Kinetics and Mechanism of the Pyridinolysis of Diphenyl Phosphinic and Thiophosphinic Chlorides in Acetonitrile

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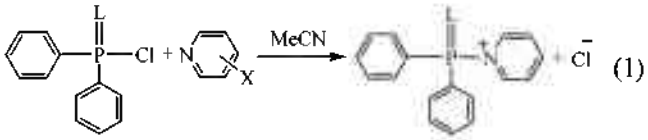
The kinetics and mechanism of the nucleophilic substitution reactions of diphenyl phosphinic (**1**) and thiophosphinic (**2**) chlorides with substituted X-pyridines are investigated kinetically in acetonitrile at 35.0 and 55.0 °C, respectively. A concerted mechanism with backside nucleophilic attack is proposed for the pyridinolysis of **1**, on the basis of the linear Brönsted plot with the β_X value of 0.68. In the case of the pyridinolysis of **2**, the Hammett and Brönsted plots are biphasic concave upwards with the break point at 3-phenyl pyridine. These results indicate a change in mechanism from a concerted S_N2(P) process with direct backside nucleophilic attack for less basic nucleophiles (X = 3-CN-3-Ph) to a stepwise process with frontside attack for more basic nucleophiles (X = 4-MeO-3-Ph). Apparent secondary inverse kinetic isotope effects with deuterated pyridine (C_5D_5N), $k_H/k_D < 1$, are observed for the pyridinolysis of **1** and **2**.

Key Words : Pyridinolysis, Diphenyl phosphinic chloride, Diphenyl thiophosphinic chloride, Biphasic Hammett and Brönsted plots, Deuterium kinetic isotope effects

Introduction

Nucleophilic substitution reactions of tetracoordinate phosphorus have been studied extensively and the proposed mechanism is either stepwise through a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate or concerted through a single TBP-5C transition state (TS).[1-6] In previous work, we reported several phosphoryl transfer reactions.[7-14] We proposed that the pyridinolysis of aryl phenyl chlorophosphates proceeds concertedly with an early TS in which the extent of both bond formation and leaving group departure is small.[7] We also reported the reactions of Z-aryl bis(4-methoxyphenyl) phosphates [(4-MeOPhO)$_2$P(O)-OPhZ] with X-pyridines in acetonitrile.[8] In the case of more basic phenolate leaving groups, the mechanism changes from a concerted process for less basic pyridines to a stepwise process with rate-limiting formation of a TBP-5C intermediate for more basic pyridines. In the case of less basic phenolate leaving groups, the reaction proceeds through a direct backside attack TBP-5C TS. In the pyridinolysis of Y-aryl phenyl isothiocyanophosphate [(YPhO)(PhO)P(O)-NCS] in acetonitrile,[9] the Hammett plots are biphasic concave downwards for substituent (Y) variations in the substrate and biphasic concave upwards for substituent (X) variations in the nucleophile.

To clarify the phosphoryl transfer mechanism as well as to compare the reactivity of diphenyl chlorophosphate (**3**)[7] and diphenyl chlorothiophosphate (**4**),[12] we have investigated the pyridinolysis of diphenyl phosphinic (**1**) and thiophosphinic (**2**) chlorides with substituted pyridines (XC_5H_4N) in acetonitrile at 35.0 °C (**1**) and 55.0 °C (**2**), respectively, as in eq. (1) (CA index name of **2**: *P,P*-diphenyl phosphinothioic chloride; commercial name: diphenylphosphinothioyl chloride). We also investigated the kinetic isotope effects (KIEs) of the pyridinolysis of **1** and **2** with deuterated pyridine (C_5D_5N).



