Research Article

Journal of Physical Organic Chemistry

Received: 11 September 2008, Revised: 14 October 2008, Accepted: 15 October 2008, Published online in Wiley InterScience: 11 December 2008

(www.interscience.wiley.com) DOI 10.1002/poc.1478

Kinetics and mechanism of the aminolysis of dimethyl and methyl phenyl phosphinic chlorides with anilines

Nilay Kumar Dey[a], Md. Ehtesham Ul Hoque[a], Chan Kyung Kim[a], Bon-Su Lee[a] and Hai Whang Lee[a]*

The reactions of dimethyl phosphinic chloride (1) and methyl phenyl phosphinic chloride (2) with X-anilines have been studied kinetically in acetonitrile at 15.0 and 55.0 °C, respectively. The deuterium kinetic isotope effects (KIEs) involving deuterated aniline nucleophiles ($XC_6H_4ND_2$) are also reported for the same reactions. The obtained KIEs for 1 are secondary inverse ($k_H/k_D = 0.703–0.899 < 1$), while those for 2 are primary normal ($k_H/k_D = 1.62–2.10 > 1$). A concerted mechanism involving predominantly backside nucleophilic attack is proposed for the anilinolysis of 1. A concerted mechanism involving predominantly frontside attack via a hydrogen-bonded four-center-type transition state is proposed for the anilinolysis of 2. The degree of steric hindrance is the major factor that determines both the reactivity of the phosphinates and the direction of the nucleophilic attack on the phosphinates. Copyright © 2008 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: deuterium kinetic isotope effect; anilinolysis; dimethyl phosphinic chloride; methyl phenyl phosphinic chloride; steric effect; frontside attack

INTRODUCTION

Phosphoryl transfer reactions are known to proceed via two main types of mechanisms: a stepwise mechanism involving a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate and a concerted mechanism via a single TBP-5C transition state (TS).[1,2] When the nucleophile attacks the reaction center from the side opposite the leaving group (backside attack), the configuration is inversed. However, when the nucleophile attacks from the leaving group side (frontside attack), the configuration is retained. When backside and frontside nucleophilic attacks occur simultaneously, the relative extents of these reaction pathways lead to products with inversion or retention of the configuration. The relative extents of the pathways depend on the nucleophile, the leaving group and the reaction conditions.[3,4]

In our preceding papers, frontside nucleophilic attack was suggested to take place in the following reactions: aryl bis(4-methoxyphenyl) phosphates [$(4\text{-MeOPhO})_2P(O)OPhZ$] with less basic pyridines,[5] aryl phenyl isothiocyanophosphates [(YPhO)(PhO)P(O)NCS] with more basic pyridines,[6] aryl phenyl chlorothiophosphates [(YPhO)(PhO)P(S)Cl] with anilines,[7] aryl ethyl chlorophosphates [**6**; (YPhO)(EtO)P(O)Cl] and aryl ethyl chlorothiophosphates [(YPhO)(EtO)P(S)Cl] with anilines,[8] diphenyl phosphinic chloride [**3**; $Ph_2P(O)Cl$] with anilines,[9] diphenyl thiophosphinic chloride [$Ph_2P(S)Cl$] with more basic pyridines[10] and anilines,[11] dimethyl chlorothionophosphate [$(MeO)_2P(S)Cl$] with more basic anilines,[12] and diethyl chlorothionophosphate [$(EtO)_2P(S)Cl$] with anilines.[12] These deductions were based mainly on deuterium primary normal kinetic isotope effects (KIEs) and cross-interaction constants.[13–15]

In this work, we investigate the aminolysis of dimethyl phosphinic chloride [**1**; $Me_2P(O)Cl$] and methyl phenyl phosphinic chloride [**2**; MePhP(O)Cl] with substituted anilines ($XC_6H_4NH_2$) in acetonitrile at 15.0 and 55.0 °C, respectively (Eqn (1)). The same reactions were repeated using the corresponding deuterated anilines ($XC_6H_4ND_2$). This work aims to clarify the phosphoryl transfer mechanism, as well as to compare the anilinolysis of diphenyl phosphinic chloride (**3**),[9] dimethyl chlorophosphate [**4**; $(MeO)_2P(O)Cl$],[12] diethyl chlorophosphate [**5**; $(EtO)_2P(O)Cl$],[12] aryl ethyl chlorophosphate (**6**),[8] and aryl phenyl chlorophosphate [**7**; (YPhO)(PhO)P(O)Cl].[16]

$$R_1R_2P(O)Cl + 2XC_6H_4NL_2 \xrightarrow{MeCN} R_1R_2P(O)NLC_6H_4X + XC_6H_4NL_3^+Cl^- \quad (1)$$

