The Methanolysis of Bromo Diphenylphosphine

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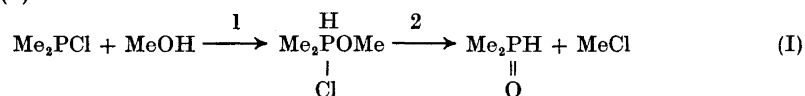*Chemical Institute, University of Bergen, N-5000 Bergen, Norway*

The rate of methanolysis of bromo diphenylphosphine has been examined in toluene by the spectrophotometric stopped flow technique. The rate of the reaction has been found to depend both on the square and on the cube of the methanol concentration. In the presence of various pyridines at constant methanol concentration the rate of reaction depends linearly on the concentration of the pyridines. The mechanism for these reactions has been discussed and reaction schemes are proposed.

Phosphinous halides, R_2P-X, are known to react with alcohols in the presence of a tertiary amine to form the corresponding phosphinites, R_2P-OR'.

Arbuzov and Nikonorov[1] made methyl diphenylphosphinite from chloro diphenylphosphine and methanol in the presence of pyridine. Similarly, Quin and Anderson[2] made the bisphosphinites from chloro diphenylphosphine and diols in the presence of diethylaniline. In the absence of an amine, Seel and Velleman[3] found that chloro dimethylphosphine and methanol first formed dimethyl methoxyphosphonium chloride, which decomposed at temperatures above $-10°C$ to dimethyl phosphinoxide and methyl chloride, while the same substrate and sodium methoxide readily reacted to form methyl dimethylphosphinite. They also found that dimethyl fluorophosphine and methanol gave methyl dimethylphosphinite and dimethyl difluorophosphorane.[4]

With regard to the mechanism of the reaction between phosphinous halides and alcohols, very little is known as no kinetic studies appear to have been performed, probably due to the high rate of the reactions. We found that the methanolysis of bromo diphenylphosphine could be conveniently followed by the "stopped flow" technique.

Dimethyl methoxyphosphonium chloride can be isolated as an intermediate in reaction (I).[3]

$$\text{Me}_2\text{PCl} + \text{MeOH} \xrightarrow{\ 1\ } \underset{\underset{\text{Cl}}{|}}{\text{Me}_2\text{POMe}} \xrightarrow{\ 2\ } \underset{\underset{\text{O}}{\parallel}}{\text{Me}_2\text{PH}} + \text{MeCl} \qquad\qquad (I)$$

and there should probably also be an intermediate of the same kind when bromo diphenylphosphine is the substrate.

The second step in reaction (I) should be similar to the last step in the Arbuzov reaction,[5] and is thought to be rather slow compared with the rate of the measured reaction.

The methanolysis of bromo diphenylphosphine (BDP) was studied in toluene with a concentration of methanol ranging from 0.1 to 0.9 M.

The kinetics were found to be represented by:

$$- \mathrm{d[BDP]}/\mathrm{d}t = k_3\mathrm{[BDP][MeOH]}^2 + k_4\mathrm{[BDP][MeOH]}^3 \qquad (1)$$

As pseudo first order conditions were used, the reaction could be described by:

$$- \mathrm{d[BDP]}/\mathrm{d}t = k'\mathrm{[BDP]} \qquad (2)$$

This equation was found to be followed for more than 85 % of the reaction and no autocatalysis due to liberated acid could be observed. The pseudo first order rate constants obtained are listed in Table 1. A plot of $k'\mathrm{[MeOH]}^{-2}$

Table 1. Pseudo first order rate constants for the reaction between bromo diphenylphosphine and methanol in toluene.[a]

Concn. MeOH M	$k' \times 10^3$ sec^{-1}	$k'\mathrm{[MeOH]}^{-2}$ M^{-2} sec^{-1}
0.116	7.7	0.57
0.255	51.0	0.78
0.379	154	1.07
0.590	490	1.40
0.898	1400	1.73
1.00	2000 [b]	

[a] Substrate concentration ca. 4×10^{-4} M.   [b] Calculated.

