Kinetics and mechanism of the anilinolysis of dimethyl and diethyl chloro(thiono)phosphates

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The deuterium kinetic isotope effects (KIEs) involving deuterated aniline nucleophiles ($XC_6H_4ND_2$) are reported for the reactions of dimethyl chlorophosphate (1), dimethyl chlorothionophosphate (2), diethyl chlorophosphate (3) and diethyl chlorothionophosphate (4) in acetonitrile at 55.0 °C. The obtained k_H/k_D values are 0.798–0.979, 0.945–1.06, 0.714–0.919 and 1.01–1.10 for 1, 2, 3 and 4, respectively. A concerted mechanism with dominant backside nucleophilic attack is proposed for the reactions of 1 and 3. A concerted mechanism involving partial frontside attack through a hydrogen-bonded four-centre-type transition state (TS) is proposed for the reactions of 2 and 4. Copyright © 2008 John Wiley & Sons, Ltd.

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Keywords: deuterium kinetic isotope effect; anilinolysis; dimethyl and diethyl chlorophosphates; dimethyl and diethyl chlorothionophosphates
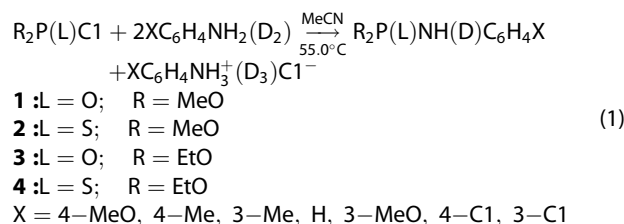
INTRODUCTION

Phosphoryl transfer reactions have been studied extensively and a considerable amount of work has been carried out to clarify the mechanism. Two main types of mechanisms, the stepwise mechanism involving a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate and the concerted mechanism through a single pentacoordinate transition state (TS), are known to occur in neutral phosphoryl transfer reactions.[1–4] When the attacking and leaving groups occupy apical positions [ap(Nu)-ap(Lg)], that is, backside nucleophilic attack, the configuration is inversed. But when the nucleophile attacks frontside towards the leaving group, that is, when nucleophile and leaving groups occupy apical and equatorial positions [ap(Nu)-eq(Lg)], respectively or when nucleophile and leaving groups occupy equatorial and apical positions [eq(Nu)-ap(Lg)], respectively, the configuration is retained.[5–16] When backside and frontside nucleophilic attacks occur simultaneously, the relative importance of the reaction pathways leads to products with inversion or retention of the configuration, depending on the nucleophile, the leaving group and the reaction conditions.[5]

In our preceding papers, partial frontside nucleophilic attack was suggested for the reactions of: aryl bis(4-methoxyphenyl) phosphates with less basic pyridines;[17] aryl phenyl isothiocyanophosphates with more basic pyridines;[18] aryl phenyl chlorothionophosphates with anilines;[19] diphenyl phosphinic chlorides with anilines;[20] diphenyl thiophosphinic chlorides with more basic pyridines[21] and aryl ethyl chlorophosphates and chlorothionophosphates with anilines.[22]

In this work, we investigate the aminolysis of dimethyl chlorophosphate (1), dimethyl chlorothionophosphate (2), diethyl chlorophosphate (3) and diethyl chlorothionophosphate (4) with

substituted anilines and deuterated anilines ($XC_6H_4NH_2$ and $XC_6H_4ND_2$) in acetonitrile at 55.0 °C, Eqn (1), to clarify the phosphoryl transfer mechanism, as well as to compare the anilinolysis of aryl ethyl chlorophosphate [5; (YPhO)(EtO)P(O)Cl],[22] aryl ethyl chlorothionophosphate [6; (YPhO)(EtO)P(S)Cl],[22] aryl phenyl chlorophosphate [7; (YPhO)(PhO)P(O)Cl][23] and aryl phenyl chlorothionophosphate [8; (YPhO)(PhO)P(S)Cl].[19]

$$R_2P(L)Cl + 2XC_6H_4NH_2(D_2) \xrightarrow[55.0°C]{MeCN} R_2P(L)NH(D)C_6H_4X$$
$$+ XC_6H_4NH_3^+(D_3)Cl^-$$

1 : L = O;   R = MeO
2 : L = S;   R = MeO   (1)
3 : L = O;   R = EtO
4 : L = S;   R = EtO
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}) for the reactions obey Eqn (2) with negligible k_0 in acetonitrile. The second-order rate constants, $k_{H(D)}$, were determined using Eqn (2) with at least five concentrations [An]. No third-order or higher-