* *Correspondence to: H. W. Lee, Department of Chemistry, Inha University, 253 Yonghyundong, Namgu, Incheon 402-751, Korea. E-mail: hwlee@inha.ac.kr*

a *N. K. Dey, M. E. U. Hoque, C. K. Kim, B.-S. Lee, H. W. Lee Department of Chemistry, Inha University, Incheon 402-751, Korea*

1: $R_1 = R_2 =$ Me at 15.0 °C
2: $R_1 =$ Me; $R_2 =$ Ph at 55.0 °C
L = H or D
X = 4-MeO, 4-Me, 3-Me, H, 3-MeO, 4-Cl, 3-Cl

RESULTS AND DISCUSSION

The observed pseudo-first-order rate constants (k_{obsd}) were found to follow Eqn (2) for all of the reactions under pseudo-first-order conditions with a large excess of aniline nucleophile.

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

The k_0 values were negligible ($k_0 = 0$) in acetonitrile. The second-order rate constants ($k_{H(D)}$) were determined for at least five concentrations of anilines ([X−An]). The linear plots of Eqn (2) suggest that there is no base-catalysis or noticeable side reactions and that the overall reaction is described by Eqn (1). The k_H and k_D values are summarized in Tables 1 and 2, together with the deuterium KIEs (k_H/k_D) and the Hammett ρ_X and Brönsted β_X selectivity parameters. The magnitudes of the ρ_X and β_X values for the reactions of **1** and **2** with the deuterated anilines are somewhat smaller than those for the reactions of these compounds with the anilines. The same tendency was observed for the anilinolysis of diphenyl phosphinic chloride (**3**),[9] diphenyl thiophosphinic chloride,[11] dimethyl and diethyl chlorophosphates (**4** and **5**),[12] and dimethyl and diethyl chlorothionophosphates.[12]

As shown in Fig. 1, the natural bond order (NBO) charges, using the B3LYP/6-311+G(d,p) level,[20] on reaction center P are 1.793 (for **1**), 1.821 (for **2**), and 1.844 (for **3**).[9] (Cartesian coordinates and absolute energies of **1**, **2**, and **3** are given in the Supporting Information.) These values are consistent with what would be expected when considering the inductive effects of the ligands: $\sum\sigma_I(\mathbf{1}) = -0.02$, $\sum\sigma_I(\mathbf{2}) = +0.11$, and $\sum\sigma_I(\mathbf{3}) = +0.24$, obtained with $\sigma_I = -0.01$ (Me) and +0.12 (Ph).[21] Solely considering the inductive effects of the ligands, the reactivities of the substrates should increase in the following order: **1** < **2** < **3**. However, the sequence of the second-order rate constants of the anilinolysis ($C_6H_5NH_2$) in acetonitrile at 55.0 °C, **1**[22] >> **2** >> **3**, is contrary to the expectations for the inductive effects of the ligands and the NBO charge on the reaction center. The anilinolysis rate of **2** is 80 times faster than that of **3**. The rate of **1** is 57 times faster than that of **2** and the rate of **1** is 4520 times faster than that of **3**. Therefore, it is clear that the rate dramatically increases upon replacing the phenyl ligand by the methyl ligand.

A plot of logk_H (for the unsubstituted aniline) against the Taft steric constants [$\sum E_s = 0.00$ (**1**), −2.48 (**2**), and −4.96 (**3**), obtained with $E_s = 0.00$ (Me) and −2.48 (Ph)][23–24] according to Eqn (3) for the three phosphinates (**1**, **2,** and **3**[9]) shows good linearity, giving $\delta = 0.737$ ($r = 0.9999$).

$$\log k_{H(D)} = \delta \sum E_s + C \quad (3)$$

Buncel and coworkers[25–27] reported that the second-order rate constants, k_{EtO}^-, for the ethanolysis of the phosphinates, $Me_2P(O)(OPh\text{-}4\text{-}NO_2)$, $MePhP(O)(OPh\text{-}4\text{-}NO_2)$, and $Ph_2P(O)(OPh\text{-}4\text{-}NO_2)$ give relative rates of 235: 69: 1. These are inconsistent with what would be expected when considering the inductive effects of the ligands. A plot of logk_{EtO}^- against $\sum E_s$ (= 0.00, −2.48, and −4.96, respectively: same values as in **1**, **2** and **3**) for the three phosphinates is roughly linear, giving $\delta = 0.478$ ($r = 0.953$). This leads to the conclusion that the relative reactivities of the phosphinates are mainly determined by steric factors. The considerably larger magnitudes of δ (= 0.737) value in the present work compared to that ($\delta = 0.478$) of 4-nitrophenyl phosphinate derivatives may be ascribed to the sizes of the nucleophiles. In other words, the steric congestion for the relatively larger aniline nucleophile would be much greater than that for the ethanol nucleophile.

