

## Kinetics and Mechanism of the Aminolysis of Dimethyl Thiophosphinic Chloride with Anilines

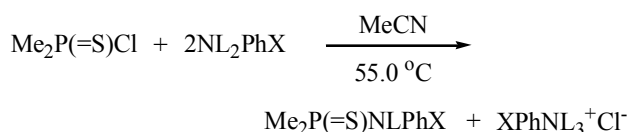
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Received February 12, 2009, Accepted March 9, 2009

**Key Words:** Anilinolysis, Dimethyl thiophosphinic chloride, Steric effect, Deuterium kinetic isotope effect

Continuing our experimental and theoretical studies on phosphoryl and thiophosphoryl transfer reactions,<sup>1</sup> nucleophilic substitution reactions of dimethyl thiophosphinic chloride with anilines are studied kinetically. To clarify the (thio)phosphoryl transfer mechanism, as well as to compare the reactivity, selectivity parameters, and deuterium kinetic isotope effects (DKIEs) of dimethyl phosphinic chloride [Me<sub>2</sub>P(=O)Cl; **2**],<sup>1i</sup> diphenyl thiophosphinic chloride [Ph<sub>2</sub>P(=S)Cl; **3**],<sup>1c</sup> and diphenyl phosphinic chloride [Ph<sub>2</sub>P(=O)Cl; **4**],<sup>1d</sup> we investigate the aminolysis of dimethyl thiophosphinic chloride [Me<sub>2</sub>P(=S)Cl; **1**] with substituted anilines (XC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>) and deuterated anilines (XC<sub>6</sub>H<sub>4</sub>ND<sub>2</sub>) in acetonitrile at 55.0 °C.



L = H or D, X = 4-MeO, 4-Me, 3-Me, H, 3-MeO, 4-Cl, 3-Cl

The second-order rate constants ( $k_{\text{H}}$  and  $k_{\text{D}}$ ) for the reactions were obtained as the slope of  $k_{\text{obsd}}$  (pseudo-first-order rate constant) against at least five concentrations of aniline nucleophiles [XC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>(D<sub>2</sub>)] in eq 1.

$$k_{\text{obsd}} = k_0 + k_{\text{H(D)}}[\text{XC}_6\text{H}_4\text{NH}_2(\text{D}_2)] \quad (1)$$

The intercept ( $k_0$ ) was negligible in all cases. No third-order kinetics was observed and no complications were found in the determination of  $k_{\text{obsd}}$ . The  $k_{\text{H}}$  values are summarized in Table 1, together with  $k_{\text{D}}$  values involving deuterated anilines. The

**Table 1.** Second-Order Rate Constants,  $k_{\text{H}}$  and  $k_{\text{D}}$  ( $\times 10^3/\text{M}^{-1}\text{s}^{-1}$ ), of the Reactions of Dimethyl Thiophosphinic Chloride (**1**) with XC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> and XC<sub>6</sub>H<sub>4</sub>ND<sub>2</sub> in Acetonitrile at 55.0 °C

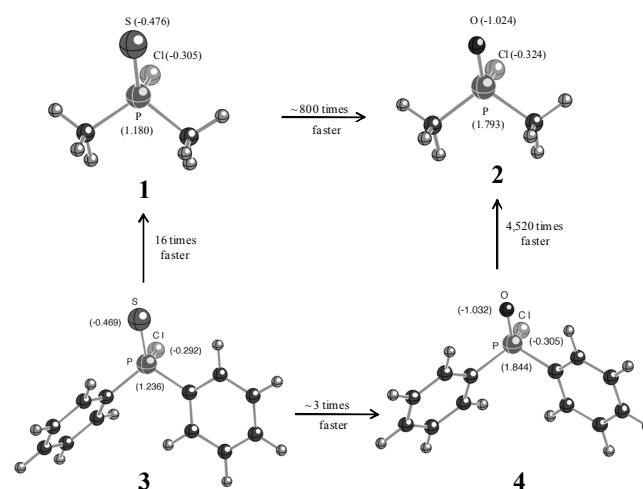
| X     | $k_{\text{H}}$          | $k_{\text{D}}$ | $k_{\text{H}}/k_{\text{D}}$ |
|-------|-------------------------|----------------|-----------------------------|
| 4-MeO | 95.6 ± 0.9 <sup>a</sup> | 101 ± 2        | 0.945 ± 0.014 <sup>b</sup>  |
| 4-Me  | 35.0 ± 1.0              | 37.9 ± 0.6     | 0.953 ± 0.030               |
| 3-Me  | 16.2 ± 0.2              | 17.8 ± 0.3     | 0.910 ± 0.019               |
| H     | 9.79 ± 0.26             | 11.1 ± 0.1     | 0.882 ± 0.025               |
| 3-MeO | 3.97 ± 0.11             | 4.58 ± 0.12    | 0.867 ± 0.033               |
| 4-Cl  | 1.47 ± 0.04             | 1.80 ± 0.07    | 0.817 ± 0.038               |
| 3-Cl  | 0.407 ± 0.003           | 0.550 ± 0.008  | 0.740 ± 0.012               |