(1)

L = O (**1**) at 35.0 °C; L = S (**2**) at 55.0 °C
X = 4-MeO, 4-Me, 3-Me, H, 3-Ph, 3-MeO, 3-Cl, 3-Ac, 4-Ac, 4-CN, 3-CN

Results and Discussion

The pseudo-first-order rate constants observed (k_{obsd}) for all reactions obey eq. (2) with negligible k_0 (≈0) in acetonitrile. The second-order rate constants were determined using eq. (2) with at least five pyridine concentrations, [Py]. No third-order or higher-order terms were detected, and no

$$k_{obsd} = k_0 + k_2[Py] \quad (2)$$

complications were found in the determination of k_{obsd} or in the linear plot of eq. (2). This suggests that there is no base-catalysis or noticeable side reactions, and the overall reaction follows the route given by eq. (1). The second-order rate constants of the pyridinolysis of **1** (at 35.0 °C) and **2** (at 55.0 °C) in acetonitrile are summarized in Table 1. The substituent effects in the nucleophiles on the rates are in accord with those for a typical nucleophilic substitution reaction, that is, a stronger nucleophile results in a faster rate.

The natural bond order (NBO) charges[15] and rate ratios of the reactions of **1**, **2**, **3**, and **4** with unsubstituted pyridine in acetonitrile at 35.0 °C are shown in Figure 1. The second-order rate constant, $k_2 = 26.6 \times 10^{-2}$ M^{-1} s^{-1}, of **3** at 35.0 °C is an extrapolated value from $k_2 = 3.71 \times 10^{-2}$, 9.40×10^{-2}, and 13.5×10^{-2} M^{-1} s^{-1} at 5.0, 15.0, and 25.0 °C, respectively,[7]

Table 1. Second-Order Rate Constants ($k_2 \times 10^3/M^{-1}s^{-1}$) of the Pyridinolysis of Diphenyl Phosphinic (**1**) and Thiophosphinic (**2**) Chlorides in Acetonitrile at 35.0 °C (**1**) and 55.0 °C (**2**), respectively

X	4-MeO	4-Me	3-Me	H	3-Ph	3-MeO	3-Cl	3-Ac	4-Ac	4-CN	3-CN
1[a]	742	414	107	54.6	32.1	26.5	1.96	1.90	0.850	0.313	0.292
2[b]	371	60.7	15.5	2.36	1.01	0.943	0.186	0.179	0.109	0.0574	0.0626

[a]35.0 °C. [b]55.0 °C.