The second-order rate constants, relative rates, NBO charges on reaction center P, KIEs, and Brönsted β_X ($= \beta_{nuc}$) values for the anilinolysis of **1**–**7** in acetonitrile at 55.0 °C are summarized in Table 3. This table shows that the NBO charges on P reaction centers (or the electrophilicities of the substrates) do not seem to play an important role in determining the reactivities of the P = O substrates, suggesting that there are great steric effects on the anilinolysis rates of the P = O systems. The large magnitudes of the Brönsted β_X (= 0.88–1.69) values for the anilinolysis of the studied reaction systems (**1**–**7**) suggest extensive bond formation in the TS. These values are considerably larger than those of the following other phosphoryl transfer reactions in which the reactions proceed by concerted mechanism: pyridi-

Table 1. Second-order rate constants ($k_{H(D)} \times 10\,M^{-1}\,s^{-1}$) and selectivity parameters[a] for the reactions of dimethyl phosphinic chloride (**1**) with $XC_6H_4NH_2$ and $XC_6H_4ND_2$ in acetonitrile at 15.0 °C

X	k_H ($\times 10\,M^{-1}\,s^{-1}$)	k_D ($\times 10\,M^{-1}\,s^{-1}$)	k_H/k_D
4-MeO	429 ± 8	477 ± 5	0.899 ± 0.019[b]
4-Me	163 ± 3	191 ± 5	0.853 ± 0.027
3-Me	70.0 ± 1.2	85.1 ± 0.7	0.823 ± 0.016
H	16.1 ± 0.4	20.4 ± 0.4	0.789 ± 0.025
3-MeO	7.58 ± 0.08	9.99 ± 0.15	0.759 ± 0.014
4-Cl	1.97 ± 0.06	2.69 ± 0.03	0.732 ± 0.024
3-Cl	0.574 ± 0.015	0.816 ± 0.020	0.703 ± 0.025
$-\rho_X$	4.59 ± 0.20 ($r = 0.995$)	4.42 ± 0.19 ($r = 0.995$)	
β_X	1.62 ± 0.10 ($r = 0.990$)	1.56 ± 0.10 ($r = 0.990$)	

[a] The σ and pK_a (in water) values were taken from References [17] and [18], respectively.
[b] Standard error $\{= 1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}\}$[19].

Table 2. Second-order rate constants ($k_{H(D)} \times 10^2\,M^{-1}\,s^{-1}$) and selectivity parameters[a] for the reactions of methyl phenyl phosphinic chloride (**2**) with $XC_6H_4NH_2$ and $XC_6H_4ND_2$ in acetonitrile at 55.0 °C

X	k_H ($\times 10^2\,M^{-1}\,s^{-1}$)	k_D ($\times 10^2\,M^{-1}\,s^{-1}$)	k_H/k_D
4-MeO	56.1 ± 1.4	26.7 ± 0.3	2.10 ± 0.06[b]
4-Me	33.7 ± 0.9	16.2 ± 0.2	2.08 ± 0.06
3-Me	18.4 ± 0.4	9.01 ± 0.10	2.04 ± 0.05
H	13.8 ± 0.4	6.80 ± 0.04	2.03 ± 0.06
3-MeO	6.24 ± 0.12	3.54 ± 0.05	1.76 ± 0.04
4-Cl	3.35 ± 0.09	2.01 ± 0.03	1.67 ± 0.05
3-Cl	1.46 ± 0.02	0.900 ± 0.010	1.62 ± 0.03
$-\rho_X$	2.49 ± 0.04 ($r = 0.999$)	2.28 ± 0.03 ($r = 0.999$)	
β_X	0.88 ± 0.02 ($r = 0.999$)	0.81 ± 0.02 ($r = 0.999$)	

[a] The σ and pK_a (in water) values were taken from References [17] and [18], respectively.
[b] Standard error $\{= 1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}\}$[19].

