Kinetics and Mechanism of the Anilinolysis of *O*-Ethyl Phenyl Phosphonochloridothioate in Acetonitrile

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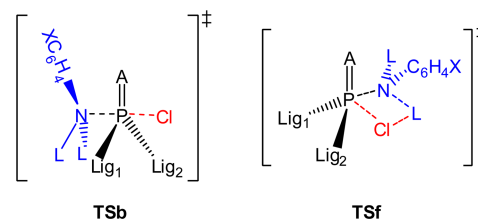*Received April 1, 2012, Accepted May 23, 2012*

The nucleophilic substitution reactions of *O*-ethyl phenyl phosphonochloridothioate with substituted anilines $(XC_6H_4NH_2)$ and deuterated anilines $(XC_6H_4ND_2)$ are kinetically investigated in acetonitrile at 55.0 °C. The deuterium kinetic isotope effects (DKIEs) invariably increase from a secondary inverse DKIE ($k_H/k_D = 0.93$) to a primary normal DKIE ($k_H/k_D = 1.28$) as the substituent of nucleophile (X) changes from electron-donating to electron-withdrawing. These can be rationalized by the gradual transition state (TS) variation from a backside to frontside attack. A concerted S_N2 mechanism is proposed. A trigonal bipyramidal TS is proposed for a backside attack while a hydrogen-bonded, four-center-type TS is proposed for a frontside attack.

Key Words : Phosphoryl transfer reaction, Anilinolysis, *O*-Ethyl phenyl phosphonochloridothioate, Deuterium kinetic isotope effect

Introduction

In previous work, this lab reported upon various types of phosphoryl and thiophosphoryl transfer reactions, experimentally and theoretically. The kinetics and mechanism of the anilinolyses of $(Lig_1)(Lig_2)P(=O$ or $=S)Cl$-type substrates in acetonitrile (MeCN) were investigated by means of the deuterium kinetic isotope effects (DKIEs) involving deuterated anilines $(XC_6H_4ND_2)$, selectivity parameters, and steric effects of the two ligands (Lig_1 and Lig_2).
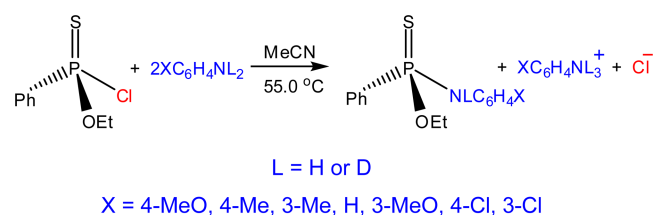
It is well known that the DKIEs are one of the strong tools to clarify the reaction mechanism. The DKIEs can be only secondary inverse ($k_H/k_D < 1$) in a normal S_N2 reaction, since the N–H(D) vibrational frequencies invariably increase upon going to the transition state (TS) (in-line-type TSb in Scheme 1; backside nucleophilic attack), given the increase in steric hindrance in the bond formation step; the greater the bond formation, the greater the steric congestion occurs, and the smaller the k_H/k_D value becomes.[1] In contrast, when partial deprotonation of the aniline occurs in a rate-limiting step by hydrogen bonding (hydrogen-bonded, four-center-type TSf in Scheme 1; frontside nucleophilic attack), the DKIEs are primary normal ($k_H/k_D > 1$); the greater the extent of the hydrogen bond that occurs, the greater the k_H/k_D value becomes.[2] The real primary normal DKIE due to the hydrogen bond between the hydrogen of the N–H(D) moiety and Cl leaving group should be greater than the observed value since the observed DKIEs would be the sum of: (i) the primary normal DKIE, $k_H/k_D > 1$, because of the partial deprotonation of one of the two N–H(D) bonds in the TSf for a frontside attack; (ii) the secondary inverse DKIE, $k_H/k_D < 1$, because of the steric hindrance that increases the out-of-plane bending vibrational frequencies of the other N–H(D) bond in TSf for a frontside attack; (iii) lowering the k_H/k_D value because of the nonlinear and unsymmetrical structure of $N \cdots H(D) \cdots Cl$ in TSf; and finally (iv) lowering the k_H/k_D

Scheme 1. Backside attack TSb and frontside attack involving hydrogen-bonded, four-center-type TSf (L = H or D; A = O or S; Lig_1 and Lig_2 represent the two ligands).

value because of heavy atom (N in the nucleophile and Cl in the leaving group) contribution to the reaction-coordinate motion. When the reaction proceeds simultaneously through both pathways, backside (TSb) and frontside (TSf) attack, the observed DKIEs are the sum of both effects, secondary inverse and primary normal, and the obtained value of k_H/k_D can be greater or lesser than unity depending on the proportion of the two pathways.