<sup>a</sup>Standard deviation <sup>b</sup>Standard error  $\{= 1/k_{\text{D}}[(\Delta k_{\text{H}})^2 + (k_{\text{H}}/k_{\text{D}})^2 \times (\Delta k_{\text{D}})^2]^{1/2}\}^2$

rate increases 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).

As shown in Figure 1, the reactivity of the P=O system is greater than that of its P=S counterpart [ $k_{\text{H}}(\mathbf{2})/k_{\text{H}}(\mathbf{1}) \approx 800$  and  $k_{\text{H}}(\mathbf{4})/k_{\text{H}}(\mathbf{3}) \approx 3$ ]. It is well known that the P=O systems are generally more reactive than their P=S counterparts for several reasons, the so-called “thio effect”, which is mainly the electronegativity difference between O and S and favors O over S.<sup>3</sup> The natural bond order (NBO) charges<sup>4</sup> of the reaction center P in the gas phase are 1.180 (**1**), 1.793 (**2**),<sup>1i</sup> 1.236 (**3**),<sup>1c</sup> and 1.844 (**4**),<sup>1d</sup> which are consistent with the inductive effects of Ph ( $\sigma_1 = +0.12$ )<sup>5</sup> and Me ( $\sigma_1 = -0.01$ )<sup>5</sup> ligands. Solely considering the positive charge of the reaction center P atom in the P=S (and P=O) system, the anilinolysis rate of **1** (and **2**) should be slower than that of **3** (and **4**), *i.e.*,  $k_{\text{H}}(\mathbf{1})/k_{\text{H}}(\mathbf{3}) < 1$  [and  $k_{\text{H}}(\mathbf{2})/k_{\text{H}}(\mathbf{4}) < 1$ ]. However, the observed rate ratios of  $k_{\text{H}}(\mathbf{1})/k_{\text{H}}(\mathbf{3}) = 16$  and  $k_{\text{H}}(\mathbf{2})/k_{\text{H}}(\mathbf{4}) = 4,520$  are completely opposite to expectations from the inductive effects of the ligands, strongly suggesting that the inductive effects of the ligands do not play an important role to decide the reactivity in each reaction system, P=S or P=O system.<sup>6</sup>

The values of second-order rate constants ( $k_{\text{H}}$ ), selectivity parameters ( $\rho_{\text{X}}$  and  $\beta_{\text{X}}$ <sup>9</sup>; see Figure 2), and DKIEs ( $k_{\text{H}}/k_{\text{D}}$ ) of



**Figure 1.** The B3LYP/6-311+G(d,p)<sup>4</sup> geometries and NBO charges of **1**, **2**,<sup>1i</sup> **3**,<sup>1c</sup> and **4**<sup>1d</sup> in the gas phase. The anilinolysis (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>) rate ratios in acetonitrile at 55.0 °C are displayed next to the arrows.

**Table 2.** The  $k_H$  ( $\times 10^4/\text{M}^{-1}\text{s}^{-1}$ ),  $\rho_X$ ,  $\beta_X$ , and  $k_H/k_D$  Values of the Reactions of  $\text{Me}_2\text{P(=S)Cl}$  (**1**),  $\text{Me}_2\text{P(=O)Cl}$  (**2**),  $\text{Ph}_2\text{P(=S)Cl}$  (**3**), and  $\text{Ph}_2\text{P(=O)Cl}$  (**4**) with X-Anilines in Acetonitrile at 55.0 °C

| Substrate             | $k_H^a$             | $-\rho_X^b$                          | $\beta_X^c$                          | $k_H/k_D$     | ref.      |
|-----------------------|---------------------|--------------------------------------|--------------------------------------|---------------|-----------|
| <b>1</b>              | 97.9                | 3.60 <sup>d</sup> /3.45 <sup>e</sup> | 1.28 <sup>f</sup> /1.22 <sup>g</sup> | 0.740 - 0.945 | This work |
| <b>2</b> <sup>h</sup> | 78,200 <sup>i</sup> | 4.59/4.42                            | 1.62/1.56                            | 0.703 - 0.899 | 1i        |
| <b>3</b>              | 6.01                | 3.97/3.94                            | 1.40/1.40                            | 1.00 - 1.10   | 1e        |
| <b>4</b>              | 17.3                | 4.78/4.56                            | 1.69/1.62                            | 1.42 - 1.82   | 1d        |