nium-*N*-phosphonate with pyridines (0.53);[28] 3-methoxy pyridino-*N*-phosphate with pyridines (0.17);[29] isoquinolino-*N*-phosphonate with pyridines (0.15);[30] phosphorylated 3-methoxypyridine with primary amines (0.19);[31] acetyl phosphate dianion with pyridines (0.10);[32] 4-nitrophenyl diphenyl phosphate with phenoxides (0.53);[33] 2,4-dinitrophenyl diphenyl phosphate with phenoxides (0.12);[34] *O,O*-dimethyl-*O*-(3-methyl-4-nitrophenyl) phosphorothioate with phenoxides (0.49);[35] 2-aryloxy-2-oxo-1,3,2-dioxaphosphorinans with various oxyanions (0.32–0.48);[36] 2,4-dinitrophenyl methyl phosphate monoanion with primary amines (0.31);[37] and bis-2,4-dinitrophenyl phosphate monoanion with pyridines (0.54).[38] For the studied phosphoryl transfer reactions, the large β_X values seem to be the characteristic for the anilinolysis of phosphates and phosphinates with the Cl leaving group. Large β_X values imply extensive bond formation in the TS or a late TS.

In our previous work on the anilinolysis of **7**, a backside nucleophilic attack concerted mechanism with a late, product-like TS (TS II) was proposed on the basis of the large ρ_X (and β_X) values, the large negative cross-interaction constant ($\rho_{XY} = -1.31$) and the considerably small values of the secondary inverse KIEs ($k_H/k_D = 0.61$–0.87) with deuterated aniline nucleophiles.[16] A concerted mechanism involving predominantly backside nucleophilic attack in the TS (TS II) was also proposed for the anilinolysis of **4** and **5** based on the secondary inverse KIEs.[12] On the other hand, for the anilinolysis of **6**, a concerted

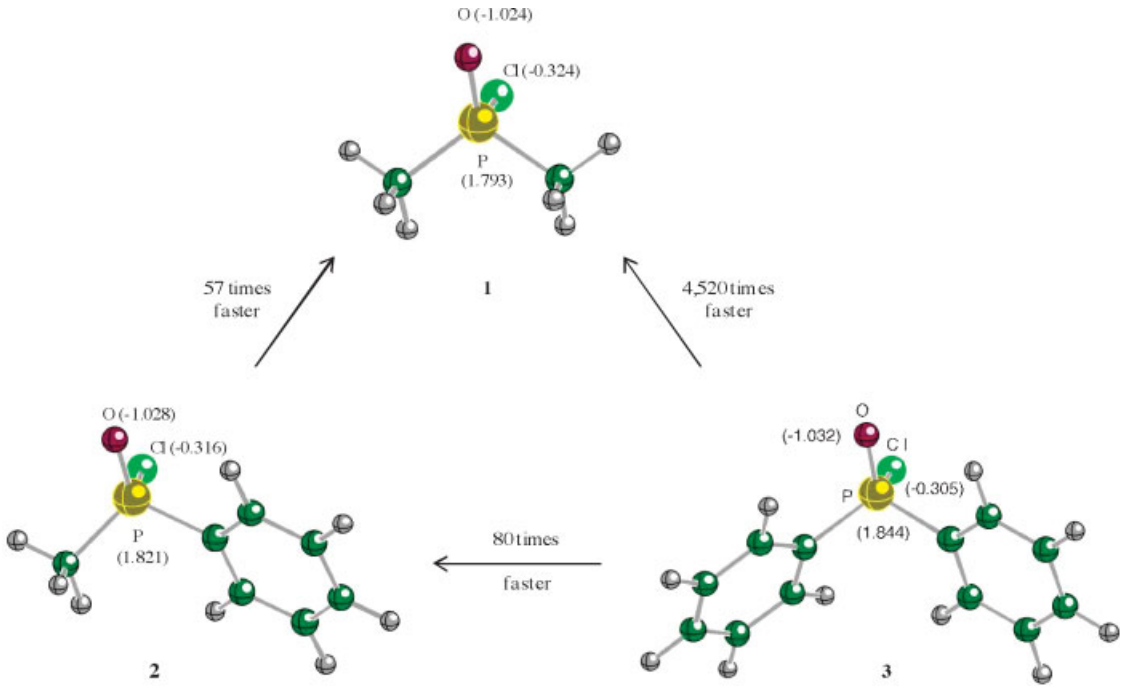


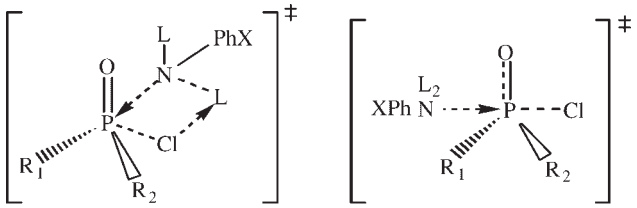
Figure 1. B3LYP/6-311+G(d,p)[20] geometries and NBO charges of **1**, **2**, and **3**[9] in the gas phase. The anilinolysis ($C_6H_5NH_2$) rate ratios in acetonitrile at 55.0 °C are displayed next to the arrows.