as a function of the concentration of methanol, [MeOH], was found to be linear with an intercept of k_3 (0.38 M^{-2} sec^{-1}) and a slope of k_4 (1.63 M^{-3} sec^{-1}). (Fig. 1).
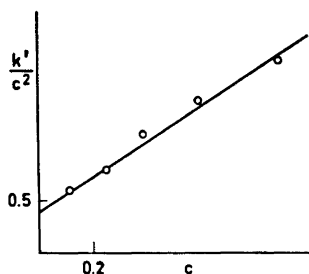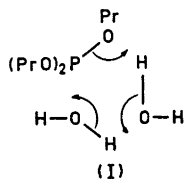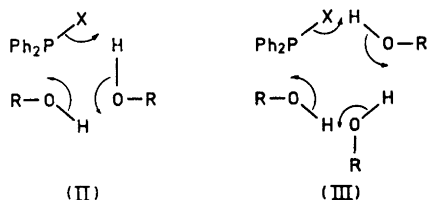

Fig. 1. Pseudo first order rate constants divided by the square of the methanol concentration as a function of the methanol concentration for the methanolysis of bromo diphenylphosphine.
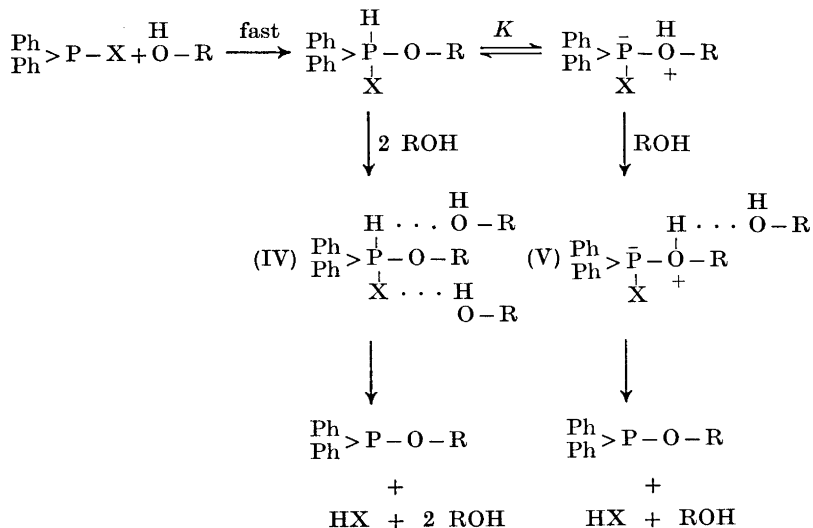
Aksnes and Aksnes [6] found a third order reaction which was second order in water for the hydrolysis of tripropyl phosphite in acetonitrile and suggested a sixmembered cyclic transition state (I).

$$
\begin{array}{c}
\text{Pr} \\
\text{O} \\
(\text{PrO})_2\text{P} \overset{\frown}{} \text{H} \\
\text{H} - \text{O} \text{O} - \text{H} \\
\text{H} \\
(\text{I})
\end{array}
$$

As alcohols are known to be extensively associated in nonpolar solvents,[7] intermediates like II and III may be responsible for both the third and the fourth order terms in rate eqn. (1).

$$
\begin{array}{cc}
\begin{array}{c}
\text{X} \\
\text{Ph}_2\text{P} \overset{\frown}{} \text{H} \\
\text{R} - \text{O} \text{O} - \text{R} \\
\text{H} \\
(\text{II})
\end{array}
&
\begin{array}{c}
\text{X} \; \text{H} \\
\text{Ph}_2\text{P} \text{O} - \text{R} \\
\text{R} - \text{O} \text{H} \\
\text{H} \; \text{O} \\
\text{R} \\
(\text{III})
\end{array}
\end{array}
$$

If we assume that the phosphorus-halogen bond is not completely broken in the transition state leading to the ionic intermediate, another reaction sequence may be set up:

$$
\overset{\text{Ph}}{\underset{\text{Ph}}{}}\!\!> \text{P} - \text{X} + \overset{\text{H}}{\text{O}} - \text{R} \xrightarrow{\text{fast}} \overset{\text{Ph}}{\underset{\text{Ph}}{}}\!\!> \underset{\overset{|}{\text{X}}}{\overset{\overset{\text{H}}{|}}{\text{P}}} - \text{O} - \text{R} \overset{K}{\rightleftharpoons} \overset{\text{Ph}}{\underset{\text{Ph}}{}}\!\!> \underset{\overset{|}{\text{X}} \; +}{\overset{\overset{\text{H}}{|}}{\bar{\text{P}}}} - \text{O} - \text{R}
$$