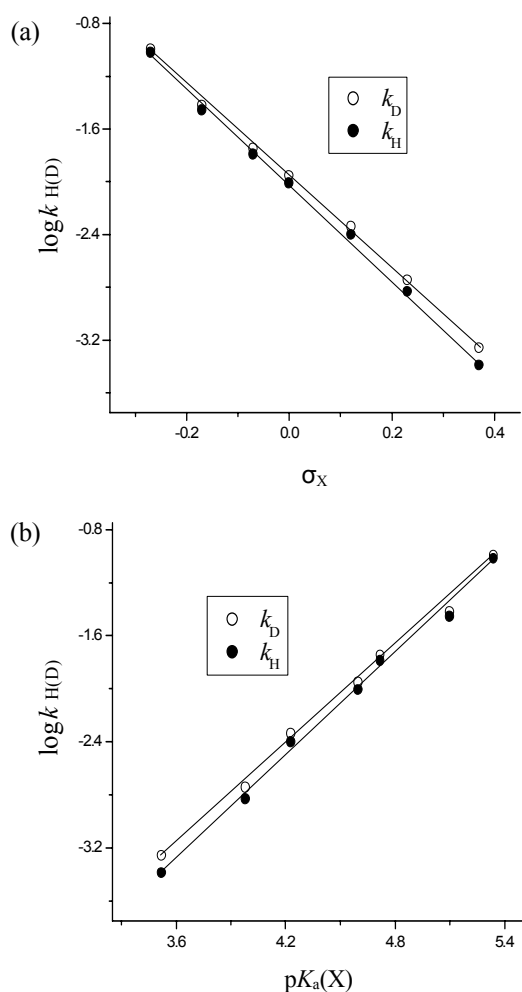
<sup>a</sup>When X = H <sup>b</sup>The  $\sigma$  values were taken from ref. 7 <sup>c</sup>The  $\text{pK}_a$  values in water were taken from ref. 8 <sup>d</sup>Calculated from  $k_H$  values. Correlation coefficient ( $r$ ) = 0.999 <sup>e</sup>Calculated from  $k_D$  values.  $r$  = 0.999 <sup>f</sup>Calculated from  $k_H$  values.  $r$  = 0.997 <sup>g</sup>Calculated from  $k_D$  values.  $r$  = 0.997 <sup>h</sup>The values of  $\rho_X$ ,  $\beta_X$ , and  $k_H/k_D$  are at 15.0 °C <sup>i</sup>The  $k_H$  value of  $7.82 \text{ M}^{-1} \text{ s}^{-1}$  at 55.0 °C was calculated by extrapolation in the Arrhenius plot ( $r$  = 0.999) with empirical kinetic data:  $k_H = 0.776$  (0.0 °C), 1.01 (5.0 °C) and  $1.61 \text{ M}^{-1} \text{ s}^{-1}$  (15.0 °C) from ref. 1i

the reactions of **1**, **2**, **3**, and **4** with X-anilines in acetonitrile are summarized in Table 2. The observed rate ratios of  $k_H(\mathbf{1})/k_H(\mathbf{3}) = 16$  and  $k_H(\mathbf{2})/k_H(\mathbf{4}) = 4,520$  can be rationalized by the degree of steric hindrance. Two phenyl groups are bonded to the reaction center P atom in **3** (and **4**) while two methyl groups are bonded in **1** (and **2**). As a result, the steric hindrance in **3** (and **4**) would be much greater than that in **1** (and **2**) when the aniline nucleophile attacks opposite

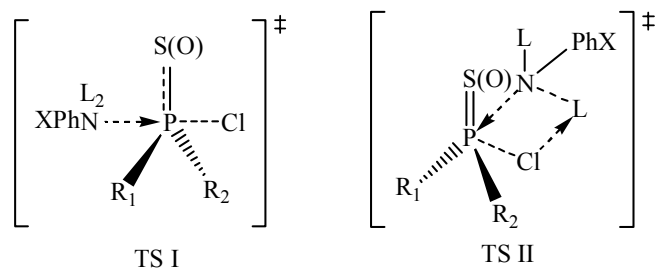
the Cl leaving group, *i.e.*, backside nucleophilic attack.

