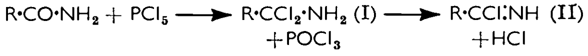
404. *An Investigation of the Reaction of Phosphorus Pentachloride with Benzamide with Oxygen-18 as Tracer.*

By A. Lapidot and David Samuel.

The reaction of phosphorus pentachloride and benzamide has been investigated with oxygen-18 as tracer. An unstable intermediate *N*-benzoylphosphorimidic trichloride $Ph{\cdot}CO{\cdot}N{:}PCl_3$ is first formed, which can be hydrolysed in two steps to *N*-benzoylphosphoramidic acid in which the original oxygen of the carbonyl group is retained. When this intermediate is decomposed thermally to phosphorus oxychloride and benzonitrile the oxygen atom migrates from carbon to phosphorus.

A cyclic mechanism for this rearrangement is suggested.

Wallach[1] investigated the reaction between phosphorus pentachloride and carboxyamides originally discovered by Gerhardt.[2] Wallach suggested that a dichloroamine (I) and phosphorus oxychloride were first formed, the former then losing hydrogen chloride to form an imidoyl chloride (II) which then recombined with the phosphorus oxychloride to give compound (III); however, neither intermediate (I or II) could be isolated.



$$R{\cdot}CO{\cdot}NH_2 + PCl_5 \longrightarrow \underset{+POCl_3}{R{\cdot}CCl_2{\cdot}NH_2\ (I)} \longrightarrow \underset{+HCl}{R{\cdot}CCl{:}NH\ (II)}$$

$$(II) + POCl_3 \longrightarrow R{\cdot}CCl{:}N{\cdot}POCl_2\ (III) + HCl.$$

Titherley and Worral[3] studied the reaction of benzamide and phosphorus pentachloride and identified a product of the reaction as *N*-benzoylphosphoramidic dichloride which, since it contained two oxygen atoms, was presumably formed by the action of moisture on an unstable intermediate.

Kirsanov[4] re-examined this reaction more recently and showed by analysis and molecular weight determinations that one intermediate was a trichloro-compound. He found that this intermediate could be hydrolysed in two steps to *N*-benzoylphosphoramidic

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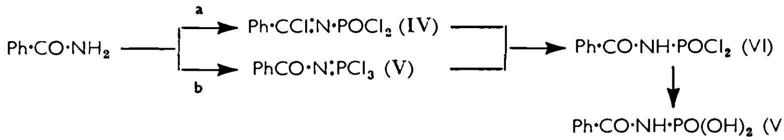
[1] Wallach, *Annalen*, 1877, **184**, 1.

[2] Gerhardt, *Annalen*, 1858, **108**, 214.

[3] Titherley and Worral, *J.*, 1909, **95**, 1143.

[4] Kirsanov, *Isvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, **1954**, 646; Kirsanov and Makirta, *J. Gen. Chem.* (*U.S.S.R.*), 1956, **26**, 1029, 1033; *Zhur. obshchei Khim.*, 1957, **27**, 450.

acid (VII) and that when heated it decomposed quantitatively to phosphorus oxychloride and benzonitrile. On the basis of these reactions Kirsanov proposed alternative mechanisms for the reaction of phosphorus pentachloride with benzamide:



He was unable to distinguish between the two mechanisms or suggest a pathway for the decomposition by pyrolysis.

We have now investigated both these reactions by using oxygen-18 as tracer.

Mechanism of Reaction of Benzamide and Phosphorus Pentachloride.—Benzamide and phosphorus pentachloride were caused to react in dry benzene, and the intermediate trichloro-compound (IV or V) partially hydrolysed by the addition of an equimolar quantity of water enriched in oxygen-18. The resulting *N*-benzoylphosphoramidic dichloride (VI) was then hydrolysed with an excess of ordinary water, first to *N*-benzoylphoramidic acid (VII) and then to benzamide and phosphoric acid (see Halmann, Lapidot, and Samuel [5]). Both products were purified and analysed for isotopic oxygen content. The benzamide contained no excess of oxygen-18; the phosphoric acid contained approximately one-quarter of the oxygen-18 content of the water used in the first hydrolytic step (see Table).

^{18}O Results.

Compound analysed	Atom % excess of ^{18}O	Compound analysed	Atom % excess of ^{18}O
A. Water used in partial hydrolysis	10·4	B. Benzamide used for synthesis	8·5
Benzamide from total hydrolysis	0·0	Phosphorus oxychloride from pyrolysis	8·5
Phosphate from total hydrolysis	2·16		

Under the conditions used for these reactions and for the separation of the products there is no isotopic exchange of oxygen between water and benzamide [6] or phosphoric acid.[7] From these results it appears that the oxygen in the benzamide finally isolated is the same oxygen initially in the carbonyl group of benzamide and in the carbonyl group of *N*-benzoylphosphoramidic trichloride (V). This result demonstrates that mechanism (b) is the correct one and, at the same time, disproves the mechanism proposed by Wallach.[1]

Evidence from the infrared and nuclear magnetic resonance spectra for structures of this type has been presented [8] for the products of the reaction of phosphorus pentachloride and amidophosphoric acids.

Mechanism of Thermal Decomposition of N-*Benzoylphosphorimidic Trichloride.*—*N*-Benzoylphosphorimidic trichloride (V) labelled with ^{18}O in the carbonyl group was prepared from [^{18}O]benzamide and phosphorus pentachloride and was decomposed by heat into phosphorus oxychloride and benzonitrile. The oxychloride was found, on analysis, to contain oxygen of the same isotopic composition as the [^{18}O]benzamide used as starting material (see Table). The oxygen of the oxychloride atom cannot, therefore, come from the air or from water accidentally present as moisture.