Table 3. Summary of the second-order rate constants, relative rate ratios, NBO charges on reaction center P, kinetic isotope effects (KIEs) and Brönsted β_X values for the anilinolysis of $R_1R_2P(O)Cl$ in acetonitrile at 55.0 °C

No.	R_1	R_2	k_H[a] ($\times 10^4\ M^{-1}\ s^{-1}$)	k_{rel}[b]	NBO charge of P	k_H/k_D	β_X	References
1[c]	Me	Me	782 00[d]	8777	+1.793	0.703–0.899	1.62	This work
2	Me	Ph	1380	155	+1.821	1.62–2.10	0.88	This work
4	MeO	MeO	42.8	4.8	+2.226	0.798–0.979	0.96	[12]
5	EtO	EtO	28.2	3.2	+2.236	0.714–0.919	1.06	[12]
6[e]	YPhO	EtO	20.0	2.2	+2.233[f]	1.10–1.28	1.13	[8]
3	Ph	Ph	17.3	1.9	+1.844	1.42–1.82	1.69	[9]
7[e]	YPhO	PhO	8.91	1	+2.230[f]	0.71–0.77	1.36	[16]

[a] For the reactions of the unsubstituted aniline, X = H. For compounds **6** and **7**, Y = H.
[b] $k_{rel} = k_{R1,R2}/k_{PhO,PhO}$ (for the reactions of the unsubstituted aniline).
[c] The k_H/k_D and β_X values are at 15.0 °C.
[d] Extrapolated value at 55.0 °C[22].
[e] The k_H/k_D and β_X values are for the anilinolysis of unsubstituted substrate (Y = H).
[f] Y = H.

mechanism involving a partial frontside attack via a hydrogen-bonded four-center-type TS (TS I) was suggested for several reasons, mainly based on the primary normal KIEs.[8]



TS I TS II

In the present anilinolysis studies, the KIEs for **1** are secondary inverse ($k_H/k_D = 0.703–0.899$; relatively small values), whereas the KIEs for **2** are primary normal ($k_H/k_D = 1.62–2.10$).[39] In an S_N2 mechanism, a secondary inverse KIE ($k_H/k_D < 1$) is ascribed to an increment in the vibrational frequencies of the N—L (L = H or D) in the TS II. This, in turn, results from the increased steric crowding that occurs during the bond making process.[40–43] As a nucleophile attacks the reaction center, the two N—L vibrations (both bending and stretching modes) are sterically hindered and force constants (and hence the vibrational frequencies) increase in the TS. This results in a secondary inverse KIE in all S_N2-type reactions. The magnitudes of secondary inverse KIEs reflect the degree of steric hindrance and hence the degree of bond formation; the smaller the secondary inverse KIE, the greater the extent of bond formation. By contrast, a primary normal KIE ($k_H/k_D > 1$) indicates that partial deprotonation of the aniline nucleophile occurs by hydrogen bonding in the rate-limiting step.[44] More hydrogen bond formation will result in a greater degree of deprotonation in the TS, and as a consequence, a greater k_H/k_D value.

Therefore, the secondary inverse KIEs in **1**, $k_H/k_D = 0.703–0.899$, imply that the steric congestion in TS II is severe due to the backside nucleophilic attack toward the Cl leaving group and that the extent of bond formation is great. In other words, the TS is very late. The degree of steric crowding in the TS increases as the nucleophile changes from a stronger nucleophile (X = 4-MeO; $k_H/k_D = 0.899$) to weaker one (X = 3-Cl; $k_H/k_D = 0.703$), i.e., the degree of bond formation is larger for the weaker nucleophile. The same tendencies were observed for the anilinolysis of **4**,[12] **5**,[12] and **7**[16] in which the proposed mechanism is S_N2 with backside nucleophilic attack via TBP-5C TS. The smaller k_H/k_D value for a weaker nucleophile may coincide with greater degrees of bond cleavage and bond making, since the negative charge on the reaction center P should be smaller for the weaker nucleophile. This is expected from the More O'Ferrall–Jencks diagram.[45–46]

