Anilinolysis of *S*-Aryl Phenyl Phosphonochloridothioates in Acetonitrile

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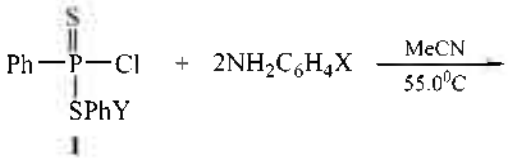
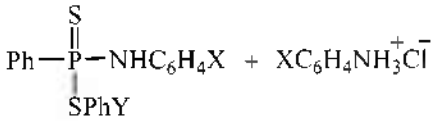
In our preceding papers,[1] we reported various phosphoryl and thiophosphoryl transfer reactions. Continuing our studies on thiophosphoryl transfer reactions, we have carried out kinetic studies of the reactions of Y-*S*-aryl phenyl phosphonochloridothioates (**1**) with X-anilines in acetonitrile at 55.0 °C to clarify the anilinolysis mechanism and stereochemistry by comparing the reactivity, the sign of the cross-interaction constants,[2] the steric effects, and finally the deuterium kinetic isotope effects (KIEs) with those obtained in the previous work.



(1)



X = 4-MeO, 3-Me, H, 4-Cl, 3-Cl
Y = 4-MeO, 4-Me, 3-Me, H, 3-MeO

The pseudo-first-order rate constants observed (k_{obsd}) for all reactions obeyed eq. (2) with negligible k_0 (≈ 0) in acetonitrile. The clean second-order rate constants, $k_{H(D)}$, were obtained as the slope of the plot of k_{obsd} against aniline concentration.

$$k_{obsd} = k_0 + k_H[\text{X-An}] \quad (2)$$

The second-order rate constants (k_H) for the reactions of **1** with X-anilines in acetonitrile at 55.0 °C are summarized in Table 1 together with selectivity parameters, ρ_X, β_X, ρ_Y, and ρ_{XY}. The rate increases with a more electron-withdrawing substituent Y in the substrate and with a more electron-donating substituent X in the nucleophile which is consistent with a typical nucleophilic substitution reaction with negative charge development at the reaction center P in the transition state (TS).

Figure 1 shows the plot of ρ_X *vs* σ_Y and ρ_Y *vs* σ_X (eqs. 3) for the anilinolysis of **1** with good linearities. The negative ρ_{XY} (= −0.31) value implies the rate-limiting nucleophilic bond formation.[2] A more electron-withdrawing substituent ($\partial\sigma_Y > 0$) in the substrate leads to a greater degree of bond formation ($\hat{c}\rho_X < 0$ or $|\hat{c}\rho_X| > 0$), resulting in $\rho_{XY} = \partial\rho_X/\partial\sigma_Y < 0$. A stronger nucleophile ($\partial\sigma_X < 0$) leads to greater negative charge development at the reaction center ($\hat{c}\rho_Y > 0$) because of greater bond formation, resulting in $\rho_{XY} = \hat{c}\rho_Y/\partial\sigma_X < 0$. The negative sign of ρ_{XY} is in agreement with the concerted mechanism,[2] as observed in the anilinolysis of aryl phenyl chlorothiophosphates ($\rho_{XY} = -0.22$)[1c] and aryl ethyl chlorothiophosphates ($\rho_{XY} = -0.28$).[1f]

$$\log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \quad (3a)$$

$$\rho_{XY} = \hat{c}\rho_X/\partial\sigma_Y = \partial\rho_Y/\partial\sigma_X \quad (3b)$$

The KIEs with deuterated anilines in the present work are summarized in Table 2. The obtained primary normal KIEs (k_H/k_D = 1.15-1.59 > 1) indicate that partial deprotonation of the aniline nucleophile occurs in the rate-limiting step by hydrogen bonding. A concerted mechanism involving a partial frontside nucleophilic attack through a hydrogen-bonded, four-center-type TS I accompanied by a backside nucleophilic attack with a trigonal bipyramidal pentacoordinate (TBP-5C) TS II is proposed in the present work, for