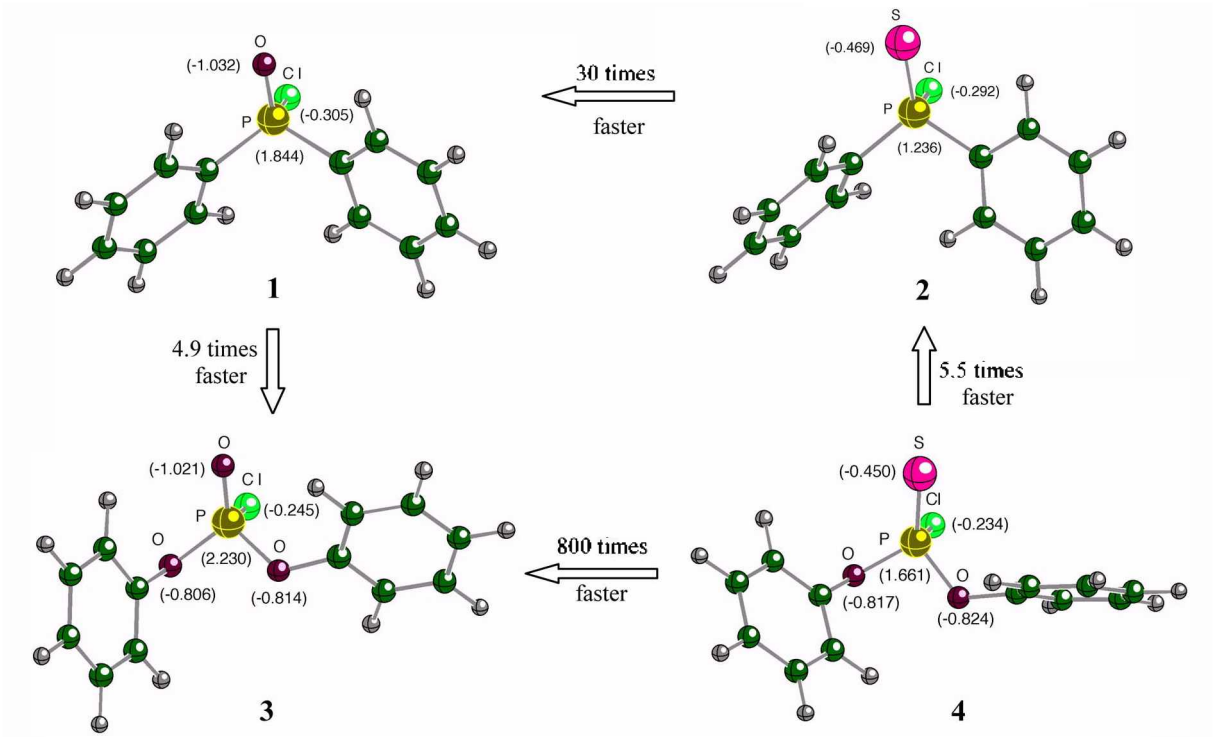


Figure 1. The B3LYP/6-311+G(d,p)[15] geometries and natural bond order (NBO) charges of **1**, **2**, **3**, and **4**. The relative rate ratios are for unsubstituted pyridine in acetonitrile at 35.0 °C.

and the second-order rate constant, $k_2 = 3.33 \times 10^{-4}$ $M^{-1}s^{-1}$, of **4** at 35.0 °C is unpublished data. The NBO charges on the reaction center P are 1.844 in **1** and 2.230 in **3** (P=O systems); 1.236 in **2** and 1.661 in **4** (P=S systems). Considering the inductive effects of Ph ($\sigma_I = 0.12$) and PhO ($\sigma_I = 0.40$) ligands,[16] the NBO charges on the reaction center P are in accord with expectations for the electronic influence of the ligands. However, the rate ratio of $k_{P=O}$(**2**)/$k_{P=S}$(**4**) = 5.5 (at 35.0 °C) is not consistent with the magnitudes of NBO charges on the reaction center P atom, while the rate ratio of $k_{P=O}$(**3**)/$k_{P=O}$(**1**) = 4.9 (at 35.0 °C) is in accord with expectations for the inductive effects of the ligands. The slower rate of **2** and **4** (P=S systems) than those of **1** and **3** (P=O systems) is attributed to several reasons, so-called "thio effect", which is mainly the electronegativity difference between O and S, that favors O over S.[6,17-19]

Some phosphate systems are more reactive than their thiophosphate counterparts by two or more orders of magnitude.[20-22] Phosphinate systems are generally less sensitive to S substitution in the P=O bond than phosphate systems: $k_{P=O}/k_{P=S} < 10$ for the alkaline hydrolysis in 60% DME-H_2O and H_2O in a series of alkyl phosphinates;[23] $k_{P=O}/k_{P=S} < 1$ for the hydrolysis of $Et_2P(O)OEt$ and $Et_2P(S)OEt$;[24] $k_{P=O}/k_{P=S}$ = 2.4-5.2 for the hydrolysis of $Me_2P(O)OPhX$ and $Me_2P(S)OPhX$;[25,26] $k_{P=O}/k_{P=S}$ = 5-13 for the aminolysis of $Ph_2P(O)OPhX$ and its thio analog;[27] $k_{P=O}/k_{P=S}$ = 42 (third-order rate constant) for the butylaminolysis of $Ph_2P(O)OPhX$ (X = 4-NO_2) and its thio analog.[28]