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Table 1. Second-order rate constants, $k_{H(D)} \times 10^4 \, M^{-1} \, s^{-1}$, and selectivity parameters[a] for the reactions of dimethyl chlorophosphate (**1**) with $XC_6H_4NH_2$ and $XC_6H_4ND_2$ in acetonitrile at 55.0 °C

X	k_H^b ($\times 10^4 \, M^{-1} \, s^{-1}$)	k_D^b ($\times 10^4 \, M^{-1} \, s^{-1}$)	k_H/k_D
4-MeO	229 ± 3	234 ± 5	0.979 ± 0.026
4-Me	126 ± 4	132 ± 5	0.955 ± 0.048
3-Me	62.4 ± 1.3	66.8 ± 1.1	0.934 ± 0.024
H	42.8 ± 1.5	46.4 ± 1.4	0.922 ± 0.042
3-MeO	21.4 ± 0.5	25.4 ± 0.5	0.843 ± 0.025
4-Cl	10.6 ± 0.2	13.0 ± 0.2	0.815 ± 0.020
3-Cl	3.99 ± 0.01	5.00 ± 0.20	0.798 ± 0.030
ρ_X	-2.72 ± 0.04 ($r = 0.999$)	-2.56 ± 0.05 ($r = 0.999$)	
β_X	0.962 ± 0.019 ($r = 0.999$)	0.907 ± 0.020 ($r = 0.999$)	

[a] The σ and pK_a values were taken from References [24] and [25], respectively.
[b] Correlation coefficients (r) were better than 0.998.

Table 3. Second-order rate constants, $k_{H(D)} \times 10^4 \, M^{-1} \, s^{-1}$, and selectivity parameters[a] for the reactions of diethyl chlorophosphate (**3**) with $XC_6H_4NH_2$ and $XC_6H_4ND_2$ in acetonitrile at 55.0 °C

X	k_H^b ($\times 10^4 \, M^{-1} \, s^{-1}$)	k_D^b ($\times 10^4 \, M^{-1} \, s^{-1}$)	k_H/k_D
4-MeO	170 ± 1	185 ± 4	0.919 ± 0.022
4-Me	83.6 ± 1.0	93.0 ± 1.5	0.899 ± 0.018
3-Me	40.4 ± 0.9	47.4 ± 0.7	0.852 ± 0.022
H	28.2 ± 0.1	33.4 ± 1.1	0.844 ± 0.043
3-MeO	12.2 ± 0.3	16.0 ± 0.4	0.763 ± 0.027
4-Cl	5.40 ± 0.20	7.40 ± 0.2	0.730 ± 0.033
3-Cl	2.00 ± 0.01	2.80 ± 0.11	0.714 ± 0.028
ρ_X	-2.99 ± 0.04 ($r = 0.999$)	-2.80 ± 0.04 ($r = 0.999$)	
β_X	1.06 ± 0.03 ($r = 0.999$)	0.993 ± 0.023 ($r = 0.999$)	

[a,b] Same as in Table 1.

order terms were detected,

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

and no complications were found in the determination of k_{obsd} or in the linear plots of Eqn (2). This suggests that there is no base-catalysis or noticeable side reaction and that the overall reactions follow the route given by Eqn (1). The k_H and k_D values are summarized in Tables 1–4, together with the deuterium kinetic isotope effects (KIEs), k_H/k_D, and the selectivity parameters, ρ_X and β_X. The magnitudes of ρ_X and β_X values of the reactions of **1**–**4** with deuterated anilines ($XC_6H_4ND_2$) are somewhat smaller than those with anilines ($XC_6H_4NH_2$), suggesting less sensitivity to substituent effect of deuterated anilines than of anilines.

Figure 1 shows the rate ratios of the anilinolysis ($C_6H_5NH_2$) of **1**, **2**, **3** and **4** in acetonitrile at 55.0 °C. The reaction rate of **1** is 3.9 times faster than that of **2** and the rate of **3** is 5.5 times faster than that of **4**. Phosphate systems are more reactive than their thionophosphate counterparts for several reasons, the so-called thio effect, which is mainly the electronegativity difference between O and S that favours O over S.[26–29]

