

CHROMATOGRAPHIC STUDIES ON THE HYDROLYSIS
OF PHOSPHORUS COMPOUNDSPART VII. THE HYDROLYSIS OF PHOSPHORUS TRIHALIDES
AND PSEUDOHALIDES

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It has been reported¹ that the phosphorus trihalides and pseudohalides may be hydrolysed in alkaline solution, giving rise to a variety of lower oxy-acids of phosphorus. A number of these acids have been reported to contain phosphorus-phosphorus bonds, *e.g.* hypophosphate, and such a hydrolytic reaction is one of the few methods of synthesizing such bonds, starting from monomeric materials. If the mode of formation can be elucidated, it may prove possible to synthesize compounds containing such bonds. Using the combined techniques of paper and anion-exchange chromatography, this paper describes a study of the hydrolysis, in sodium hydroxide solution, of phosphorus trichloride, tribromide and triiodide, and the pseudohalides, phosphorus triisocyanate, triisothiocyanate, and tricyanide.

EXPERIMENTAL

Preparation of the phosphorus trihalides and pseudohalides

1. Phosphorus trichloride, B.D.H. reagent grade was twice redistilled under a stream of dry nitrogen, and the fraction boiling between 75° and 76° collected.
2. Phosphorus tribromide, B.D.H. reagent grade was twice redistilled under reduced pressure, and the fraction boiling at 20–21° at 0.1 mm pressure was collected.
3. Phosphorus triiodide was prepared by the direct union of the elements in purified carbon disulphide², and was twice recrystallised from this solvent before use.

$$\text{PI}_3: \text{P calc.}, 7.53\%; \text{P found}, 7.51\%.$$

4. Phosphorus triisocyanate $\text{P}(\text{NCO})_3$, was prepared by distillation of a sample of polymerized compound. When freshly prepared, phosphorus triisocyanate is a liquid ($d = 1.439$), which upon standing polymerizes to a yellow-white solid which is insoluble in common organic solvents³.

The phosphorus triisocyanate which was in the polymerized form was twice distilled under dry nitrogen, and the fraction boiling at 169° collected. The resulting liquid was hydrolysed immediately.

5. Phosphorus triisothiocyanate $\text{P}(\text{NCS})_3$ was synthesized by the addition of freshly distilled phosphorus trichloride to a solution of ammonium thiocyanate in

liquid sulphur dioxide. Ammonium chloride precipitates leaving phosphorus triisothiocyanate in solution⁴. After filtering off the ammonium chloride, the sulphur dioxide was allowed to partially evaporate, whereupon the phosphorus triisothiocyanate separated out as a colourless oil. The oil was separated from the remaining sulphur dioxide, dissolved in a fresh sample of solvent, and the separation process repeated. All attempts to distil the oil resulted in the formation of the deep brown coloured polymer reported by DIXON⁵, this polymer also formed on standing. The substance was freshly prepared and treated three times with liquid sulphur dioxide before use.

$P(NCS)_3$: P calc., 15.10 %; P found, 14.98 %.

6. Phosphorus tricyanide $P(CN)_3$ was prepared by the reaction between phosphorus trichloride and silver cyanide in benzene⁶. The phosphorus tricyanide was resublimed (98° , 0.1 mm) before use.

$P(CN)_3$: P calc., 28.42 %; P found, 28.49 %.

During all the work described above, precautions were taken to exclude moisture by handling the materials in a dry-nitrogen filled, dry box.

Hydrolysis of the phosphorus trihalides and pseudohalides

All hydrolysis experiments were carried out under identical conditions using a stock solution of 5.063N sodium hydroxide solution and keeping the ratio: moles of $P(X)_3$ /moles of NaOH constant at ratio of 1:7.