A large rate ratio of $k_{P=O}$(**3**)/$k_{P=S}$(**4**) = 800 is observed for the pyridinolysis of diphenyl chlorophosphate and its thio analog in acetonitrile at 35.0 °C, while $k_{P=O}$(**3**)/$k_{P=S}$(**4**) = 8.8 is obtained for the anilinolysis in acetonitrile at 55.0 °C.[10,12] The rate ratio of $k_{P=O}$(**1**)/$k_{P=S}$(**2**) = 30 is observed for the pyridinolysis of diphenyl phosphinic chloride and its thio analog. The pyridinolysis rate ratio of $k_{P=O}$(**3**)/$k_{P=O}$(**1**) = 4.9 at 35.0 °C shows the opposite tendency to the anilinolysis rate ratio of $k_{P=O}$(**1**)/$k_{P=S}$(**3**) = 1.9 in acetonitrile at 55.0 °C.[13]

The Hammett ρ_X (ρ_{nuc}) and Brönsted β_X (β_{nuc}) values of **1**, **2**, and **3**[7] are summarized in Table 2. The Brönsted β_X values were obtained by correlating $\log k_2$(MeCN) with $pK_a(H_2O)$, which was justified theoretically and experimentally.[29] The magnitudes of ρ_X and β_X values of **1** ($\rho_X = -3.86$, $\beta_X = 0.68$) and **2** (biphasic: $\rho_X = -7.84$, -2.28 and $\beta_X = 1.53$, 0.38) are much larger than those of **3** ($\rho_X = -0.89$, $\beta_X = 0.16$).[7] Moreover, the Hammett and Brönsted plots of **2** are biphasic concave upwards with break point at 3-phenyl pyridine as

Table 2. Hammett and Brönsted Coefficients[a] of the Pyridinolysis of **1**, **2**, and **3** in Acetonitrile

Substrate	t / °C	$-\rho_X$	β_X
1	35.0	3.86 (0.995)[b]	0.68 (0.995)
2	55.0	7.84[c] (0.995); 2.28[d] (0.990)	1.53[c] (0.998); 0.38[d] (0.992)
3[e]	25.0	0.89 (0.999)	0.16 (0.999)

[a]The σ values were taken from ref. 31; The pK_a values in water were taken from ref. 32. [b]Correlation coefficient (r). [c]X = 4-MeO-3-Ph. [d]X = 3-Ph-3-CN. [e]Ref. 7.

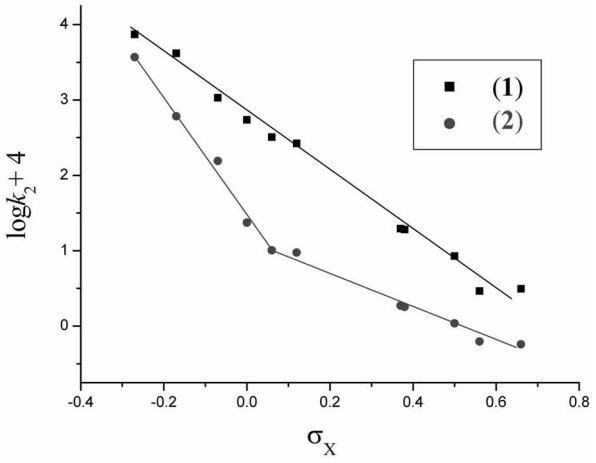


Figure 2. Hammett plots of the pyridinolysis of **1** and **2** in acetonitrile at 35.0 °C (**1**) and 55.0 °C (**2**), respectively.

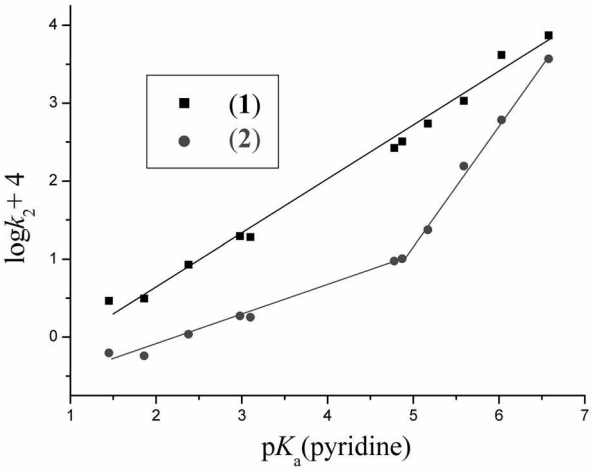


Figure 3. Brönsted plots of the pyridinolysis of **1** and **2** in acetonitrile at 35.0 °C (**1**) and 55.0 °C (**2**), respectively.