Table 1. Second-Order Rate Constants ($k_H \times 10^5/M^{-1}\,s^{-1}$) and Selectivity Parameters[a] of the Aminolysis of Y-*S*-aryl Phenyl Phosphonochloridothioates (**1**) with X-Anilines in Acetonitrile at 55.0 °C

X \ Y	4-MeO	4-Me	3-Me	H	3-MeO	ρ_Y[c]
4-MeO	107 ± 3	119 ± 3	128 ± 1	144 ± 3	168 ± 1	0.50 ± 0.01
3-Me	16.1 ± 0.1	18.0 ± 0.1	19.9 ± 0.2	21.9 ± 0.1	24.0 ± 0.5	0.45 ± 0.01
H	12.6 ± 0.2	14.6 ± 0.3	16.7 ± 0.1	17.5 ± 0.4	18.4 ± 0.1	0.43 ± 0.02
4-Cl	2.66 ± 0.05	2.75 ± 0.03	2.88 ± 0.07	3.17 ± 0.01	3.72 ± 0.05	0.37 ± 0.02
3-Cl	0.613 ± 0.002	0.665 ± 0.005	0.697 ± 0.004	0.742 ± 0.010	0.798 ± 0.017	0.29 ± 0.01
$-\rho_X$[b]	3.35 ± 0.10	3.39 ± 0.09	3.42 ± 0.09	3.45 ± 0.09	3.47 ± 0.10	ρ_{XY}[e] = −0.31 ± 0.08
β_X[c]	1.21 ± 0.05	1.22 ± 0.04	1.23 ± 0.04	1.24 ± 0.04	1.25 ± 0.05	

[a]The σ values were taken from ref. 3. The pK_a values were taken from ref. 4. [b]Correlation coefficients (r) were better than 0.995. [c]r ≥ 0.999. [d]r ≥ 0.955. [e]r = 0.991.

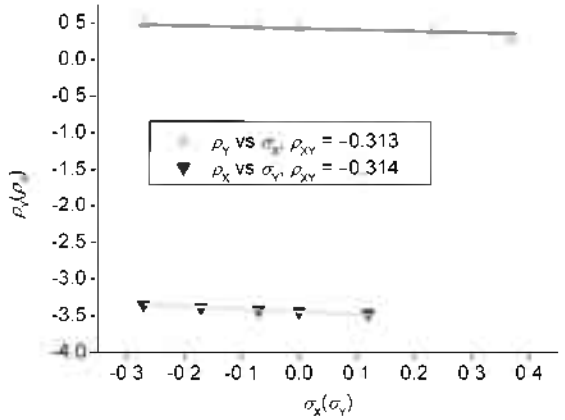


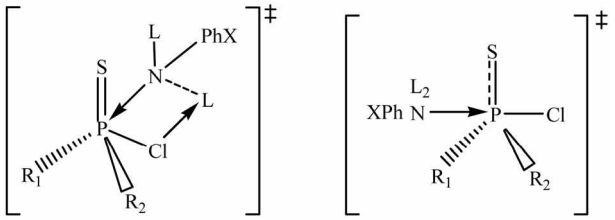
Figure 1. The ρ_{XY} (= $\partial\rho_X/\partial\sigma_Y = \partial\rho_Y/\partial\sigma_X$) plot of ρ_X *vs* σ_Y and ρ_Y *vs* σ_X of the reactions of Y-*S*-aryl phenyl phosphonochloridothioates (**1**) with X-anilines in acetonitrile at 55.0 °C.