The calculated volume of sodium hydroxide solution, equivalent (subject to the above criterion) to 5.0 ml of the halides or pseudohalide to be hydrolysed was contained in a three-necked reaction vessel under a stream of dry nitrogen. The reaction vessel was surrounded by ice-water and its contents stirred with a magnetic stirrer. The sample to be hydrolysed was introduced from a 5 ml syringe pipette fitted with a ground-glass joint, so effectively stoppering the reaction vessel. After passing through the reaction vessel, the nitrogen stream was passed through a series of four traps, each containing 20 ml of 5.0 % w/v mercuric chloride solution. This solution was to precipitate any phosphine that may be formed during the hydrolysis, as the yellow complex $P(HgCl)_3$ which was then estimated by the method reported by BEYER⁷. After completion of the hydrolysis reaction, the resultant solution was analysed by paper and anion-exchange chromatographic techniques.

Analysis

(1) *Anion-exchange chromatography.* 5 ml of the solution obtained after the hydrolysis were diluted to 50 ml in a graduated flask with distilled water, giving Solution A. 5 ml of the solution were then pipetted on to the anion-exchange column, and analysed using the procedure reported in a previous communication⁸.

In some cases, the concentration of orthophosphite present in 5.0 ml of Solution A is too large to allow a satisfactory analysis; due to column overloading with respect to this anion. In these cases, it was found necessary to dilute a 5 ml aliquot of Solution A to 25 ml, and to pipette 5 ml of this solution on to the anion-exchange column.

Thus by carrying out two analyses:

- (i) for anions with retention volumes greater than orthophosphite; and
 (ii) for anions with a lower retention volume than orthophosphite, and including orthophosphite,

a complete and accurate estimation of the products can be obtained.

Anions with a retention volume greater than pyrophosphate, that is after passage of 1.1 l of the potassium chloride eluant, were eluted by passage of 4 N hydrochloric acid down the column. All anions containing two atoms of phosphorus were assumed to have retention volumes greater than pyrophosphate.

All chromatographic analyses were performed as soon as possible after hydrolysis thus minimising any errors due to breakdown of unstable anions formed during the hydrolysis.

(2) *Paper chromatography.* One spot, approximately 3 mm diameter, of the solution obtained after hydrolysis was run on to the starting line of a paper chromatogram measuring 3 in. \times 15 in. and using Whatman No. 541 chromatographic paper. The spot was allowed to dry, and equilibrated in a glass tank containing the solvent to be used. The chromatograms were developed by a downward elution technique using both acid and basic solvents as described by EBEL^{9,10}. After eluting for 13 h, the chromatograms were dried and sprayed with KARL-KROUPA's reagent¹¹. The identity of hydrolysis products was then determined by comparison with a standard separation of a known mixture of phosphorus oxy-acids, developed on the same chromatogram.

RESULTS AND DISCUSSION

The relative percentages of phosphorus oxy-anions formed during the hydrolysis of the phosphorus trihalides and pseudohalides estimated by anion-exchange chromatography are given in Table I (see Figs. 1 and 2), whilst Table II gives the species detected by paper chromatography.

TABLE I

RELATIVE PERCENTAGES OF PHOSPHORUS OXY-ANIONS FORMED DURING THE HYDROLYSIS OF PHOSPHORUS TRIHALIDES AND PSEUDOHALIDES

Species*	PCl_3	PBr_3	PI_3	$P(NCO)_3$	$P(NCS)_3$	$P(CN)_3$
P^1	—	1.3	0.9	10.6	—	3.7
P^3	84.3	41.9	42.3	84.7	92.5	79.0
P^5	6.1	8.9	18.6	—	—	—
P^2-P^4	4.9	17.1	3.6	3.8	3.3	3.8
P^4-P^4	2.4	5.9	4.6	—	0.1	—
P^3-O-P^5	—	—	3.6	—	—	**
P^5-O-P^5	—	—	1.6	—	—	—
Anions containing more than 2 atoms of phosphorus	2.9	23.8	24.7	1.0	3.2	4.20

* The nomenclature used to describe the oxidation state of oxy-acids of phosphorus is that proposed by BLASER AND WORMS¹².