The methoxy group ($\sigma_I = 0.30$)[30] has slightly stronger electron withdrawing ability inductively than the ethoxy group ($\sigma_I = 0.28$).[30] Solely considering the difference of inductive effects between methoxy and ethoxy groups, the positive charge of the reaction centre P in **1** (and **2**) would be a little greater than that in **3** (and **4**). Figure 1 shows the natural bond order (NBO) charges,
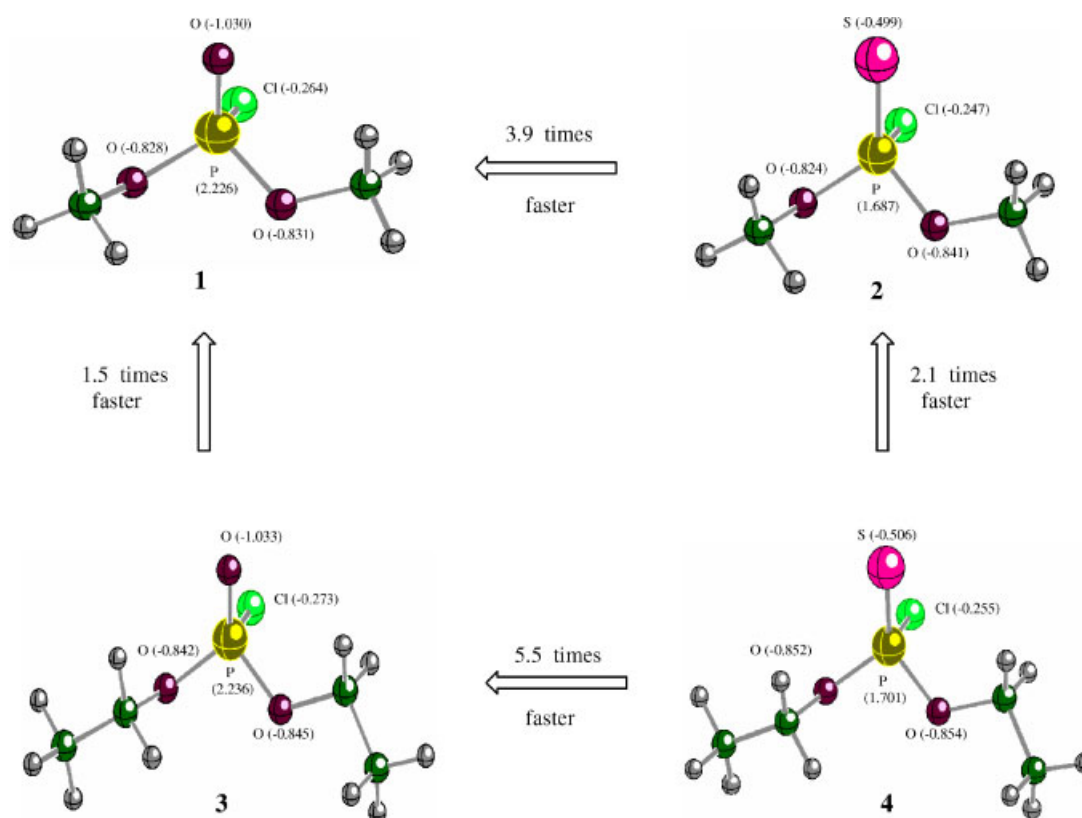
Table 2. Second-order rate constants, $k_{H(D)} \times 10^4 \, M^{-1} \, s^{-1}$, and selectivity parameters[a] for the reactions of dimethyl chlorothionophosphate (**2**) with $XC_6H_4NH_2$ and $XC_6H_4ND_2$ in acetonitrile at 55.0 °C

X	k_H^b ($\times 10^4 \, M^{-1} \, s^{-1}$)	k_D^b ($\times 10^4 \, M^{-1} \, s^{-1}$)	k_H/k_D
4-MeO	77.9 ± 1.1	73.4 ± 0.8	1.06 ± 0.02
4-Me	31.0 ± 0.6	29.8 ± 0.7	1.04 ± 0.03
3-Me	16.8 ± 0.2	16.3 ± 0.1	1.03 ± 0.02
H	10.9 ± 0.2	11.0 ± 0.2	0.991 ± 0.026
3-MeO	4.95 ± 0.14	5.08 ± 0.08	0.974 ± 0.031
4-Cl	2.33 ± 0.08	2.44 ± 0.04	0.955 ± 0.036
3-Cl	1.20 ± 0.03	1.27 ± 0.03	0.945 ± 0.029
ρ_X	-2.81 ± 0.10 ($r = 0.997$)	-2.73 ± 0.10 ($r = 0.997$)	
β_X	0.993 ± 0.050 ($r = 0.994$)	0.963 ± 0.047 ($r = 0.994$)	

[a,b] Same as in Table 1.