Table 2. Second-Order Rate Constants ($k_{H(D)} \times 10^5$/M^{-1} s^{-1}) and Kinetic Isotope Effects (k_H/k_D) for the Aminolysis of Y-*S*-Aryl Phenyl Phosphonochloridothioates with $XC_6H_4NH_2$ and $XC_6H_4ND_2$ in Acetonitrile at 55.0 °C

X	Y	$k_H \times 10^5$/M^{-1} s^{-1}	$k_D \times 10^5$/M^{-1} s^{-1}	k_H/k_D
4-MeO	4-Me	119 ± 3	77.8 ± 0.6	1.53 ± 0.04[a]
4-MeO	H	144 ± 3	90.4 ± 0.4	1.59 ± 0.03
4-MeO	3-MeO	168 ± 1	108 ± 1	1.56 ± 0.02
H	4-Me	14.6 ± 0.3	10.2 ± 0.1	1.43 ± 0.03
H	H	17.5 ± 0.4	12.0 ± 0.1	1.46 ± 0.04
H	3-MeO	18.4 ± 0.1	13.3 ± 0.3	1.38 ± 0.03
3-Cl	4-Me	0.665 ± 0.005	0.534 ± 0.009	1.25 ± 0.02
3-Cl	H	0.742 ± 0.010	0.597 ± 0.004	1.24 ± 0.02
3-Cl	3-MeO	0.798 ± 0.017	0.695 ± 0.018	1.15 ± 0.04

[a]Standard error {= $1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$}.[6]

the same reasons as in the anilinolysis of aryl phenyl chlorothiophosphates [**2**: (YPhO)(PhO)P(S)Cl],[1c] diphenyl thiophosphinic chloride [**3**: $Ph_2P(S)Cl$],[1e] aryl ethyl chlorothiophosphates [**4**: (YPhO)(EtO)P(S)Cl],[1f] diethyl chlorothiophosphate [**5**: $(EtO)_2P(S)Cl$],[1g] and dimethyl chlorothiophosphate [**6**: $(MeO)_2P(S)Cl$].[1g]



L = H or D

The observed primary normal KIEs may be proportional to the degree of hydrogen bond formation. Greater deprotonation would occur with greater bond formation, that is, the stronger nucleophile ($\partial\sigma_X < 0$) leads to a greater hydrogen bond formation ($\partial\rho_Y > 0$), resulting in $\rho_{XY} = \partial\rho_Y/\partial\sigma_X < 0$. This deduction is consistent with the obtained sequence of k_H/k_D values as shown in Table 2. The observed k_H/k_D values

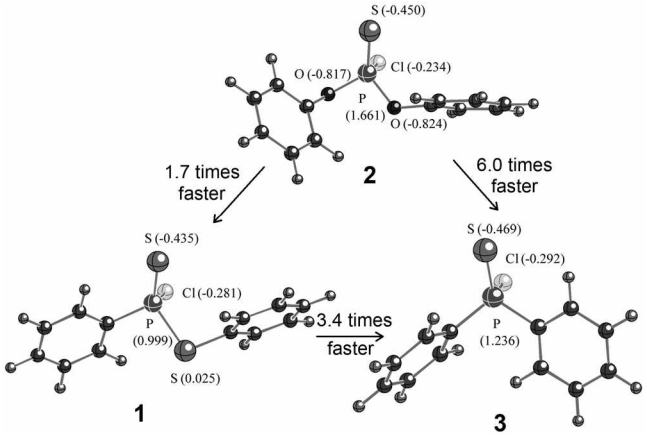


Figure 2. The B3LYP/6-311+G(d,p)[7] geometries and NBO charges of *S*-phenyl phenyl phosphonochloridothioate [**1** with Y = H: (PhS)PhP(S)Cl], diphenyl chlorothiophosphate [**2** with Y = H: $(PhO)_2P(S)Cl$],[1c] and diphenyl thiophosphinic chloride [**3**: $Ph_2P(S)Cl$][2d] in the gas phase. The anilinolysis ($C_6H_5NH_2$) rate ratios in acetonitrile at 55.0 °C are displayed next to the arrows.