The anilinolysis of **2** yields the primary normal KIEs ($k_H/k_D = 1.62–2.10$), as opposed to the secondary inverse KIEs of **1** ($k_H/k_D = 0.703–0.899$). This implies partial deprotonation in TS I which involves the formation of a hydrogen bond between the Cl leaving group and the hydrogen (deuterium) atom of the N—H(D) moiety of the aniline. Predominantly frontside nucleophilic attack (four-center-type TS I over the four-membered ring strain) was also proposed for the anilinolysis of **3**,[9] mainly based on the primary normal KIEs ($k_H/k_D = 1.42–1.82$). Partial participation of four-center-type TS for the anilinolysis of **6**[8] was based on the relatively small primary normal KIEs ($k_H/k_D = 1.10–1.28$). Taking the relatively small Cl leaving group into account, these results can be rationalized by the following steric effects: (i) the two large phenyl ligands in **3** prohibit backside attack by the aniline nucleophile toward the Cl leaving group, thereby resulting in frontside attack and primary KIEs.[9] (ii) the single phenyl and methyl ligands in **2** still prohibit the backside attack by the aniline, thereby resulting in primary KIEs. (iii) however, the two methyl ligands in **1** permit space available for backside nucleophilic attack, resulting in the secondary inverse KIE. (iv) the larger k_H/k_D value of **2** than that of **3**, despite the larger Brönsted β_X value (= 1.69) of **3** than that ($\beta_X = 0.88$) of **2**, may be due to less steric hindrance in **2** than in **3** for frontside attack. As shown in Table 2, the degree of deprotonation in the TS I of **2** is proportional to the nucleophilicity of the aniline. The same was observed for the anilinolysis of **3**, i.e., the stronger nucleophile leads to the greater primary KIE. It should be noted that the observed primary KIE is smaller than the real one due to the formation of the hydrogen bond between only one of the hydrogen (deuterium) atom of the two N—H(D) moieties and the

Cl leaving group, since the other hydrogen (deuterium) atom will give rise to the secondary inverse KIE ($k_H/k_D < 1$).

The reactivities of the P = O substrates mainly depend on the degree of steric hindrance as mentioned earlier. The reaction rate of **3**[9] (which has two phenyl ligands) is almost twice that of **7**[16] (which has two phenoxy ligands), because the phenoxy group is bulkier than the phenyl group. The sequence of reaction rates in Table 3 seems to be in accordance with the degree of steric hindrance. However, the anilinolysis of **7** proceeds via backside nucleophilic attack despite its two bulky phenoxy groups, while the reaction of **3** proceeds via frontside attack. Furthermore, the anilinolysis of **6**[8] (which has single ethoxy and phenoxy ligands) proceeds via backside and frontside attack. These results were substantiated as follows. The intervening oxygen atom between the reaction center P atom and the phenyl ring in **7** may render enough space to permit backside attack. By contrast, the two phenyl rings directly bonded to the reaction center in **3** inhibit backside attack. The fast rotation of the ethyl group of **6**, more or less, sterically inhibits backside attack, thereby resulting in a *partial* frontside attack.[8] Therefore, in comparison with **2** and **3**, smaller primary normal KIEs are obtained.

EXPERIMENTAL

Materials

Dimethyl and methyl phenyl phosphinic chlorides (97%) and HPLC-grade acetonitrile (water content < 0.005%) were used without further purification for kinetic studies. Anilines were redistilled or recrystallized before use. Deuterated anilines were prepared by heating the anilines with D_2O and one drop of HCl catalyst at 85 °C for 72 h. After numerous attempts, the anilines were more than 98% deuterated, as confirmed by ^{1}H NMR analysis.

Kinetic procedure

Rates were measured conductometrically as described previously.[16] For the present work, the following concentrations were used: [substrate **1**] = 1×10^{-4} M and [X−An] = 4–6 × 10^{-3} M; [substrate **2**] = 2×10^{-4} M and [X−An] = 1–9 × 10^{-2} M. We tried at least five concentrations of anilines. Each pseudo-first-order rate constants value (k_{obsd}) was averaged from the values obtained from three separate runs, which were reproducible within ±3%.

