Kinetic Evidence for a Dipyridine Complex with Tervalent Phosphorus

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The rates of reaction between pyridines and diphenylhalophosphines have been examined by the spectrophotometric stopped flow technique. In a toluene − acetonitrile mixture the reaction is found to have a reaction order of both one and two with respect to pyridine, while in a toluene − dioxane mixture the rate is found to be dependent on the square of the pyridine concentration. The mechanism for these reactions has been discussed and reaction schemes are proposed.

Recently the reactions of a series of alkyl- and arylphosphines, -arsines, or -stibines with a variety of halo- and haloalkyl- (or haloaryl) phosphines, -arsines, or -stibines have been reported.[1] In most instances the formation of adducts of the general formula $R_nMX_{3-n}.yM'R'_3$, where $y = 1$ or 2, were obtained. Similarly a relatively unstable compound $(CH_3)_3P_{1.96}.PCl_3$ has been isolated as a solid from the reaction between 2 mol trimethylphosphine and one mol of phosphorus trichloride.[2] There is reason to believe that tervalent nitrogen may act as a ligand atom on phosphorus in this kind of 1:2 complexes, and in a recent article Boal and Ozin have given spectroscopical evidence for the formation of the complex $Cl_3P.2N(CH_3)_3$.[3]

The present work was undertaken in order to shed some light on the reaction mechanism for the formation of 1:1 complexes between phosphorus compounds and amines. These complexes have for a long time been known to exist.[4-7] The kinetic experiments were, however, done under pseudo first order conditions with the amines in excess, and the results indicate that not only one but two nitrogen atoms were accepted as ligands on each phosphorus atom.

RESULTS

The rate of reaction of three different pyridines with bromo diphenylphosphine (BDP) has been measured in 10 vol % acetonitrile in toluene (Table 1). The reaction rates have also been measured for the reaction between pyridine and bromo diphenylphosphine in 30 vol. % dioxane in toluene (Table 2), and for the reaction between pyridine and chloro diphenylphosphine (CDP) in 10 vol. % acetonitrile in toluene (Table 3). The disappearance of the phosphines was used in following the kinetics. The cosolvent was added to toluene to avoid precipitation of the complex formed.

The measurements were all made at pseudo first order conditions with pyridine in excess and the kinetic plots were linear up to 90 % of reaction.

By plotting the obtained pseudo first order rate constants divided by the pyridine concentration $(k' \times [Py]^{-1})$ as a function of the pyridine concentration straight lines were obtained. For all reactions measured with acetonitrile as a cosolvent there were interceptions and the rate law is given by eqn. 1.

$$\text{Rate} = k_2[\text{substrate}][\text{Py}] + k_3[\text{substrate}][\text{Py}]^2 \quad (1)$$

For the reaction between pyridine and BDP in 30 % dioxane there was no such interception and the rate may be given by eqn. 2.

$$\text{Rate} = k_3[\text{substrate}][\text{Py}]^2 \quad (2)$$

By plotting the logarithms of the rate constants obtained in the reactions between BDP and different pyridines, *versus* the pK_a's of the pyridines, Brønsted coefficients of 0.53 and

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Table 1. Pseudo first order rate constants for the reaction of bromo diphenylphosphine with pyridines in 10 % acetonitrile-toluene mixture.[a,b]

Nucleophile	Conc. nucl. $\times 10^2$ M	k' s^{-1}	k'/Conc.nucl. M^{-1} s^{-1}	$pK_a{}^c$
4-Methyl-pyridine	2.64	0.445	16.9	6.40
	5.22	1.10	21.0	
	7.04	1.78	25.2	
	9.89	2.99	30.3	
	10.35	3.00	29.0	
	15.72	6.54	41.6	
	15.76	6.79	43.1	
	21.10	11.52	54.6	
Pyridine	5.44	0.32	5.8	5.54
	9.37	0.75	8.0	
	15.57	1.93	12.4	
	21.90	3.12	14.3	
Ethyl-pyridine-3-carboxylate	8.65	0.028	0.32	3.45
	16.60	0.051	0.31	
	25.00	0.099	0.39	
	32.03	0.123	0.39	

[a] The percentage is by volume. [b] The substrate concentration is *ca.* $5-7 \times 10^{-4}$ M. [c] In water at 25 °C.