in Table 2 would be the sum of (i) the primary normal KIE, $k_H/k_D > 1$, because of the partial deprotonation of one of the two N-H(D) bonds in the TS I for a frontside attack, (ii) the secondary inverse KIE, $k_H/k_D < 1$, because of the steric hindrance that increases the out-of-plane bending vibrational frequencies of the other N-H(D) bond in TS I for a frontside attack, (iii) the secondary inverse KIE, $k_H/k_D < 1$, because of the steric congestion that increases the vibrational frequencies of both of the N-H(D) bonds in TS II for a back-side attack.[5] Thus, the real primary KIE due to the hydrogen bond between the hydrogen of the N-H(D) moiety and the Cl leaving group should be greater than the observed value.

As shown in Figure 2, the natural bond order (NBO) charges, using the B3LYP/6-311+G(d,p) level,[7] on the reaction center P are 0.999 (for **1**), 1.661 (for **2**),[1c] and 1.236 (for **3**).[1e] Solely considering the NBO charge on the reaction center, the reactivities of the substrates should increase in the following order: **1** < **3** < **2**. However, the sequence of the second-order rate constants, **2** < **1** < **3**, is not consistent with the expectations for the NBO charge on the reaction center P. The anilinolysis rate of **1** is 1.7 times faster than that of **2**. The rate of **3** is 6.0 times faster than that of **2** and the rate of **3** is 3.4 times faster than that of **1**. The rate increases upon replacing a larger ligand (PhO or PhS) into a smaller ligand (Ph), suggesting that the steric effects play an important role to determine the reactivities of P=S systems.

The second-order rate constants, relative rate ratios, NBO charges on P reaction centers, KIEs (k_H/k_D), Brönsted β_X values, and cross-interaction constant ρ_{XY} values for the anilinolysis of **1**-**6** in acetonitrile at 55.0 °C are summarized in Table 3. Relatively large Brönsted β_X (β_{nuc} = 0.9-1.4) values of the anilinolysis of the studied reaction systems (**1**-**6**) suggest extensive bond formation in the TS. These values are considerably larger than those of other nucleophilic substitution reactions of P=O and P=S systems in which the reactions proceed by a concerted mechanism. The large β_X

Table 3. Summary of the Second-Order Rate Constants, Relative Rate Ratios, NBO Charges on P Reaction Centers, Kinetic Isotope Effects (k_H/k_D), Brönsted β_X Values, and Cross-Interaction Constant ρ_{XY} values for the Anilinolysis of $R_1R_2P(S)Cl$ in Acetonitrile at 55.0 °C

No	R_1	R_2	$k_H \times 10^4$/M^{-1}s^{-1}[a]	k_{rel}[b]	NBO charge on P	k_H/k_D	β_X	$-\rho_{XY}$	ref.
6	MeO	MeO	10.9	11	1.687	0.95–1.06	0.993	–	1g
3	Ph	Ph	6.01	6.0	1.236	1.00–1.10	1.40	–	1e
5	EtO	EtO	5.12	5.0	1.701	1.01–1.10	0.977	–	1g
4	YPhO	EtO	2.80	2.8	1.687	1.06–1.27	1.10–1.19	0.28	1f
1	YPhS	Ph	1.75	1.7	0.999	1.15–1.59	1.21–1.25	0.31	This work
2	YPhO	PhO	1.01	1	1.661	1.11–1.33	1.34–1.41	0.22	1c

[a]X = Y = H. [b]$k_{rel} = k_{R_1R_2}/k_{PhO,PhO}$.

values seem to be characteristic of the anilinolysis of P=O and P=S systems with the Cl leaving group.[1d,f] When we compare the reactivities of the thiophosphates [$(R_1'O)$-$(R_2'O)P(S)Cl$], the NBO charges of P reaction centers do not explain the obtained rate ratios explicitly. The rates increase as the sizes of the ligands are getting smaller: **2** (with two PhO) < **4** (with single PhO and EtO) < **5** (with two EtO) < **6** (with two MeO), *i.e.*, the relative rate ratios of **2**, **4**, **5**, and **6** are 1:2.8:5.0:11. Therefore, it is clear that the steric effect is a major factor to determine the reactivities of P=S systems, as well as P=O systems.[1c,f,g]