The DKIEs can only be secondary inverse ( $k_H/k_D < 1.0$ ) in a normal  $\text{S}_\text{N}2$  reaction, since the N-H(D) vibrational frequencies invariably increase on going to the TS because of an increase in steric congestion in the bond-making process, and the greater the extent of bond formation occurs, the smaller the  $k_H/k_D$  value becomes.<sup>10</sup> In contrast, when partial deprotonation of the aniline occurs in rate-limiting step by hydrogen bonding, the  $k_H/k_D$  values would be greater than unity.<sup>11</sup>

A backside nucleophilic attack concerted mechanism with a late, product-like TS (in-line type TS I) in the anilinolysis of Y-aryl phenyl chlorophosphates [(YPhO)(PhO)P(=O)Cl] in acetonitrile at 55.0 °C was proposed based on large  $\rho_X$  (and  $\beta_X$ ), large negative cross-interaction constant<sup>12</sup> ( $\rho_{XY} = -1.31$ ), and the secondary inverse DKIEs ( $k_H/k_D = 0.61 - 0.87$ ).<sup>1a</sup> In contrast, a partial participation of frontside attack concerted mechanism through a hydrogen-bonded four-center type TS II was suggested for the anilinolysis of Y-aryl phenyl chlorothiophosphates [(YPhO)(PhO)P(=S)Cl] in acetonitrile at 55.0 °C based on several reasons, mainly the primary normal DKIEs ( $k_H/k_D = 1.11 - 1.33$ ) and  $\rho_{XY} = -0.22$ .<sup>1c</sup> In the anilinolysis of **3** in acetonitrile at 55.0 °C,<sup>1c</sup> a partial frontside attack concerted mechanism through a hydrogen-bonded four-center type TS II was suggested on the basis of relatively small value of primary normal DKIEs,  $k_H/k_D = 1.00 - 1.10$ , the same as in Y-aryl phenyl chlorothiophosphates. In the anilinolysis of **4** in acetonitrile at 55.0 °C,<sup>1d</sup> the relatively large primary normal  $k_H/k_D$  values,  $k_H/k_D = 1.42 - 1.82$ , imply that the reaction proceeds predominantly through TS II. In the anilinolysis of **2** in acetonitrile at 15.0 °C,<sup>1i</sup> the large secondary inverse DKIEs,  $k_H/k_D = 0.703 - 0.899$ , suggest that the reaction proceeds mainly through TS I.



**Figure 2.** The Hammett (a) and Brønsted (b) plots of the reactions of dimethyl thiophosphinic chloride with  $\text{XC}_6\text{H}_4\text{NH}_2$  ( $\bullet$ ) and  $\text{XC}_6\text{H}_4\text{ND}_2$  ( $\circ$ ) in acetonitrile at 55.0 °C. The  $\sigma$  and  $\text{pK}_a$  values of  $\text{XC}_6\text{H}_4\text{ND}_2$  are assumed to be the same as the  $\sigma$  and  $\text{pK}_a$  values of  $\text{XC}_6\text{H}_4\text{NH}_2$ .



In the present work, the DKIEs,  $k_H/k_D = 0.740 - 0.945$ , are large secondary inverse similar to the anilinolysis of its P=O counterpart, **2**. Thus, a backside nucleophilic attack concerted

mechanism through TS I is proposed for the anilinolysis of **1**. We can say that the steric effect is the major factor to determine not only the reactivity but also the direction of the nucleophilic attack, *i.e.*, two large phenyl ligands lead to a partial participation of frontside nucleophilic attack whereas two small methyl ligands lead to backside attack, especially because of the relatively large size of aniline nucleophile.

When the backside nucleophilic attack is major direction, which leads to the secondary inverse DKIEs,  $k_H/k_D < 1$ , more bond formation will result in smaller  $k_H/k_D$  value. The observed sequence of the  $k_H/k_D$  values of  $X = 4\text{-MeO} > 4\text{-Me} > 3\text{-Me} > \text{H} > 3\text{-MeO} > 4\text{-Cl} > 3\text{-Cl}$  indicates that the weaker nucleophile approaches closer to the reaction center P in the TS compared to the stronger nucleophile, the same tendency as in **2**.

