—	738 m	732 m
675 wsh	640 w	—	—
625 s	595 m	—	—
550 s	532 m	—	535 w
—	—	—	505 w
410 s	470 m	—	445 vw
—	382 w	—	385 w

agitated with water (7 ml). Samples were removed from both the aqueous and ethereal layers at intervals and chromatographed using BIBERACHER's basic solvent[11]. Samples from the aqueous layer gave well defined spots, but a great deal of streaking and tailing occurred with the samples from the ethereal layers for the reasons discussed above. However, the course of the reaction is given in Table II.

Interpretation of the chromatograms

The chlorohydrines formed as intermediates are extremely soluble in ether and were found with the phosphonitrilic chloride. The aqueous layer contained trimetaphosphimic acid and hydrochloric acid formed during the hydrolysis. In the presence of such acid, the trimetaphosphimic acid was further hydrolysed, accounting for the presence of ortho-, trimeta-, diimido-trimetaphosphate, and chain phosphates. (This decomposition is discussed in Part II.)

The identification of species present in the ethereal layer was made difficult by the tailing of the triphosphonitrilic chloride.

DISCUSSION

The exact location of the substituted hydroxyl groups in the chlorohydrines has not been discovered, but the formation of large amounts of the di-substituted and tetra-substituted compounds generally, with very little, if any, of the mono-, tri- and penta-sub-

TABLE II

PHOSPHATE SPECIES DETECTED DURING THE HETEROGENEOUS HYDROLYSIS OF TRIPHOSPHONITRILIC CHLORIDE

Time(h)	Aqueous layer		Ether layer	
	Species	R_x value	Species	R_x value
0	None	—	$(PNCl_2)_3$	1.5–3.5 (streak)
3	Ortho (trace)	1.00	TMPm (trace)	1.20
	TMPm	1.20	$(PNCl_2)_3$	1.5–3.5 (streak)
9	Chain phosphates	0.45	TMPm (trace)	1.20
	Ortho	1.00	$P_3N_3Cl_4(OH)_2$ (trace)	2.50
	TMPm	1.20	$(PNCl_2)_3$	3.10 (tailing)
24	Chain phosphates	0.45	$P_3N_3Cl_2(OH)_4$ (trace)	0.55
	Ortho	1.00	TMPm (trace)	1.20
	TMPm	1.20	$P_3N_3Cl_4(OH)_2$	2.50
	DITMP (trace)	1.45	$(PNCl_2)_3$	3.10
48	Same species as 24 h			
72	Same species as 48 h			
100	Chain phosphates	0.45	$P_3N_3Cl_2(OH)_4$	0.55
	Ortho	1.00	TMPm (trace)	1.20
	TMPm	1.20	$P_3N_3Cl_4(OH)_2$ (trace)	2.50
	DITMP	1.45	$(PNCl_2)_3$ (trace)	3.10
	TMP (trace)	2.40		

Abbreviations: TMPm = trimetaphosphimate; DITMP = diimidotrimetaphosphate; TMP = trimetaphosphate.

stituted compounds indicates that substitution probably occurs in pairs. Whether substitution of a pair of chlorine atoms attached to the same phosphorus atom, or two chlorine atoms attached to different phosphorus atoms occurs, has been argued for substitution of numerous types of groups[16-18], and it is now obvious that the order of substitution depends upon the nature of the group being substituted. BECKE-GOEHRING et al.[17] suggested that strongly nucleophilic reagents attacked the trimer in the 2- or 4-position, with further substitution in the 6-position, but with weak electron donors, substitution occurred in another sequence. Proton magnetic resonance[19] has recently shown that with dimethylamine, substitution occurs in the order 2-mono; 2,4-di; 2,4,6-tri; 2,2,4,6-tetra; 2,2,4,4,6-penta and 2,2,4,4,6,6-hexa.

However, HEFFERNAN AND WHITE[20] have shown from nuclear magnetic resonance data, that when chlorine atoms are replaced by fluorine atoms, substitution of first two atoms occurs on the same phosphorus atom. They also showed that in the more rare trisubstituted compound, two of the substituted fluorine atoms reside on one phosphorus atom and the third fluorine atom on one of the neighbouring phosphorus atoms, the third phosphorus still retaining two chlorine atoms. Whilst it is also possible that steric effects must be taken into account; and that pairwise substitution of dimethylamine on the same phosphorus atom does not occur because of the steric strain which would be caused by substituting two large groups on one atom.

Some relationship usually exists between structure and R_x value when a series of related compounds are considered, and in the same way some relationship usually

exists between structure and retention volume in ion-exchange chromatography. In both these separational techniques, trimetaphosphimate appeared between the spots or peaks assigned to $P_3N_3Cl_4(OH)_2$ and $P_3N_3Cl_2(OH)_4$. At first sight it appears that no correlation exists, but if we consider the number of replaceable hydrogen atoms, we see that it rises from two for $P_3N_3Cl_4(OH)_2$, to three for $P_3(NH)_3O_3(OH)_3$ to four for $P_3N_3Cl_2(OH)_4$. (Trimetaphosphimic acid is tribasic, only 3 of its 6 hydrogen atoms being replaceable by sodium atoms.) Triphosphonitrilic chloride, whilst not chromatographing satisfactorily shows a centre of gravity of the spot at an R_x value of 3.1, which fits satisfactorily with above correlation.

Water is a nucleophilic reagent because of its unshared electron pair, but only a weak one, and because of this, substitution of the hydroxyl groups in pairs takes place. However, nuclear magnetic resonance measurements are needed to prove whether this is possible, and the following structures are proposed:
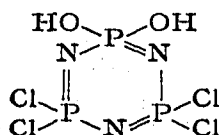
Tetrachlorohydrine
2 replaceable H's
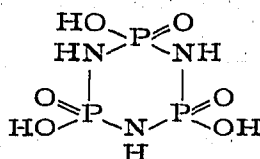
Trimetaphosphimate
3 replaceable H's
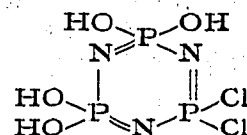
Dichlorohydrine
4 replaceable H's

This work has shown that paper chromatography and ion-exchange chromatography may be used to study the chlorohydrines, but other techniques are needed to confirm these results. Raman spectroscopy should be a useful technique in following the formation of intermediates during the hydrolysis of the polymeric chlorides. A study of the hydrolysis of the phosphonitrilic fluorides and bromides to the corresponding metaphosphimic acids through the analogous intermediate fluoro- or bromo-hydrines may prove more successful. Both of these suggestions are under active study in these laboratories, and the results will be published later.

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SUMMARY

The paper describes a paper- and anion-exchange chromatographic investigation of the heterogeneous hydrolysis of triphosphonitrilic chloride under neutral conditions, when trimetaphosphimic acid is the final product. Evidence concerning the order in which the chlorine atoms are replaced by hydroxyl groups is also given.

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