The anilinolyses of phosphonochloridothioates showed surprising results of DKIEs in MeCN:[3] (i) In Y-*O*-aryl methyl phosphonochloridothioates [**1**: $Me(YC_6H_4O)P(=S)Cl$],[3a] nonlinear free-energy correlations, biphasic concave downward Hammett and Brönsted plots with a break region between X = H and 4-Cl, were observed. The DKIEs are distinctly divided into two parts, *unprecedented* great secondary inverse ($k_H/k_D = 0.37$-$0.57 \ll 1$) with less basic anilines (X = 4-Cl, 3-Cl, 3-NO_2) and primary normal ($k_H/k_D = 1.03$-1.30) with more basic anilines (X = 4-MeO, 4-Me, H), rationalized by backside attack TSb with less basic anilines while frontside attack TSf with more basic anilines. The extraordinary secondary inverse DKIEs with less basic anilines suggest that the steric congestion in the TS is huge and the degree of bond formation is really extensive; (ii) In Y-*O*-aryl phenyl phosphonochloridothioates [**3**: $Ph(YC_6H_4O)P(=S)Cl$],[3b] the DKIEs invariably increase from

L = H or D

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

Scheme 2. The nucleophilic substitution reactions of *O*-ethyl phenyl phosphonochloridothioate (**2**) with $XC_6H_4NH_2(D_2)$ in MeCN at 55.0 °C.

an extremely large secondary inverse ($k_H/k_D = 0.44$; min) to a primary normal ($k_H/k_D = 1.34$; max) as both substituents of nucleophile (X) and substrate (Y) change from electron-donating to electron-withdrawing, substantiated by the gradual TS variation from backside attack TSb to frontside attack TSf; (iii) In Y-*S*-aryl phenyl phosphonochloridothioates [**4**: Ph(YC_6H_4S)P(=S)Cl],[3c] the DKIEs are secondary inverse ($k_H/k_D = 0.65$-0.98), rationalized by predominant backside attack TSb.

In the present work, the kinetics and mechanism of the reactions of *O*-ethyl phenyl phosphonochloridothioate (**2**) with anilines ($XC_6H_4NH_2$) and deuterated anilines ($XC_6H_4ND_2$) in MeCN at 55.0 ± 0.1 °C (Scheme 2) are examined on the basis of the DKIEs, selectivity parameters, and steric effects of the two ligands on the rate. The purpose of this work is to gain further information on the anilinolyses of phosphonochloridothioates depending upon the two ligands as well as to compare with the kinetic results of **1**, **3**, and **4**. The numbering of the substrates follows the size of the two ligands.

Results and Discussion

The B3LYP/6-311+G(d,p) geometry, bond angles, and natural bond order (NBO) charges of **2** in the gas phase are shown in Figure 1.[4] The MO theoretical structure shows that the sulfur, oxygen, carbon, and chlorine have more or less distorted tetrahedral geometry with the phosphorus atom at the center.