shown in Figures 2 and 3. Non-linear free energy correlation of concave upward plots is diagnostic of a change in the reaction mechanism, *e.g.*, parallel reactions where the reaction path is changed depending on the substituents, while non-linear free energy correlation of concave downward plots is diagnostic of a rate-limiting step change from bond-breaking with less basic nucleophiles to bond-formation with more basic nucleophiles.[30]

The β_X values of pyridinolysis of phosphate systems in which the reactions proceed by a concerted mechanism are known between 0.1-0.6: pyridinolysis of pyridinium-*N*-phosphonates (0.53),[33] isoquinolino-*N*-phosphonate (0.15),[34] phosphorylated 3-methoxy pyridine (0.17),[35] acetyl phosphate dianion (0.10),[36] 2-aryloxy-2-oxo-1,3,2-dioxaphosphorinanes (aryl = 2,4-dinitrophenyl) (0.61),[37] and bis 2,4-dinitrophenyl phosphate monoanion (0.54).[38] The β_X value of the reaction of 4-nitrophenyl diphenyl phosphinate with aryl oxide ions, which proceeds through a concerted mechanism, is 0.46.[39]

Anilinolysis of aryl phenyl chlorophosphates **[**(YPhO)-(PhO)P(O)Cl**]**[10] and aryl 4-chlorophenyl chlorophosphates [(YPhO)(4-ClPhO)P(O)Cl][11] in acetonitrile were investigated. We proposed a concerted mechanism with a late, product-like TS, in which bond making and leaving group departure are extensive, and the aniline nucleophile and the Cl leaving group occupy apical positions in the TS. The obtained β_X values are 1.24-1.68 and 1.43-1.49 for aryl phenyl[10] and 4-chlorophenyl[11] chlorophosphates, respectively. The inverse secondary kinetic isotope effects (KIEs), $k_H/k_D < 1$, with deuterated anilines ($XC_6H_4ND_2$) are observed; k_H/k_D = 0.61-0.87 and 0.64-0.87 for aryl phenyl[10] and 4-chlorophenyl[11] chlorophosphates, respectively. For the anilinolysis of aryl phenyl chlorothiophosphates **[**(YPhO)-(PhO)P(S)Cl**]** and aryl 4-chlorophenyl chlorothiophosphates [(YPhO)(4-ClPhO)P(S)Cl],[12] partial participation of a frontside attack concerted mechanism through a hydrogen-bonded four-center-type TS is proposed, mainly on the basis of the primary normal KIEs, $k_H/k_D > 1$, with deuterated anilines; k_H/k_D = 1.11-1.33 and 1.10-1.46 for aryl phenyl and 4-chlorophenyl chlorothiophosphates, respectively.[12] The obtained β_X values are 1.34-1.41 and 1.23-1.38 for aryl phenyl and 4-chlorophenyl chlorothiophosphates, respectively.[12]

In the present work, we propose a concerted mechanism for the pyridinolysis of **1** in which the pyridine nucleophile and the Cl leaving group occupy apical positions (backside nucleophilic attack) in the TS, on the basis of the linear Brönsted plot with the β_X value of 0.68. Comparing the β_X value of 0.68 in **1** with that of 0.16 in **3**, the degree of bond formation would be much larger in **1** than in **3**. In the case of the pyridinolysis of **2**, we propose a concerted mechanism with backside nucleophilic attack **[**ap(Nu)-ap(Lg)**]** for less basic nucleophiles (X = 3-CN-3-Ph), and a stepwise mechanism in which the pyridine and Cl occupy the adjacent spaces, because of frontside (equatorial) nucleophilic attack [eq(Nu)-ap(Lg)], in the TS for more basic nucleophiles (X = 4-MeO-3-Ph), on the basis of the concave upwards non-linear Brönsted plot with a β_X value of 0.38 for less basic nucleophiles and 1.53 for more basic nucleophiles. The