$$\downarrow 2\;\text{ROH} \qquad\qquad \downarrow \text{ROH}$$

$$
\begin{array}{cc}
(\text{IV}) \;
\overset{\text{Ph}}{\underset{\text{Ph}}{}}\!\!> \underset{\overset{|}{\text{X}} \cdots \text{H}}{\overset{\text{H} \cdots \overset{\text{H}}{\text{O}} - \text{R}}{\text{P}}} - \text{O} - \text{R}
&
(\text{V}) \;
\overset{\text{Ph}}{\underset{\text{Ph}}{}}\!\!> \underset{\overset{|}{\text{X}} \; +}{\overset{\text{H} \cdots \overset{\text{H}}{\text{O}} - \text{R}}{\bar{\text{P}}}} - \text{O} - \text{R} \\
\\
\downarrow & \downarrow \\
\\
\overset{\text{Ph}}{\underset{\text{Ph}}{}}\!\!> \text{P} - \text{O} - \text{R} & \overset{\text{Ph}}{\underset{\text{Ph}}{}}\!\!> \text{P} - \text{O} - \text{R} \\
+ & + \\
\text{HX} + 2\;\text{ROH} & \text{HX} + \text{ROH}
\end{array}
$$

The intermediate V would carry a formal negative charge on the phosphorus atom, while intermediate IV will not. Because of this the intermediate V will not have any need for assistance to eliminate the halogen while intermediate IV will have. As a result, these two species may give rise to the two different terms in the rate equation.

THE PYRIDINE CATALYZED METHANOLYSIS

The base catalyzed methanolysis of bromo diphenylphosphine was studied in toluene at pseudo first order conditions. The concentration of methanol was kept constant at 1 M while the concentrations of the three pyridines, 4-methyl-pyridine, pyridine, and ethyl pyridine-3-carboxylate were varied from 3.75×10^{-2} M to 25.5×10^{-2} M. All the reactions were found to follow the following rate equation:

$$- d[BDP]/dt = k_2(BDP) \, (pyridine) = k'(BDP) \tag{3}$$

When k' was plotted as a function of the pyridine concentrations, linear plots without intercepts were obtained (Fig. 2). The results are listed in Table 2.
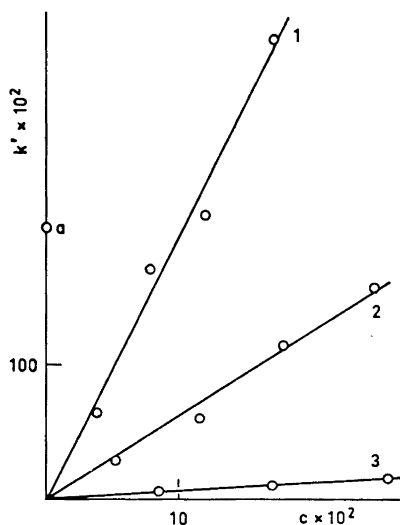

Fig. 2. Pseudo first order rate constants as a function of the pyridine concentration for the pyridine catalyzed methanolysis of bromo diphenylphosphine. (a) The uncatalyzed methanolysis. (1) 4-Methyl-pyridine. (2) Pyridine. (3) Ehtyl pyridine-3-carboxylate.
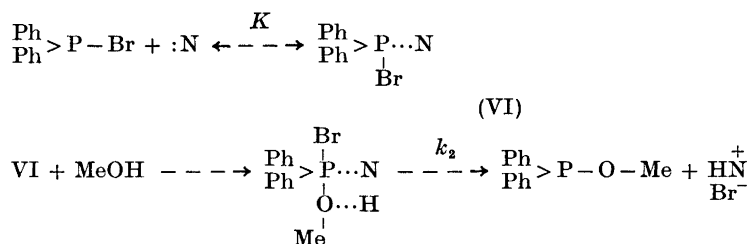
The presence of a tertiary amine in the alcoholysis of halogeno phosphines will give the desired product.[1,2] This might be thought to be caused by the ability of the amine to form an ammonium salt with the halo acid liberated during the reaction. If the catalysis by the amine is general base catalyzed, an increase in rate should be expected.[8] In our reaction there was a lowering in k' from the pure methanolysis for almost every pyridine concentration examined. Aksnes and Aksnes[6] also found that a small amount of pyridine