The observed pseudo-first-order rate constants (k_{obsd}) were found to follow Eq. (1) for all the reactions under pseudo-first-order conditions with a large excess of aniline nucleophile. The k_0 values were negligible ($k_0 \approx 0$) in MeCN. The
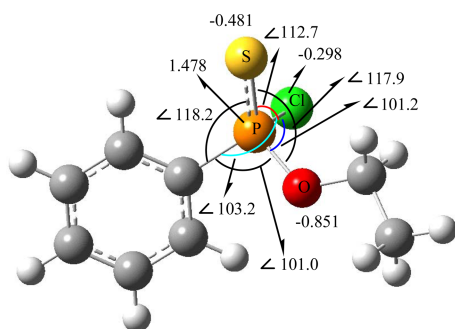
second-order rate constants ($k_{H(D)}$) were determined with at least five concentrations of anilines. The linear plots of Eq. (1) suggest that there is no base-catalysis or noticeable side reaction and that the overall reaction is described by Scheme 2.

$$k_{obsd} = k_0 + k_{H(D)}[XC_6H_4NH_2(D_2)] \qquad (1)$$

The second-order rate constants (k_H and k_D) are summarized in Table 1, together with the deuterium kinetic isotope effects (DKIEs; k_H/k_D) and Hammett ρ_X and Brönsted β_X selectivity parameters. The pK_a(X) values of the X-anilines in water were used to obtain the Brönsted β_X values in MeCN, and this procedure was justified experimentally and theoretically.[5] The values of pK_a(X) and σ_X of the deuterated X-anilines are assumed to be identical to those of the X-anilines. Perrin and coworkers reported that the basicities of β-deuterated analogs of benzylamine, *N,N*-dimethylaniline and methylamine increase roughly by 0.02 pK_a units per deuterium, and that these effects are additive.[6] Thus, the

Table 1. The Second-Order Rate Constants ($k_{H(D)} \times 10^3$/M^{-1} s^{-1}), Selectivity Parameters (ρ_X and β_X),[a] and DKIEs (k_H/k_D) of the Reactions of *O*-Ethyl Phenyl Phosphonochloridothioate (**2**) with $XC_6H_4NH_2(D_2)$ in MeCN at 55.0 °C

X	$k_H \times 10^3$	$k_D \times 10^4$	k_H/k_D
4-MeO	61.5 ± 0.1^b	66.1 ± 0.3	0.930 ± 0.005^g
4-Me	28.3 ± 0.1	28.8 ± 0.1	0.983 ± 0.005
3-Me	10.9 ± 0.1	10.4 ± 0.1	1.05 ± 0.01
H	6.93 ± 0.01	5.93 ± 0.01	1.17 ± 0.01
3-MeO	2.77 ± 0.01	2.30 ± 0.01	1.20 ± 0.01
4-Cl	1.07 ± 0.01	0.883 ± 0.002	1.21 ± 0.01
3-Cl	0.370 ± 0.001	0.290 ± 0.001	1.28 ± 0.01
$-\rho_{X(H \text{ and } D)}$	3.47 ± 0.03^c	3.69 ± 0.03^e	
$\beta_{X(H \text{ and } D)}$	1.23 ± 0.04^d	1.31 ± 0.05^f	

[a]The σ values were taken from ref. 7. The pK_a values of X-anilines in water were taken from ref. 8. [b]Standard deviation. [c]Correlation coefficient, r = 0.999. [d]r = 0.999. [e]r = 0.999. [f]r = 0.998. [g]Standard error {= 1/ $k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$} from ref. 9.
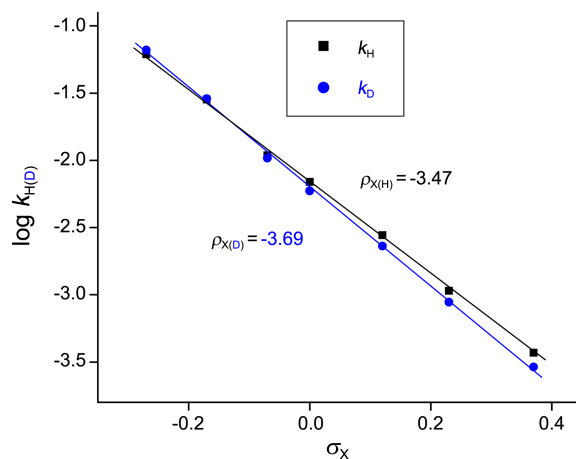

Figure 2. The Hammett plots (log $k_{H(D)}$ *vs* σ_X) of the reactions of *O*-ethyl phenyl phosphonochloridothioate (**2**) with $XC_6H_4NH_2(D_2)$ in MeCN at 55.0 °C.