Table 2. Pseudo first order rate constants for the reaction of bromo diphenylphosphine with pyridine in 30 % dioxane-toluene mixture.[a,b]

Conc. of pyridine $\times 10^2$ M	k' s^{-1}	k'/Conc. pyridine M^{-1} s^{-1}
6.30	2.39	0.379
14.42	6.30	0.437
18.85	15.05	0.799
26.35	28.30	1.074

[a] The percentage is by volume. [b] The substrate concentration is *ca.* $5-7 \times 10^{-4}$ M.

Table 3. Pseudo first order rate constants for the reaction of chloro diphenylphosphine with pyridine in 10 % acetonitrile-toluene mixture.[a,b]

Conc. of pyridine $\times 10^2$ M	k' s^{-1}	k'/Conc. pyridine M^{-1} s^{-1}
2.64	1.05	0.398
7.04	3.75	0.532
10.35	6.08	0.587
15.76	11.18	0.709
21.10	19.00	0.900

[a] The percentage is by volume. [b] The substrate concentration is *ca.* 6×10^{-4} M.

1.0 are obtained for k_2 and k_3 respectively.

The ratio between the rate constants (eqn. 1) for the reactions of pyridine with BDP and CDP is 8.5 in the second order term and 22 in the third order term, and k_3 is 11 times greater in 10 % acetonitrile than in 30 % dioxane for the pyridine – BDP reaction.

The pseudo first order rate constants are given in Tables 1, 2, and 3, and the second and third order rate constants are given in Table 4. The pseudo first order rate constants for the reactions between BDP and pyridines divided by the pyridine concentration are plotted in Fig. 1 as a function of the pyridine concentration.

EXPERIMENTAL

The chloro diphenylphosphine used was a commercial product. It was distilled twice under nitrogen prior to use. The procedure for the synthesis of pyridine-3-carboxylate and bromo diphenylphosphine and for the purification of these reagents together with the applied solvents has previously been described.[8]

In a typical run the pyridine was weighed in a volumetric flask and diluted to the mark with a mixture of toluene and twice the amount of the desired cosolvent. 0.1 ml of a standard solution of the substrate in toluene was injected

Table 4. Summary of the second and third order rate constants. $Ph_2PX + 2Nu \longrightarrow Ph_2PX.2Nu$

Solvent	Phosphine	Nu[a]	$k_2 M^{-1}s^{-1}$	$k_3 M^{-2}s^{-1}$
Acetonitrile, 10 %	BDP	MePy	10.3	205
		Py	3.1	54
		EtPy	0.27	0.37
	CDP	Py	0.33	2.55
Dioxane, 30 %	BDP	Py	0.00	4.14

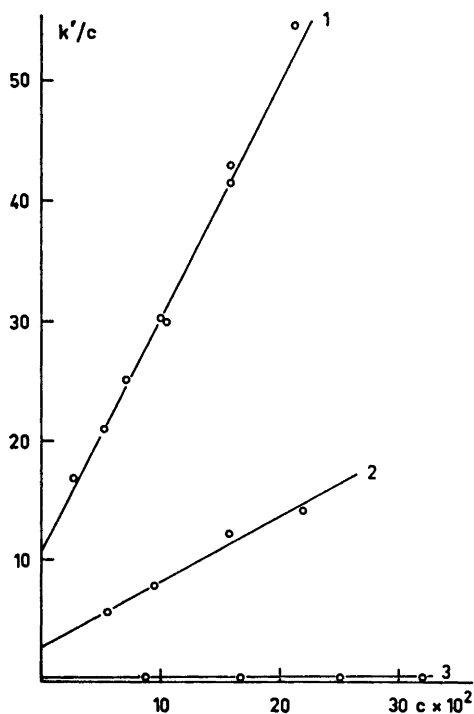[a] MePy is 4-methylpyridine, Py is pyridine, and EtPy is ethyl pyridine-3-carboxylate.