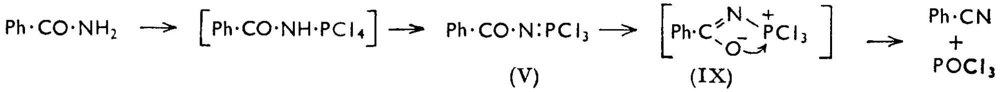
It appears, therefore, that in pyrolysis the original carbonyl-oxygen atom becomes attached to the phosphorus of the oxychloride, whereas in hydrolysis it remains as part of the carbonyl group of the final product. In order to reconcile these two observations a rearrangement of some kind must occur in one of the two reactions.

The first step in the reaction of phosphorus pentachloride with benzamide is the attack of phosphorus probably as the incipient $[PCl_4]^+$ ion on either the oxygen or the nitrogen

[5] Halmann, Lapidot, and Samuel, *J.*, 1960, **903**, 4672.
[6] Bender and Ginger, *J. Amer. Chem. Soc.*, 1955, **77**, 348.
[7] Bunton, Llewellyn, Vernon, and Welch, *J.*, 1961, 1636.
[8] Becke-Goehring, Debo, Fluck, and Goetze, *Chem. Ber.*, 1961, **94**, 1383; Fluck, *ibid.*, p. 1388.

of benzamide. This reaction is formally similar to protonation and to the reactions of the halides of other metalloids. There has been considerable discussion, which has recently been reviewed,[9] as to where protonation (and electrophilic attack in general) occurs in amides. In *NN*-disubstituted amides attack on oxygen is the only one possible, as has been shown in the reaction of phosphorochloridates with dimethylformamide.[10] For benzamide itself, it appears that attack on the unhindered nitrogen occurs as suggested[11] for reaction of phosphorus pentachloride and phosphoramides. The trichloro-intermediate (V) is formed by successive loss of two molecules of hydrogen chloride and can then be hydrolysed by path (b).

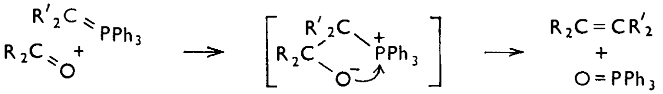
It appears that in presence of hydrogen chloride,[4] or on heating, re-arrangement takes place involving nucleophilic attack of phosphorus on oxygen, probably by a cyclic mechanism.



(V) (IX)

Polar forms of phosphorimidic trichlorides similar to (IX) have been described by Zhmurova and Kirsanov[12] in connexion with the structure of arylphosphorimidic trichlorides $Ar{\cdot}N{:}PCl_3$.

This mechanism seems also analogous to the reaction[13] of triphenylphosphinemethylenes (" ylides ") with carbonyl compounds (the Wittig reaction):



The partial deoxygenation[14] of *o*-quinones and α-diketones by phosphorous triesters may also proceed by a similar rearrangement.

EXPERIMENTAL

Water enriched in oxygen-18 from the separation plant of the Weizmann Institute was used. Isotopic oxygen analyses were done by the method of Anbar and Guttmann.[15]

N-*Benzoylphosphorimidic Trichloride*.—This was prepared by Titherley and Worral's method,[3] by heating benzamide (3·5 g.) and phosphorus pentachloride (6 g.) in dry benzene (15 ml.) for 20 min. at 50°.

Partial Hydrolysis of N-*Benzoylphosphorimidic Trichloride with* $H_2{}^{18}O$.—A benzene solution (15 ml.) of the trichloride prepared as described above was shaken with $H_2{}^{18}O$ (10·4 atom % excess of ^{18}O; 1 ml.) at 0°. The reaction is very fast and the white precipitate of *N*-benzoylphosphoramidic dichloride (5 g.) was filtered off, washed with benzene, and dried in a desiccator. It had m. p. 110° (lit.,[3] 110°).

Hydrolysis of N-*Benzoylphosphoramidic Dichloride*.—The dichloride was shaken with ordinary water (50 ml.) at 50°, then warmed for a few minutes at 90°. The benzamide formed was extracted with ether, washed with dilute aqueous sodium hydrogen carbonate, and dried (Na_2SO_4). On removal of the solvent, benzamide (2 g.), m. p. 127—128°, was isolated and analysed for its ^{18}O content (see Table). The phosphoric acid was isolated by precipitation as the barium salt at pH 9, washed, dried, and analysed for its ^{18}O content.

N-[^{18}O]Benzoylphosphorimidic trichloride was prepared as described above by using benzamide (8·7 atom % of ^{18}O) prepared as described by Pinchas *et al.*[16]

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[9] Katritzky and Jones, *Chem. and Ind.*, 1961, 722.

[10] Cramer and Winter, *Chem. Ber.*, 1961, **94**, 989.

[11] Becke-Goehring, Mann, and Euler, *Chem. Ber.*, 1961, **94**, 193.

[12] Zhmurova and Kirsanov, *Zhur. obshchei Khim.*, 1960, **30**, 3044, 4048.

[13] Schöllkopf, *Angew. Chem.*, 1959, **71**, 260.

[14] Ramirez and Desai, *J. Amer. Chem. Soc.*, 1960, **82**, 2652.

[15] Anbar and Guttmann, *Internat. J. Radiation Isotopes*, 1959, **3**, 233; Samuel, *J.*, 1960, 1318.

[16] Pinchas, Samuel, and Weiss-Broday, *J.*, 1961, 1688.

Thermal Decomposition of Labelled N-*Benzoylphosphorimidic Trichloride*.—The trichloride was heated in a microdistillation apparatus until the phosphorus oxychloride, b. p. 107°, distilled over; this was collected and analysed for its chlorine content (Found: Cl, 66·5. Calc.: 69·2%) and for its ^{18}O content [15] (see Table).

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