In the anilinolysis of **6**,[1g] the k_H/k_D values of the weaker nucleophiles (X = 3-Cl, 4-Cl, 3-MeO, and H) are less than unity, while those of the stronger nucleophiles (X = 4-MeO, 4-Me, and 3-Me) are larger than unity. In an S_N2 mechanism, the secondary inverse KIE (k_H/k_D < 1) is ascribed to the increment of the vibrational frequencies of N-H(D) in the TS II due to an increase in steric crowding in the bond-making process.[8] This implies that a backside nucleophilic attack is dominant for the weaker nucleophiles, while a frontside nucleophilic attack is dominant for the stronger nucleophiles. The backside nucleophilic attack for the weaker nucleophiles is possible because of the relatively small sizes of two MeO ligands.[1g]

The small $\Delta H^{\neq}$ values and large negative $\Delta S^{\neq}$ values are characteristic of relatively late TS with a large degree of bond formation and breaking.[9] Since the Cl leaving group is a strong nucleofuge, a large degree of bond breaking will not require a lot of energy and a large degree of bond formation will provide partial bond energy in the TS, resulting in small positive $\Delta H^{\neq}$ values. The large negative $\Delta S^{\neq}$ values may result from a large degree of bond breaking and also steric hindrance in the bond formation of aniline.

Summary

The reactions of *S*-aryl phenyl phosphonochloridothioates with anilines and deuterated anilines are investigated kinetically in acetonitrile at 55.0 °C. A negative cross-interaction constant (ρ_{XY} = −0.31) and primary normal kinetic isotope effects (k_H/k_D = 1.15-1.59) are consistent with a concerted process with a partial frontside nucleophilic attack through a hydrogen-bonded, four-center-type TS accompanied by a backside nucleophilic attack with a trigonal bipyramidal pentacoordinate TS.

Experimental Section

Materials. GR grade phenyl thiophosphonic dichloride, anilines, thiophenols, triethylamine, and deuterium oxide (D_2O; 99.9 atom% D) were used without further purification except anilines. Anilines were generally recrystallized or distilled for further purification before use. HPLC-grade MeCN (water content is less than 0.005%) were used without further purification for kinetics study. Deuterated anilines were prepared by heating anilines with D_2O at 85 °C for 72 h and confirmed by ^{1}H-NMR. Y-*S*-aryl phenyl phosphonochloridothioates were prepared by the following single step reaction. The equimolar starting materials, phenyl thiophosphonic dichloride, thiophenols, and triethyl amine were mixed and stirred in methylene chloride solvent, keeping in an ice bath for 18-20 hrs. The physical constants of substrates after isolation by column chromatography are as follows.

***S*-(4-Methoxyphenyl) phenyl phosphonochloridothioate.** White solid; mp 68-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 16.6, 6.4 Hz, 2H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.33-7.29 (m, 2H), 6.84 (d, J = 7.6 Hz, 2H), 3.80 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, J = 4.6 Hz), 137.9 (d, J = 4.6 Hz), 135.9 (d, J_{P-C} = 94.0 Hz), 132.9 (d, J = 3.8 Hz), 131.0 (d, J = 12.1 Hz), 128.4 (d, J = 15.2 Hz), 117.3 (d, J = 7.6 Hz), 114.9 (d, J = 3.0 Hz), 55.4 (s, OCH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 94.1 (s, 1P); IR (KBr, cm^{-1}) 3061 (C-H, aromatic), 2947, 2841 (-CH_3), 1493 (C=C, Ar), 1438 (P-C, Ar), 828 (P=S); GCMS: m/z, 314 (M^-); Anal. Calcd for $C_{13}H_{12}OPS_2Cl$: C, 49.60; H, 3.84; Found: C, 49.90; H, 3.88.