larger β_X value (1.53) for more basic nucleophiles also suggests a frontside attack with greater bond-formation compared to backside attack towards the Cl leaving group for the less basic pyridines. It is well known that a weakly basic group has a greater apicophilicity so that apical approach is favored for such nucleophiles.[8,40,41] Since the apical bonds are longer than the equatorial bonds,[8,40] the apical nucleophilic attack should lead to a looser P-N bond in the TBP-5C TS structure and hence a smaller magnitude of β_X as well as ρ_X is obtained.[8]

The proposed mechanism for the present work can be supported from the following results. Concave upward biphasic-type Hammett and Brönsted plots for substituent (X) variations in the nucleophiles of the reactions of Y-aryl phenyl isothiocyanophosphate with X-pyridines in acetonitrile was interpreted as a change in the nucleophilic attacking direction from backside (apical) for weaker basic pyridines (X = 4-CN, 4-Ac, 3-Cl, and 3-Ac) to frontside (equatorial) for stronger basic pyridines (X = 4-MeO, 4-Me, 3-Me, H, and 3-Ph).[9] Gorenstein and Rowell investigated the reactions of epimeric 2-(aryloxy)-2-oxydioxaphosphorinanes in 30% dioxane/water with a variety of nucleophiles and interpreted the results in terms of a change in mechanism from a concerted S_N2(P) process for less basic (or weaker) nucleophiles to a stepwise process for very basic (or stronger) nucleophiles, and, as a result, some retention of configuration at phosphorus was observed because of a frontside nucleophilic attack.[40]

The large β_X value (1.53) for more basic nucleophiles in the pyridinolysis of **2** is ascribed to the frontside (equatorial) attack TS, and the stepwise mechanism with the rate-limiting bond-formation would be more favorable than with rate-limiting leaving group expulsion, despite the large β_X value could be an indication of a rate-limiting leaving group expulsion process.[42] But the stepwise mechanism with rate-limiting leaving group expulsion cannot be completely neglected. This suggestion is supported from the results of the reactions of Y-aryl phenyl isothiocyanophosphate with X-pyridines in acetonitrile, yielding non-linear free energy correlation of concave upward Hammett and Brönsted plots as in the present work of **2**.[9] For stronger nucleophiles (X = 4-MeO, 4-Me, 3-Me, H, and 3-Ph), we proposed that the nucleophiles attack frontside (equatorial position) and the rate-determining step is changed from leaving group expulsion with electron withdrawing groups in the substrates (Y = H, 3-MeO, and 4-Cl) (ρ_{XY} = +3.16 and β_X = 1.13-1.28) to bond-formation with electron donating groups in the substrates (Y = 4-MeO, 4-Me, H) (ρ_{XY} = −1.42 and β_X = 1.21-1.28).[9]