Figure 1. The B3LYP/6-311+G(d,p) geometry of *O*-ethyl phenyl phosphonochloridothioate (**2**) in the gas phase.
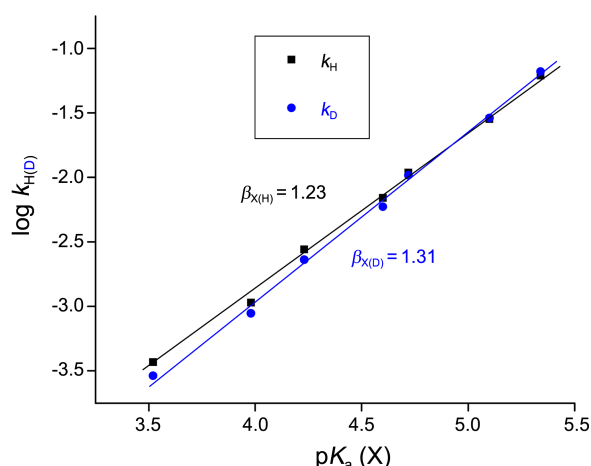
Figure 3. The Brönsted plots [log $k_{H(D)}$ *vs* pK_a(X)] of the reactions of *O*-ethyl phenyl phosphonochloridothioate (**2**) with XC$_6$H$_4$NH$_2$(D$_2$) in MeCN at 55.0 °C.

pK_a(X) values of deuterated X-anilines may be slightly greater than those of X-anilines, however, the difference is too small to be taken into account. Figures 2 and 3 show the Hammett (log $k_{H(D)}$ *vs* σ_X) and Brönsted [log $k_{H(D)}$ *vs* pK_a(X)] plots with X, respectively. The stronger nucleophile leads to the faster rate as observed in a typical nucleophilic substitution reaction with positive charge development at the nucleophilic N atom in the TS. The DKIEs invariably increase from the secondary inverse (k_H/k_D = 0.93-0.98 < 1) with X = (4-MeO, 4-Me) to primary normal (k_H/k_D = 1.05-1.28 > 1) with X = (3-Me, H, 3-MeO, 4-Cl, 3-Cl) as the aniline becomes less basic. The magnitudes of ρ_X and β_X values with anilines are slightly smaller than those with deuterated anilines, suggesting less sensitive to substituent X effect of anilines compared to that of deuterated anilines.

The second-order rate constants (k_H) with unsubstituted aniline (C$_6$H$_5$NH$_2$) at 55.0 °C, NBO charges at the reaction center P atom [B3LYP/6-311+G(d,p) level of theory] in the gas phase,[5] Brönsted coefficients ($\beta_{X(H)}$), cross-interaction constants (CICs, ρ_{XY}),[10] and DKIEs (k_H/k_D) of the reactions of **1-4** with XC$_6$H$_4$NH$_2$(D$_2$) in MeCN at 55.0 °C are summarized in Table 2. There is no correlation between the anilinolysis rates of **1-3** and positive charges at the reaction center P atom, implying that the inductive effects of the two ligands do not play any role to decide the reactivity of anilinolyses of R$_1$(R$_2$O)P(=S)Cl-type substrates. The anilinolysis rates of **1-3** are inversely proportional to the size of the

two ligands, **3**(Ph,PhO) > **2**(Ph,EtO) > **1**(Me,PhO), suggesting that the steric effects of the two ligands are the major factor to determine the anilinolysis rates. The larger the two ligands, the steric effects become greater in the TS, and the rate becomes slower. The size of PhS is more or less larger than that of PhO and, thus, the steric effects of the two ligands of **4** with PhS are somewhat greater than those of **3** with PhO in the TS. However, the anilinolysis rate of **4** is nine times slower than that of **3** which cannot be rationalized by the steric effects of the two ligands. The considerably slower rate of **4** compared to that of **3** may be due to the difference of NBO charge at P atom, (NBO charge) = 1.462(**3**)-0.999(**4**) = 0.463.