Table 2. Summary of the pseudo first order and second order rate constants for the pyridine catalyzed reaction between bromo diphenylphosphine and methanol.[a,b]

Nucleophile	Concn. of nucl. $\times 10^2$ M	$k' \times 10^2$ sec^{-1}	k_2 M^{-1}sec^{-1}
4-Methyl-pyridine	3.75	63	
	7.66	169	
	11.84	210	
	16.96	338	19.6
Pyridine	5.32	27.2	
	11.54	59.2	
	17.70	113.6	
	24.20	157.6	6.4
Ethyl-pyridine-3-carboxylate	8.40	5.48	
	16.87	9.76	
	25.52	15.23	0.6

[a] Methanol concentration 1 M. [b] Substrate concentration *ca.* 4×10^{-4} M.

present, retarded the rate of hydrolysis of tripropylphosphite considerably. The following mechanism is proposed for the catalyzed reaction:

$$\begin{array}{c}\text{Ph}\\\text{Ph}\end{array}\!\!> \text{P} - \text{Br} + :\text{N} \xleftarrow{\quad K \quad}\begin{array}{c}\text{Ph}\\\text{Ph}\end{array}\!\!> \overset{\displaystyle |}{\underset{\displaystyle \text{Br}}{\text{P}}} \cdots \text{N}$$

(VI)

$$\text{VI} + \text{MeOH} \;\text{---}\!\!\rightarrow\; \begin{array}{c}\text{Ph}\\\text{Ph}\end{array}\!\!> \overset{\displaystyle \overset{\text{Br}}{|}}{\underset{\displaystyle \underset{\text{Me}}{\overset{|}{\text{O}}\cdots\text{H}}}{\text{P}}} \cdots \text{N} \;\xrightarrow{\;k_2\;}\; \begin{array}{c}\text{Ph}\\\text{Ph}\end{array}\!\!> \text{P} - \text{O} - \text{Me} + \overset{+}{\text{HN}} \;\;\text{Br}^-$$

Association constants for hydrogen bonding between phenol and pyridines [9] are known to increase with increasing pK_a values of the pyridines.

A hydrogen bonded complex between methanol and pyridine may be expected to react more rapidly with both the phosphinous halide and the intermediate than the free methanol. No competition from the general base catalyzed reaction between methanol and the phosphinous halide is observed and we may conclude that K has to be large.

When $\log k_2$ is plotted *versus* pK_a of the pyridines, a Brønsted β-coefficient of 0.5 is obtained. This Brønsted coefficient has been related to the amount of bond formation in the transition state of nucleophilic substitution reactions.[10,11] In our reaction, however, more than one bond being formed or broken in the transition state, little significance can be given this figure.

<div align="center">EXPERIMENTAL</div>

Reagent grade toluene was refluxed over sodium and fractionated. Acetonitrile, reagent grade, was first distilled from phosphorus pentoxide and then refluxed and fractionated from anhydrous potassium carbonate.

The pyridines were commercial products except for ethyl pyridine-3-carboxylate. The commercial pyridines were twice distilled from potassium hydroxide pellets. The ethyl pyridine-3-carboxylate was prepared by esterification of nicotinic acid with ethanol in the presence of sulfuric acid as described by Gilman and Broadbent.[12] Dry methanol was prepared as described by Vogel.[13] Bromo diphenylphosphine was prepared as described by Kuchen and Grünewald.[14] The pale yellow liquid thus obtained solidified when placed in the refrigerator, and did not melt until the temperature had reached $23-24°C$.

The reactions were followed at 310 nm with a Durrum stopped flow apparatus by measuring the disappearance of the halophosphine. In a typical run, the pyridine was weighed in a 25 ml volumetric flask and diluted to the mark with a previously made 2 M solution of methanol in toluene. The solution of phosphine was made by injecting about 0.1 ml of a standard solution of substrate in toluene into 5 ml of toluene. Solutions of nucleophile and substrate were then mixed in the stopped flow apparatus and the reaction measured. Dry nitrogen had been bubbled through the solutions beforehand.

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