The observed KIEs, k_H/k_D, of the pyridinolysis of **1** and **2** with deuterated pyridine (C_5D_5N) are summarized in Table 3. The observed k_H/k_D values of **1** (0.78) and **2** (0.83) are less than unity. The origin of these secondary inverse KIEs might be the results of the anharmonicity of C-H and C-D bonds. This is manifested in a reduced C-D bond length, which results in increased electron density on a carbon atom bearing D relative to H.[43] So the deuterated pyridine is more basic than pyridine. Perrin and coworkers reported that the basicities of β-deuterated analogs of benzylamine, *N,N*-dimethylaniline and methylamine increase roughly 0.02 pK_a units per deuterium and these effects are additive.[43] For five deuterium atoms in *d*-5 pyridine this gives an expected ΔpK_a of approximately +0.1 unit. Considering the β_X value of 0.68 in **1**, the k_D value of *d*-5 pyridine can be estimated as k_D =1.17 × 54.6 × 10^{-3} = 63.9 × 10^{-3} M^{-1} s^{-1} since $\Delta\log k_2$ = 0.68 × ΔpK_a = 0.68 × 0.1 = 0.068 or Δk_2 = 1.17, and an expected k_H/k_D value is 0.85. The observed k_D value of *d*-5 pyridine is 69.8 × 10^{-3} M^{-1} s^{-1} and the observed k_H/k_D value is 0.78 which is very close to the expected value of 0.85. In the same way, considering the β_X value of 1.53 (for the region of X = H) in **2**, an expected k_D value of *d*-5 pyridine is 3.35 × 10^{-3} M^{-1} s^{-1} and an expected k_H/k_D value is 0.70 while the observed k_D value is 2.84 × 10^{-3} M^{-1} s^{-1} and the observed k_H/k_D value is 0.83 which is larger than the expected value of 0.70. These results show that the observed secondary inverse KIEs of the studied systems are not current secondary inverse KIEs.

Table 3. Kinetic Isotope Effects, k_H/k_D, of the Pyridinolysis of **1** and **2** with Deuterated Pyridine (C_5D_5N) in Acetonitrile

Substrate	t / °C	$k_H \times 10^5$ /$M^{-1}s^{-1}$	$k_D \times 10^5$ /$M^{-1}s^{-1}$	k_H/k_D
1	35.0	54.6 ± 1.5	69.8 ± 2.2	0.78 ± 0.02
2	55.0	2.36 ± 0.06	2.84 ± 0.08	0.83 ± 0.03

Table 4. Activation Parameters[a] for the Pyridinolysis of **1**, **2**, and **3** with Pyridine (C_5H_5N) in Acetonitrile

Substrate	t / °C	$k_2 \times 10^5$ /$M^{-1}s^{-1}$	$\Delta H^{\neq}$ (kcal mol^{-1})	$-\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
1	25	47.3		
	35	54.6	2.0 ± 0.1[b]	58 ± 1
	45	62.3		
2	35	1.83		
	45	2.14	1.9 ± 0.2	65 ± 1
	55	2.36		
3[c]	5	37.1		
	15	94.0	10.2 ± 2	28 ± 7
	25	135		

[a]Calculated by the Eyring equation. [b]Standard deviation. [c]Ref. 7.

The activation enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, of the pyridinolysis of **1**, **2**, and **3** are summarized in Table 4. The $\Delta H^{\neq}$ values of **1** (2.0 kcal/mol) and **2** (1.9 kcal/mol) are much smaller than that of **3** (10.2 kcal/mol),[7] while $\Delta S^{\neq}$ values of **1** (−58 e.u.) and **2** (−65 e.u.) are much more negative than that of **3** (−28 e.u.).[7] The large negative activation entropies of **1**and **2** seem to be characteristic of a relatively late TS with large bond formation and cleavage.

Summary

The kinetic studies of the reactions of diphenyl phosphinic (**1**) and thiophosphinic (**2**) chlorides with substituted X-pyridines have been carried out in acetonitrile at 35.0 and

55.0 °C, respectively. A concerted mechanism with backside nucleophilic attack is proposed for the pyridinolysis of **1**. In the case of the pyridinolysis of **2**, the Hammett and Brönsted plots are biphasic concave upwards with the break point at 3-phenyl pyridine indicating a change in mechanism from a concerted S_N2(P) process with direct backside nucleophilic attack for less basic nucleophiles (X = 3-CN-3-Ph) to a stepwise process with frontside attack for more basic nucleophiles (X = 4-MeO-3-Ph). The larger magnitudes of ρ_X and β_X for stronger nucleophiles are considered to arise from the frontside (equatorial) nucleophilic attack, whereas the smaller values arise from the backside (apical) nucleophilic attack in the TS. The stepwise mechanism with the rate-limiting bond formation is proposed for more basic nucleophiles in the pyridinolysis of **2** on the basis of greater β_X value (1.53). Apparent secondary inverse kinetic isotope effects with deuterated pyridine (C_5D_5N), $k_H/k_D < 1$, for the pyridinolysis of **1** and **2** are interpreted with the more basic properties of *d*-5 pyridine compared to pyridine.