The magnitudes of Hammett  $\rho_X$  and Brønsted  $\beta_X$  values are both large, suggesting extensive bond formation in the TS. The larger magnitudes of  $\rho_X$  and  $\beta_X$  values of P=O systems (**2** and **4**) compared to P=S systems (**1** and **3**) suggest that P=O system has a later, more product-like TS than P=S system. The magnitudes of  $\rho_X$  and  $\beta_X$  values with deuterated anilines ( $\text{XC}_6\text{H}_4\text{ND}_2$ ) are somewhat smaller than those with anilines ( $\text{XC}_6\text{H}_4\text{NH}_2$ ), suggesting less sensitivity to substituent effect of deuterated anilines than of anilines.

### Summary

The aminolysis of dimethyl thiophosphinic chloride with substituted anilines and deuterated anilines is investigated kinetically in acetonitrile at 55.0 °C. When substituents in the nucleophiles were varied, the rate changes were consistent with the nature of a typical nucleophilic substitution reaction. Structure-reactivity relationship between **1**, **2**, **3**, and **4** was discussed based on NBO charges and steric effects. Large Hammett  $\rho_X$  ( $\rho_{\text{nuc}} = -3.60$ ) and Brønsted  $\beta_X$  ( $\beta_{\text{nuc}} = 1.28$ ) values suggest extensive bond formation in the transition state. The relatively large secondary inverse DKIEs ( $k_H/k_D = 0.740 - 0.945$ ) involving deuterated aniline nucleophiles indicate that the aniline nucleophile attacks backside toward the reaction center P atom through trigonal bipyramidal pentacoordinate TS.

### Experimental Section

**Materials.** Dimethyl thiophosphinic chloride, 97% (substrate), and HPLC grade acetonitrile (water content is less than 0.005%) were used for kinetic studies without further purification. Anilines were redistilled or recrystallized before use as previously described.<sup>1</sup> Deuterated anilines were prepared by heating anilines with D<sub>2</sub>O (99.9 atom % D), and one drop of HCl catalyst at 90 °C for 72 hrs and, after numerous attempts, were more than 98% deuterated, as confirmed by <sup>1</sup>H-NMR.<sup>1a-i</sup>

**Kinetic Measurements.** Rates were measured conductometrically using a computer controlled conductivity bridge constructed in this laboratory as described previously.<sup>1</sup> The pseudo-first-order rate constants were determined with large excess of nucleophiles, [substrate] =  $5 \times 10^{-4}$  M and [An] =

0.01 - 0.05 M. The pseudo-first-order rate constant values were the average of three runs, which were reproducible within  $\pm 3\%$ .

**Product Analysis.** Dimethyl thiophosphinic chloride was reacted with excess amount of 4-methyl aniline for more than 15 half-lives in acetonitrile at 55.0 °C. The products were isolated by a work-up process with diethyl ether and dilute HCl. The MgSO<sub>4</sub> was added and kept for two hours. The products finally were isolated by solvent evaporation under reduced pressure after filtration. The products were passed through column chromatography (30% ethyl acetate and n-hexane). The analytical data are as follows.

**(CH<sub>3</sub>)<sub>2</sub>P(=S)NHC<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>.** Brown solid; mp 122-124 °C; <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  1.88-2.01 (6H, m, CH<sub>3</sub>), 2.24-2.34 (3H, m, CH<sub>3</sub>), 4.41 (1H, s, NH), 6.89-7.10 (4H, m, aromatic); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  20.6 (s, CH<sub>3</sub>), 22.9, 23.6 (ss, CH<sub>3</sub>), 120.7, 120.8, 130.0, 132.8, 137.4 (C=C, aromatic); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  62.3 (1P, s, P=S); m/z, 199 (M<sup>+</sup>); found: C 54.2, H 7.3, N 6.8; C<sub>9</sub>H<sub>14</sub>NPS requires C 54.2, H 7.1, N 7.0%.

**Acknowledgments.** This work was supported by Inha University Research Grant.

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  6. Comparing the NBO charges of the reaction center P in the gas phase, the positive charge difference of P atom between P=S and P=O system is great,  $|\Delta\delta| \approx 0.6$ : 1.180 (**1**) < 1.793 (**2**) and 1.236 (**3**) < 1.844 (**4**), resulting in "thio effect". However, within each system, P=S or P=O system, the positive charge difference of P,  $|\Delta\delta| = 0.05\text{--}0.06$ , is too small to be a decisive factor to decide the reactivity over steric factor.
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