The cross-interaction constant (CIC; ρ_{XY}) is negative in a normal S$_N$2 reaction (or in a stepwise reaction with a rate-limiting bond formation) and positive in a stepwise reaction with a rate-limiting leaving group expulsion from the intermediate.[10] The magnitude of the CIC is inversely proportional to the distance between X and Y through the reaction center; the tighter the TS, the greater the magnitude of the CIC.[10] Here, X and Y denote the substituents of the nucleophile and substrate, respectively. A concerted mechanism was proposed with more basic anilines based on negative ρ_{XY} (= −0.95) value while a stepwise mechanism with a rate-limiting leaving group departure from the intermediate with less basic anilines based on the positive ρ_{XY} (= 0.77) value for the anilinolysis of **1**.[1a] A concerted mechanism was proposed on the basis of negative ρ_{XY} [= −0.38(**3**) and −0.31(**4**)] values for the anilinolyses of **3** and **4**, respectively.[1b,c]

In the present work, a concerted mechanism is proposed on the basis of: (i) the Brönsted coefficient ($\beta_{X(H)}$ = 1.23: comparable with $\beta_{X(H)}$(**3**) = 1.22-1.33 and $\beta_{X(H)}$(**4**) = 1.21-1.25);[1b,c] (ii) and the same variation trends of the DKIEs with X from secondary inverse to primary normal DKIEs as observed in **3**, where the magnitude of k_H/k_D increases with a weaker nucleophile.[1b] The DKIEs (k_H/k_D = 0.93-1.28) suggest that the nucleophile attacking direction is changed from predominant backside attack (TSb; Scheme 1) to predominant frontside attack (a hydrogen-bonded, four-center-type TSf; Scheme 1) as the aniline becomes less basic. These phenomena were also observed in the anilinolysis of **3**.[1b] These results suggest that the fraction of backside attack gradually decreases, while that of frontside attack gradually increases as the aniline becomes weaker.

Activation parameters, enthalpy and entropy of activation,

Table 2. Summary of the Second-Order Rate Constants ($k_H \times 10^3$/M^{-1} s^{-1}) with C$_6$H$_5$NH$_2$, NBO Charges at the Reaction Center P Atom, Brönsted Coefficients ($\beta_{X(H)}$), CICs (ρ_{XY}), and DKIEs (k_H/k_D) for the Reactions of **1-4** with XC$_6$H$_4$NH$_2$(D$_2$) in MeCN at 55.0 °C

Substrate	$10^3 k_H$[a]	charge at P	$\beta_{X(H)}$	ρ_{XY}	k_H/k_D
1: Me(YC$_6$H$_4$O)P(=S)Cl	7.25[b]	1.432[b]	0.14-0.46,[c] 1.31-1.54[d]	−0.95,[c] +0.77[d]	1.03-1.30,[c] 0.37-0.57[d]
2: Ph(EtO)P(=S)Cl	6.93	1.478	1.23	–	0.93-1.28
3: Ph(YC$_6$H$_4$O)P(=S)Cl	1.50[b]	1.462[b]	1.22-1.33	−0.38	0.44-1.34
4: Ph(YC$_6$H$_4$S)P(=S)Cl	0.175[b]	0.999[b]	1.21-1.25	−0.31	0.65-0.98

[a]The value with unsubstituted aniline. [b]The value with Y = H. [c]X = (4-MeO, 4-Me, H). [d]X = (4-Cl, 3-Cl, 3-NO$_2$).

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Table 3. Activation Parameters for the Reactions of *O*-Ethyl Phenyl Phosphonochloridothioate (**2**) with Aniline (C₆H₅NH₂) in MeCN

t/°C	$k_H \times 10^3$/M⁻¹ s⁻¹	$\Delta H^{\ddagger}$/kcal mol⁻¹	$-\Delta S^{\ddagger}$/cal mol⁻¹ K⁻¹
45.0	5.27 ± 0.01		
55.0	6.93 ± 0.01	4.6	55
65.0	8.63 ± 0.03		

are determined for the anilinolysis (with C₆H₅NH₂) of **2** in Table 3. The enthalpy of activation is relatively low (4.6 kcal mol⁻¹) and entropy of activation is relatively large negative values (–55 cal mol⁻¹ K⁻¹). The relatively low of activation enthalpy and large negative value of activation entropy are typical for the aminolyses of P=S systems.