Fig. 1. Pseudo first order rate constants divided by the pyridine concentration as a function of the pyridine concentration for the reaction between bromo diphenylphosphine and pyridines in 10 % acetonitrile – toluene mixture. (1) 4-Methyl pyridine. (2) Pyridine. (3) Ethyl pyridine-3-carboxylate.

into about 5 ml of toluene. After nitrogen had been bubbled through the solutions they were mixed in the stopped flow apparatus and the reaction measured as described.[8] All measurements were made at 25 °C.

DISCUSSION

There is a significant change in the rate equation (eqn. 1) when acetonitrile is exchanged with dioxane as a cosolvent. In 30 % dioxane the second order term has disappeared, and the explanation of this may be found in the different inertness towards the substrate of these two solvents.

There are two ways to explain the third order term which is common in the two rate equations. One is that two pyridine molecules attack the substrate simultaneously to form the 1:2 complex, and the other is that there exists an equilibrium between pyridine and the substrate to form a 1:1 complex which may react with a second molecule of pyridine. We think that the second explanation is the most probable because 1:1 complexes between tervalent phosphorus and amine are known [4-7] and a 1:1 intermediate between BDP and pyridine is also indicated in the pyridine catalyzed methanolysis of BDP.[8] The rate of nucleophilic attack on tervalent phosphorus is known to be fast, and the first attack on P^{III} in our reactions is assumed to be too fast to be measured with the stopped flow technique. When a 1:1 adduct has been formed, the electrophilicity of the phosphorus atom should have diminished and thus have made the rate measureable for the second attack of a pyridine molecule. The mechanism proposed should then be as shown in eqn. 3.

$$Ph_2P - X + Py \rightleftharpoons Ph_2P - X.Py \xrightarrow{Py} Ph_2P - X.2Py \qquad (3)$$
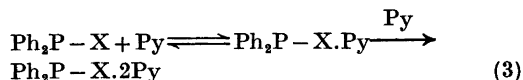
Acetonitrile is known to act as a ligand towards a series of Lewis acids [9] and we may

therefore assume that in addition to the equilibrium between the phosphine and pyridine, we also have a competitive equilibrium between the phosphine and acetonitrile. This should be reflected as a competitive reaction in the rate equation, and the reaction leading to the second order term in the rate equation (eqn. 1) should be given as shown in eqn. 4.

$$Ph_2P-X+MeCN \rightleftharpoons Ph_2P-X.MeCN \xrightarrow{Py}$$
$$Ph_2P-X.(MeCN).Py \qquad (4)$$
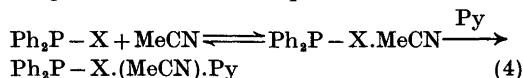
The halide is in certain cases known to be displaced from R_2P-X compounds when a 1:1 complex is formed as in the reaction between triethylphosphine and chloro dimethylphosphine in the formation of $[(C_2H_5)_3PP(CH_3)_2]Cl$.[10] In our reaction, however, we have a significant effect due to the halide. This effect should be absent if the phosphorus-halogen bond was broken prior to the rate determining step and it appears therefore that in the product-forming step the halogen must still be in the sphere of influence of the phosphorus atom.

The complexes between tervalent phosphorus compounds and amines are in general very unstable when more than one amine molecule is attached to the phosphorus atom. Their existence has been indicated by spectroscopic studies [3] and by vapor pressure measurement.[11] The structure of these complexes is not known but it might be of interest to look at similar complexes which have the same electronic configuration around the central atom. In the compound $PCl_3.2P(CH_3)_3$ the two entering phosphorus atoms have been found to be axial to each other,[12] while X-ray determination of $SbCl_3.2OAsPh_3$ has shown it to have a *cis*-pseudooctahedral stereochemistry as shown in (I).[13] Boal and Ozin suggest a similar structure for $PCl_3.2N(CH_3)_3$.[3]

(I)
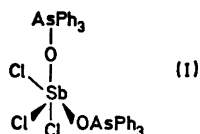
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