** Some isohypophosphate⁶ was detected in this case (retention volume 890 ml) but was not separated from an unidentified species⁹ (retention volume 810 ml) see Fig. 2F. This species was not formed in the hydrolysis of any other halide or pseudohalide and was found to be very stable to alkali at room temperature.

TABLE II
PHOSPHORUS OXY-ACIDS DETECTED BY PAPER CHROMATOGRAPHY

PCl_3	PBr_3	PI_3	$P(NCO)_3$	$P(NCS)_3$	$P(CN)_3$
—	—	—	P^1	P^1	P^1
P^3	P^3	P^3	P^3	P^3	P^3
P^5	P^5	P^5	—	P^5	P^5
P^2-P^4	P^2-P^4	P^2-P^4	P^2-P^4	P^2-P^4	P^2-P^4
P^4-P^4	P^4-P^4	P^4-P^4	—	P^4-P^4	—
$P^4-P^3-P^4$	$P^4-P^3-P^4$	$P^4-P^3-P^4$	$P^4-P^3-P^4$	$P^4-P^3-P^4$	$P^4-P^3-P^4$
		P^3-O-P^5		*	P^3-O-P^5
		P^5-O-P^5			P^5-O-P^5
**	**	**	**	**	**

* In the hydrolysis of $P(NCS)_3$, in addition to the species shown above, two unidentified species were observed on acid solvent chromatograms, having R_x values of 0.9, and 0.15 respectively. R_x = distance travelled by unknown oxy-anion/distance travelled by orthophosphate.

** In all cases, some species were formed which remained at or near the starting line and were unidentified. Presumably these are high-molecular weight phosphorus oxy-anions e.g. $-(P^3)_6^-$ (see ref. 12).

In no case was sufficient phosphine formed to cause precipitation in the mercuric chloride traps.

In addition to the hydrolyses of the trihalides and pseudohalides in caustic soda solution, hydrolyses were carried out in 2 *N* hydrochloric acid, and the resulting solutions examined qualitatively by using paper chromatography. The three trihalides formed orthophosphite and a trace of orthophosphate while the pseudohalides formed orthophosphite only.

It appears from the results that the reaction products become more complicated as the atomic number of the halide increases. This is accompanied by an increased rate

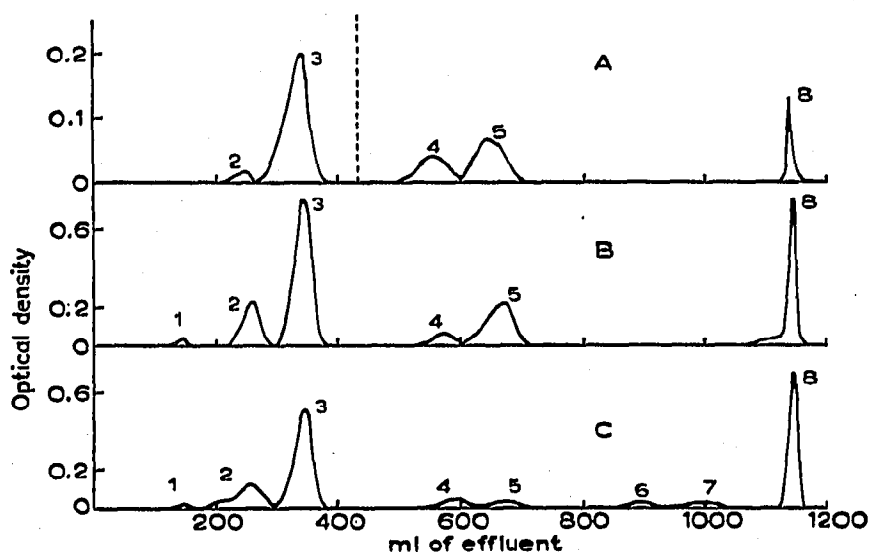


Fig. 1. Typical ion-exchange elution patterns of the phosphorus trihalides. A = PCl_3 ; B = PBr_3 ; C = PI_3 . Nomenclature: (1) hypophosphite; (2) orthophosphate; (3) orthophosphite; (4) hypophosphate; (5) diphosphite; (6) isohypophosphate; (7) pyrophosphate; (8) anions containing two or more phosphorus atoms eluted with 4*N* HCl; (9) unidentified species. The dotted line signifies that the pattern was compounded from two separate runs as described in the experimental section.