Product analysis

Dimethyl phosphonic chloride and methyl phenyl phosphinic chloride were reacted with excess 4-methylaniline and 4-methoxyaniline for more than 15 half-lives at 15 and 55.0 °C in acetonitrile, respectively. The 4-methyl and 4-methoxy aniline hydrochloride salts were separated by filtration. Analytical and spectroscopic data of the products gave the following results:

$$(CH_3)_2P(=O)NHC_6H_4-4-CH_3$$

Brown solid, mp 172–174 °C, ^{1}H NMR (400 MHz, DMSO-d6) δ 1.62–1.70 (6H, m, CH_3), 2.23–2.27 (3H, d, J = 16.0 Hz, CH_3), 4.84–4.86 (1H, d, J = 8.0 Hz, NH), 6.61–7.26 (4H, m, phenyl); ^{13}C NMR (100 MHz, DMSO-d6) δ 16.3–17.2 (CH_3, s), 20.6 (CH_3, s), 115.2, 119.2, 119.3, 129.7, 130.0, 131.8, 37.7 (C═C, aromatic); ^{31}P NMR (162 MHz, DMSO-d6) δ 39.9–40.0 (1P, d, J = 16.2 Hz, P = S); m/z, 183 (M+); (found: C 59.1, H 7.7, N 7.8; $C_9H_{14}NOP$ requires C 59.0, H 7.7, N 7.7%).

$$(CH_3)(C_6H_5)P(=O)NHC_6H_4-4-OCH_3$$

Purple gummy solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77, 1.80 (3H, ss, P-CH_3), 3.72 (3H, s, OCH_3), 4.96 (1H, d, J = 8.4 Hz, NH), 6.73 (d, J = 8.8 Hz, 2H, phenyl), 6.96 (2H, d, J = 8.8 Hz, phenyl), 7.47 (2H, t, J = 8.8 Hz, phenyl), 7.52 (1H, t, J = 8.8 Hz, phenyl), 7.86 (2H, d, J = 8.8 Hz, phenyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2–17.1 (CH_3, s), 55.5 (OCH_3), 114.6, 115.4, 120.6, 121.2, 128.3, 131.5, 132.1, 133.1, 155.2 (C═C, aromatic); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9 (s, 1P, P = O); m/z 261 (M+); (found: C 64.0, H 6.1, N, 5.7; $C_{14}H_{16}NO_2P$ requires C 64.3, H 6.2, N 5.4%).

Acknowledgements

This work was supported by a grant from the Korea Research Foundation (KRF-2008-314-C00207).

REFERENCES

[1] R. F. Hudson, *Structure and Mechanism in Organophosphorus Chemistry*, Academic Press, London, **1965**, Chapter 3.
[2] A. Williams, *Concerted Organic and Bio-organic Mechanisms*, CRS Press, Boca Raton, **2000**, Chapter 6.
[3] C. R. Hall, T. D. Inch, *Tetrahedron* **1980**, *36*, 2059–2095.
[4] R. J. P. Corriu, J. P. Dutheil, G. F. Lanneau, *J. Am. Chem. Soc.* **1984**, *106*, 1060–1065.
[5] H. W. Lee, A. K. Guha, C. K. Kim, I. Lee, *J. Org. Chem.* **2002**, *67*, 2215–2222.
[6] K. K. Adhikary, H. W. Lee, I. Lee, *Bull. Korean Chem. Soc.* **2003**, *24*, 1135–1140.
[7] M. E. U. Hoque, S. Dey, A. K. Guha, C. K. Kim, B. S. Lee, H. W. Lee, *J. Org. Chem.* **2007**, *72*, 5493–5499.
[8] M. E. U. Hoque, N. K. Dey, C. K. Kim, B. S. Lee, H. W. Lee, *Org. Biomol. Chem.* **2007**, *5*, 3944–3950.
[9] M. E. U. Hoque, H. W. Lee, *Bull. Korean Chem. Soc.* **2007**, *28*, 936–940.
[10] M. E. U. Hoque, N. K. Dey, A. K. Guha, C. K. Kim, B. S. Lee, H. W. Lee, *Bull. Korean Chem. Soc.* **2007**, *28*, 1797-1802.
[11] N. K. Dey, I. S. Han, H. W. Lee, *Bull. Korean Chem. Soc.* **2007**, *28*, 2003–2008.
[12] N. K. Dey, M. E. U. Hoque, C. K. Kim, B. S. Lee, H. W. Lee, *J. Phys. Org. Chem.* **2008**, *21*, 544–548.
[13] I. Lee, *Chem. Soc. Rev.* **1990**, *9*, 317–333.
[14] I. Lee, *Adv. Phys. Org. Chem.* **1992**, *27*, 57–117.
[15] I. Lee, H. W. Lee, *Collect. Czech. Chem. Commun.* **1999**, *64*, 1529–1550.
[16] A. K. Guha, H. W. Lee, I. Lee, *J. Chem. Soc. Perkin Trans.* **1999**, *2*, 765–769.
[17] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195.
[18] A. Streitwieser, Jr, C. H. Heathcock, *Introduction to Organic Chemistry* (3rd edn), Macmillan, New York, **1996**, 693.
[19] T. B. Crumpler, J. H. Yoh, *Chemical Computations and Errors*, John Wiley, New York, **1940**, 178.
[20] W. J. Hehre, L. Random, P. V. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**, Chapter 4.
[21] M. Charton, *Prog. Phys. Org. Chem.* **1987**, *16*, 287–315.
[22] The k_H value of 7.82 $M^{-1}s^{-1}$ at 55.0 °C was calculated by extrapolation in the Arrhenius plot (r = 0.99938) with kinetic data: k_H = 0.776 (0.0 °C), 1.01 (5.0 °C), and 1.61 $M^{-1}s^{-1}$ (15.0 °C).
[23] R. W. Taft, In *Steric Effect in Organic Chemistry*, (Ed.: M. S. Newman), Wiley, New York, **1956**, Chapter 3.
[24] A. Williams, *Free Energy Relationship in Organic and Bio-organic Chemistry*, RSC, Cambridge, UK, **2003**, Chapter 7.
[25] I. Onyido, K. Albright, E. Buncel, *Org. Biomol. Chem.* **2005**, *3*, 1468.
[26] E. J. Dunn, E. Buncel, *Can. J. Chem.* **1989**, *67*, 1440–1448.