Experimental Section

Materials. Phenyl thiophosphonic dichloride (more than 98.0%), ethanol (more than 99.8%) were used for substrate synthesis, and HPLC grade acetonitrile (water content is less than 0.005%) was used for kinetic studies without further purification. Anilines were redistilled or recrystallized before use as previously described.[3] Deuterated anilines were synthesized by heating anilines and deuterium oxide (99.9 atom %D) and one drop of HCl as catalyst at 85 °C for 72 hr, and after numerous attempts, anilines were deuterated more than 98%, as confirmed by ¹H NMR. *O*-Ethyl phenyl phosphonochloridothioate was prepared by the following one step synthetic route.[11] Phenyl thiophosphonic dichloride was added dropwise to ethanol over 10 min. After stirring for 30 min in ice-water, the reaction mixture was extracted using distilled water/ethyl acetate. The organic extract was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and a pale yellow liquid product was isolated through column chromatography [silica gel, hexane/ethyl acetate (55:1)]. Analytical and spectroscopic data of the product gave the following results (see Supporting Information):

(C₆H₅)(C₂H₅O)P(=S)Cl: Pale yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 1.45 (t, J = 7.2 Hz, 3H, CH₃, EtO), 4.36-4.47 (q, 2H, OCH₂, EtO), 7.48-7.60 (m, 3H, Ph), 8.00-8.06 (m, 2H, Ph); ¹³C NMR (100 MHz, CDCl₃) δ 15.73, 15.82 (CH₃, EtO), 63.67, 63.74 (OCH₂, EtO), 128.40, 128.56, 130.38, 130.51, 133.06, 133.10 (C=C, aromatic); ³¹P NMR (162 MHz, CDCl₃) δ 93.38 (s, 1P, P=S); MS (EI) *m/z*, 220 (M⁺).

Kinetic Procedure. Rates were measured conductometrically at 55.0 °C. The conductivity bridge used in this work was a self-made computer automated A/D converter conductivity bridge. Pseudo-first-order rate constants, k_{obsd} were measured by curve fitting analysis in origin program with a large excess of anilines, [substrate] = 1 × 10⁻³ M and [X-aniline] = (0.03-0.15) M. Second-order rate constants, $k_{H(D)}$, were obtained from the slope of a plot of k_{obsd} *vs.* [X-aniline] with at least five concentrations of anilines. The pseudo-first-order rate constant values (k_{obsd}) were the average of at least three runs that were reproducible within ± 3%.

Product Analysis. *O*-Ethyl phenyl phosphonochloridothioate was reacted with excess aniline, for more than 15 half-lives at 55.0 °C in MeCN. The aniline hydrochloride salt was separated by filtration. Acetonitrile was evaporated under reduced pressure. The product was isolated with ether by a work-up process and dried over anhydrous MgSO₄. After filtration the product was isolated by evaporating the solvent under reduced pressure. The analytical and spectroscopic data of the product gave the following results (see Supporting Information):

(C₆H₅)(C₂H₅O)P(=S)NHC₆H₅: Brown gummy substance; ¹H NMR (400 MHz, CDCl₃) δ 1.21-1.39 (m, 3H, CH₃, EtO), 4.09-4.37 (q, 2H, OCH₂, EtO), 5.48 (s, 1H, NH), 6.75-6.78 (d, J = 8.4 Hz, 2H, phenyl), 6.84-6.88 (t, J = 8.4 Hz, 1H, phenyl), 7.08-7.12 (t, J = 8.0 Hz, 2H, phenyl), 7.35-7.44 (m, 3H, phenyl), 7.78-7.84 (m, 2H, phenyl); ¹³C NMR (100 MHz, CDCl₃) δ 15.89 (CH₃, EtO), 61.15 (OCH₂, EtO), 117.68, 121.91, 128.60, 129.23, 130.64, 131.81, 139.93 (C=C, aromatic); ³¹P NMR (162 MHz, CDCl₃) δ 74.12 (s, 1P, P=S); MS (EI) *m/z*, 277 (M⁺).

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