Experimental Section

Materials. Aldrich GR grade pyridines were used without further purification. HPLC grade acetonitrile (water content is less than 0.005%) was used without further purification. Deuterated pyridine (C_5D_5N; 99 atom % D) was commercially available. The GR Grade diphenyl phosphinic chloride, diphenyl thiophosphiniic chloride were used without further purification.

Kinetic Measurements. Rates were measured conductometrically as described previously.[7-13] For the present work, [substrate] = 2×10^{-3} M and [Py] = 0.01-0.09 M for **1**, and [substrate] = 1×10^{-3} M and [Py] = 0.03-0.15 M for **2** were used. Pseudo-first-order rate constants, k_{obsd}, values were the average of at least three runs which were reproducible within ± 3%.

Product Analysis. Diphenyl phosphinic chloride (**1**) was reacted with excess pyridine at 35.0 °C and diphenyl thiophosphinic chloride (**2**) was reacted with excess 4-acetylpyridine at 55.0 °C for more than 15 half-lives in acetonitrile. Acetonitrile was evaporated under reduced pressure. Diethylether was then added. An insoluble white products were found for both **1**, and **2**. The products were isolated with diethylether after several washes with acetonitrile. The solvent was then removed under reduced pressure. The physical constants were as follows:

$[(NC_5H_5)P(=O)(C_6H_5)_2]^+Cl^-$. White solid; mp 194-196 °C; IR (KBr) 3068 (C-H, aromatic), 1434, 1178 (P-C_6H_5), 726 cm^{-1} (P=O); ^1H NMR (400 MHz, DMSO-d_6): δ 7.43-7.51 (5H, m, phenyl), 7.68-7.74 (4H, m, phenyl), 8.00 (3H, t, J = 8.8 Hz, pyridinium), 8.53 (1H, t, J = 8.8 Hz, phenyl), 8.89 (2H, d, J = 8.8 Hz, pyridinium); ^{13}C NMR (100 MHz, DMSO-d_6) δ 126.9, 128.2, 128.3, 130.7, 130.8, 131.3, 134.1, 135.5, 142.3, 145.2 (aromatic); ^{31}P NMR (162 MHz, DMSO-d_6) δ 33.52 (1P, s, P=O); Anal. Calcd for $C_{17}H_{15}NOPCl$: C, 64.67; H, 4.79; N, 4.44. Found: C, 64.67; H, 4.81; N, 4.74.

$[4\text{-}COCH_3(NC_5H_4)P(=S)(C_6H_5)_2]^+Cl^-$. White solid; mp 203-204 °C; IR (KBr) 3060 (C-H, aromatic). 2938 (CH_3), 1432, 1103 (P-C_6H_5), 730 cm^{-1} (P=S); ^1H NMR (400 MHz, $CDCl_3$) δ 2.64 (3H, s, Me), 7.36-7.40 (4H, t, J = 6.0 Hz, phenyl), 7.47 (2H, t, J = 6.0 Hz, phenyl), 7.73 (2H, d, J = 6.0 Hz, pyridinium), 7.82-7.87 (4H, m, phenyl), 8.81 (2H, d, J = 6.0 Hz, pyridinium); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2 (Me), 121.2, 128.2, 131.3, 132.0, 150.8 (aromatic); ^{31}P NMR (162 MHz, $CDCl_3$) δ 85.69 (1P, s, P=S); Anal. Calcd. for $C_{19}H_{17}NOPSCl$: C, 61.04; H, 4.58; N, 3.75; S, 8.58. Found: C, 61.34; H, 4.59; N, 3.46; S, 8.34.

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