***S*-(4-Methylphenyl) phenyl phosphonochloridothioate.** White solid; mp 87-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 16.5, 6.5 Hz, 2H), 7.57-7.53 (m, 1H), 7.49-7.43 (m, 2H), 7.28-7.24 (m, 2H), 7.11 (d, J = 7.0 Hz, 2H) 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9 (d, J = 4.5 Hz), 136.2 (d, J = 5.3 Hz), 136.0 (d, J_{P-C} = 95.5 Hz), 132.9 (d, J = 3.8 Hz), 131.0 (d, J = 12.9 Hz), 130.1 (d, J = 3.8 Hz), 128.4 (d, J = 15.2 Hz), 123.3 (d, J = 7.6 Hz), 21.4 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 93.6 (s, 1P); IR (KBr, cm^{-1}) 3056 (C-H, aromatic), 2917 (-CH_3), 1479 (C=C, Ar), 1439 (P-C, Ar), 739 (P=S); GCMS: m/z, 298 (M^+); Anal. Calcd for $C_{13}H_{12}PS_2Cl$: C, 52.26; H, 4.05; Found: C, 52.41; H, 3.83.

***S*-(3-Methylphenyl) phenyl phosphonochloridothioate.** Colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J

= 16.0, 6.4 Hz, 2H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.24-7.20 (m, 3H), 7.17 (s, 1H), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0 (d, J = 3.8 Hz), 136.7 (d, J = 5.3 Hz), 135.6 (d, J_{P-C} = 95.5 Hz), 133.1 (d, J = 4.6 Hz), 132.8 (d, J = 3.0 Hz), 131.1 (d, J = 3.8 Hz), 130.7 (d, J = 12.1 Hz), 128.9 (d, J = 3.0 Hz), 128.2 (d, J = 15.1 Hz), 126.3 (d, J = 7.6 Hz), 21.1 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 93.4 (s, 1P); IR (neat, cm^{-1}) 3054 (C-H, aromatic), 2920, 2850 (-CH_3), 1475 (C=C, Ar), 1437 (P-C, Ar), 780 (P=S); GCMS: m/z, 298 (M^+); Anal. Calcd for $C_{13}H_{12}PS_2Cl$: C, 52.26; H, 4.05; Found: C, 52.74; H, 3.80.

***S*-Phenyl phenyl phosphonochloridothioate.**[10] White solid; mp 86-87 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 16.8, 8.0 Hz, 2H), 7.60-7.55 (m, 1H), 7.50-7.40 (m, 5H), 7.35-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 135.9 (d, J_{P-C} = 94.7 Hz), 133.1 (d, J = 3.8 Hz), 131.0 (d, J = 12.9 Hz), 130.5 (d, J = 4.5 Hz), 129.3 (d, J = 3.8 Hz), 128.4 (d, J = 15.9 Hz), 127.0 (d, J = 15.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 93.2 (s, 1P); IR (KBr, cm^{-1}) 3640 (C-H, Ar), 1434 (C=C, Ar), 1396 (P-C, Ar), 806 (P=S); GCMS: m/z, 284 (M^+); Anal. for $C_{12}H_{10}PS_2Cl$: C, 50.61; H, 3.54; Found: C, 50.93; H, 3.58.

***S*-(3-Methoxyphenyl) phenyl phosphonochloridothioate.** Colourless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 16.8, 8.1 Hz, 2H), 7.60-7.56 (m, 1H), 7.51-7.46 (m, 2H), 7.23 (t, J = 8.2 Hz, 1H), 7.01-6.96 (m, 2H), 6.92-6.91 (m, 1H), 3.80 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, J = 3.8 Hz), 136.0 (d, J_{P-C} = 96.2 Hz), 133.1 (d, J = 3.1 Hz), 131.1 (d, J = 12.9 Hz), 130.0 (d, J = 8.7 Hz), 128.5 (d, J = 19.0 Hz), 127.9 (d, J = 7.6 Hz), 120.9 (d, J = 4.5 Hz), 119.6, 117.1 (d, J = 4.6 Hz), 55.6 (s, OCH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.9 (s, 1P); IR (neat, cm^{-1}) 3062 (C-H, aromatic), 2937, 2837 (-CH_3), 1479 (C=C, Ar), 1437 (P-C, Ar), 856 (P=S); GCMS: m/z, 314 (M^+); Anal. Calcd for $C_{13}H_{12}OPS_2Cl$: C, 49.60; H, 3.84;. Found: C, 49.76; H, 3.90.