[27] E. J. Dunn, R. T. Moir, E. Buncel, J. G. Purdon, R. A. B. Bannard, *Can. J. Chem.* **1990**, *68*, 1837–1845.
[28] A. Williams, *J. Am. Chem. Soc.* **1985**, *107*, 6335–6339.
[29] M. T. Skoog, W. P. Jencks, *J. Am. Chem. Soc.* **1983**, *105*, 3356–3357.
[30] N. Bourne, A. Williams, *J. Am. Chem. Soc.* **1984**, *106*, 7591–7596.
[31] M. T. Skoog, W. P. Jencks, *J. Am. Chem. Soc.* **1984**, *106*, 7597–7606.
[32] D. Herschlag, W. P. Jencks, *J. Am. Chem. Soc.* **1989**, *111*, 7587–7596.
[33] S. A. Ba-Saif, M. A. Waring, A. Williams, *J. Am. Chem. Soc.* **1990**, *112*, 8115–8120.
[34] S. A. Ba-Saif, M. A. Waring, A. Williams, *J. Chem. Soc. Perkin Trans.* **1991**, *2*, 1653–1659.
[35] B. A. Gregersen, X. Lopez, D. M. York, *J. Am. Chem. Soc.* **2003**, *125*, 7178–7179.
[36] S. A. Khan, A. J. Kirby, *J. Chem. Soc. (B)* **1970**, 1172–1182.
[37] A. J. Kirby, M. J. Younas, *J. Chem. Soc. (B)* **1970**, 1165–1172.
[38] A. J. Kirby, A. G. Varvoglis, *J. Chem. Soc. (B)* **1968**, 135–141.
[39] The value of $k_H/k_D = 2.10$ for the reaction of **2** with 4-methoxyaniline is the largest one that we have ever observed in the phosphoryl transfer reactions.
[40] J. A. Barnes, I. H. Williams, *J. Chem. Soc. Chem. Commun.* **1993**, 1286–1287.
[41] R. A. Poirier, Y. Wang, K. C. Westaway, *J. Am. Chem. Soc.* **1994**, *116*, 2526–2533.
[42] I. Lee, H. J. Koh, B. S. Lee, H. W. Lee, *J. Chem. Soc. Chem. Commun.* **1990**, 335–336.
[43] I. Lee, *Chem. Soc. Rev.* **1995**, *24*, 223–229.
[44] L. Melander, W. H. Saunders, Jr, *Reaction Rates of Isotopic Molecules*, Wiley, New York, **1981**, Chapter 5.
[45] R. A. More O'Ferrall, *J. Chem. Soc. B* **1970**, 274–277.
[46] W. P. Jencks, *Chem. Rev.* **1972**, *72*, 705–718.