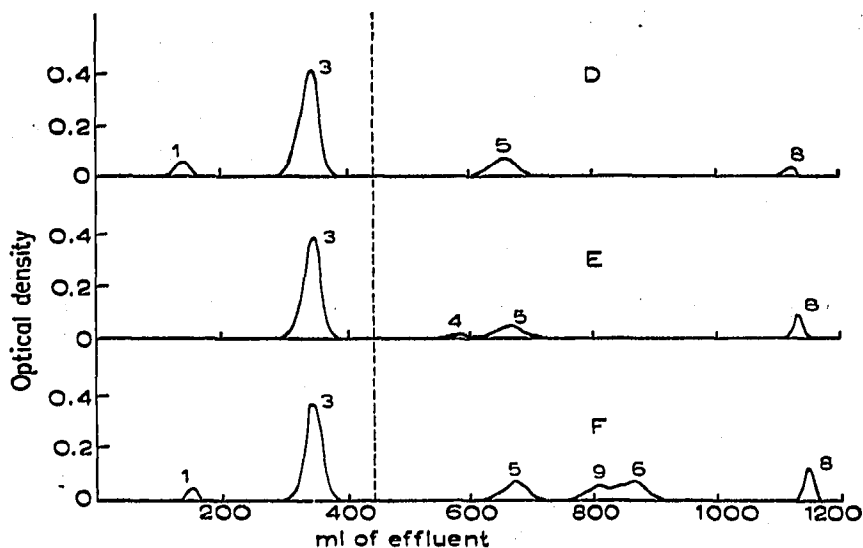


Fig. 2. Typical ion-exchange elution patterns of the phosphorus pseudohalides. D = $P(NCO)_3$; E = $P(NCS)_3$; F = $P(CN)_3$. For nomenclature see Fig. 1.

of hydrolysis and a decrease in the Pauling electronegativity value¹³ of the halide (Table III). The values for the pseudohalides were calculated from infra-red data using the method proposed by BELL¹⁴.

The analytical figures for the hydrolysis of phosphorus triiodide and phosphorus tricyanide cannot be strictly compared with those obtained for the other trihalides and pseudohalides, as they are solids and were hydrolysed in that form. This procedure increases the rate of hydrolysis, which becomes almost explosive for phosphorus tricyanide. Solutions of phosphorus triiodide in carbon disulphide, and phosphorus tricyanide in diethyl ether, were hydrolysed by dropping the solutions into caustic soda solution and violently agitating the two immiscible liquids. Phosphorus tricyanide formed only orthophosphite, while phosphorus triiodide produced orthophosphite and a trace of orthophosphate.

The formation of oxy-anions having an oxidation state different from that of the original halide is probably due to disproportionation, but the interesting facet of the reaction is the formation of phosphorus-bonds. The reason for this is by no means clear as yet and further work is being carried out, with a detailed study of the hydrolysis of phosphorus tribromide under a wide variety of differing experimental conditions in order to clarify this situation.

TABLE III

PAULING ELECTRONEGATIVITY VALUES OF THE SUBSTITUENT HALIDES AND PSEUDOHALIDES

Halide or pseudohalide	Electronegativity
Cl	3.0
Br	2.8
I	2.5
CNO	3.7
CN	3.4
CNS	3.2

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SUMMARY

Paper and anion-exchange chromatographic techniques have been employed to study the formation of a variety of phosphorus oxy-anions in the hydrolysis of phosphorus trihalides and pseudohalides in caustic soda solution.

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