Product analysis. *S*-(4-Methylphenyl) phenylphosphonochloridothioate was treated with excess 4-methoxyaniline for more than 15 half-lives at 55.0 °C in acetonitrile. 4-methoxyaniline hydrochloride salt was separated as ether insoluble part by filtration. A reddish brown gummy product was isolated from ether soluble part by a work-up process with ether and water which was dried over anhydrous $MgSO_4$ and followed by the evaporation of the solvent under reduced pressure after filtration. The physical constants are as follows.

[(4-CH_3-C_6H_4S)(C_6H_5)P(S)(NH-C_6H_4-4-OCH_3)]: Reddish brown gummy substance; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 14.5, 7.7 Hz, 2H), 7.53-7.51 (m, 1H), 7.47-7.44 (m, 2H), 7.18 (d, J = 7.2 Hz, 2H), 7.08 (d, J = 7.2 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 4.92 (d, J = 6.8 Hz, N-H, 1H), 3.76 (s, 3H, OCH_3), 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4 (s), 139.9 (d, J = 3.0 Hz), 136.2 (d, J = 3.8 Hz), 134.9 (d, J_{P-C} = 105.4 Hz), 132.6 (d, J = 4.5 Hz), 132.2 (d, J = 3.0 Hz), 130.7 (d, J = 11.4 Hz), 129.8 (d, J = 2.3 Hz), 128.6 (d, J = 14.4 Hz), 124.0 (d, J = 6.1 Hz), 121.7 (d, J = 6.0 Hz), 114.3 (s), 55.5 (s, OCH_3), 21.4 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 73.2 (s, 1P); IR (KBr, cm^{-1}) 3271 (-NH-), 3076, (C-H, aromatic), 2928, 2861 (-CH_3), 1510 (C=C, Ar) 1438 (P-C, Ar), 809 (P=S); GCMS: m/z, 385 (M^+); Anal. Calcd for $C_{20}H_{20}ONPS_2$: C, 62.31; H, 5.23; N, 3.63. Found: C, 62.59; H, 5.25; N, 3.47.

Kinetic measurements. The kinetic study was performed with a computer controlled conductivity bridge. All the reactions were carried out under pseudo-first-order conditions, using large excesses of nucleophiles: [Substrate] = 3×10^{-3} M, [X-Aniline] = 0.5-0.9 M. At least five different aniline concentrations were employed and replicate values of k_{obsd} were determined to obtain $k_{H(D)}$, reproducible to within ± 3%.

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9. The obtained activation enthalpy and entropy values from the second-order rate constants at 55.0, 60.0, and 65.0 °C are as follows: $\Delta H^{\neq}$ = 4.5 ± 0.6 kcal/mol and $\Delta S^{\neq}$ = 58 = 2 e.u. for X = 4-MeO and Y = 4-Me, $\Delta H^{\neq}$ = 2.5 ± 0.1 and $\Delta S^{\neq}$ = 64 ± 1 for X = 4-MeO and Y = 3-MeO, $\Delta H^{\neq}$ = 2.4 = 0.1 and $\Delta S^{\neq}$ = 69 = 1 for X = H and Y = 4-Me, and $\Delta H^{\neq}$ = 3.8 = 0.6 and $\Delta S^{\neq}$ = 65 = 2 for X = H and Y = H.
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