Table 4. Second-order rate constants, $k_{H(D)} \times 10^4 \, M^{-1} \, s^{-1}$, and selectivity parameters[a] for the reactions of diethyl chlorothionophosphate (**4**) with $XC_6H_4NH_2$ and $XC_6H_4ND_2$ in acetonitrile at 55.0 °C

X	k_H^b ($\times 10^4 \, M^{-1} \, s^{-1}$)	k_D^b ($\times 10^4 \, M^{-1} \, s^{-1}$)	k_H/k_D
4-MeO	41.3 ± 0.1	37.7 ± 0.4	1.10 ± 0.01
4-Me	17.4 ± 0.3	16.1 ± 0.3	1.08 ± 0.03
3-Me	7.19 ± 0.18	6.78 ± 0.12	1.06 ± 0.03
H	5.12 ± 0.07	4.86 ± 0.16	1.05 ± 0.04
3-MeO	2.51 ± 0.06	2.41 ± 0.06	1.04 ± 0.04
4-Cl	1.57 ± 0.03	1.53 ± 0.03	1.03 ± 0.03
3-Cl	0.607 ± 0.019	0.602 ± 0.011	1.01 ± 0.04
ρ_X	-2.75 ± 0.14 ($r = 0.993$)	-2.70 ± 0.14 ($r = 0.993$)	
β_X	0.977 ± 0.045 ($r = 0.995$)	0.957 ± 0.044 ($r = 0.995$)	

[a,b] Same as in Table 1.

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Figure 1. B3LYP/6-311+G(d,p)[31] geometries and NBO charges of **1**, **2**, **3** and **4** in the gas phase.

using the B3LYP/6-311+G(d,p) level,[31] on reaction centre P, 2.226 (**1**) < 2.236 (**3**) and 1.687 (**2**) < 1.701(**4**), which are not consistent with the expectations for the inductive effects of the ligands. The obtained rate ratios of k_H (**1**)/k_H(**3**) = 1.5 and k_H (**2**)/k_H(**4**) = 2.1 cannot be rationalized by the inductive effects of the ligands or the NBO charges on the reaction centre.

Moreover, taking into account the NBO charges on reaction centre P in **5** (2.233),[22] **7** (2.230),[23] **6** (1.687)[22] and **8** (1.661),[19] the sequence of reactivity for **1**: **3**: **5**: **7** = 4.8: 3.2: 2.2: 1 and **2**: **4**: **6**: **8** = 10.8: 5.1: 2.8: 1 (when X = Y = H) cannot be rationalized (refer also to Table 5). The plots of log k_H against Taft steric constants [$\sum E_s$: E_s = 0.00 (Me), −0.07 (Et) and −2.48 (Ph)][32,33] according to

Eqn (3) for the four phosphates (**1**, **3**, **5**[22] and **7**[23]) and the four thionophosphates (**2**, **4**, **6**[22] and **8**[19]) are roughly linear, giving δ = 0.12 (r = 0.967) and δ = 0.18 (r = 0.959), respectively.

$$\log k_H = \delta \sum E_s + C \qquad (3)$$

Buncel and coworkers reported that the second-order rate constants, k_{EtO}^-, for the ethanolysis of the phosphinates, $Ph_2P(O)$ (OPh-4-NO_2), $PhMeP(O)(OPh$-4-$NO_2)$ and $Me_2P(O)(OPh$-4-$NO_2)$ give relative rates of 1: 69: 235, contrary to the expectations for the inductive effects of the ligands [σ_I = −0.01(Me) and 0.12(Ph)].[34–37] A plot of log k_{EtO}^- against $\sum E_s$ for the three

Table 5. Summary of second-order rate constants and selectivity parameters for the anilinolysis of $R_1R_2P(=L)Cl$ in acetonitrile at 55.0 °C

| L		R_1	R_2	$k_H{}^a$ (×10^4 M^{-1} s^{-1})	k_H/k_D	$-\rho_X$	β_X	ρ_Y	$-\rho_{XY}$	References
O	**1:**	MeO	MeO	42.8	0.80–0.98	2.72	0.96	—	—	This work
	3:	EtO	EtO	28.2	0.71–0.92	2.99	1.06	—	—	This work
	5:	YPhO	EtO	20.0	1.07–1.80	3.09–3.40	1.09–1.20	0.41–0.90	0.60	[22]
	7:	YPhO	PhO	8.91	0.61–0.87	3.42–4.63	1.24–1.68	0.22–0.87	1.31	[23]
S	**2:**	MeO	MeO	10.9	0.95–1.06	2.81	0.99	—	—	This work
	4:	EtO	EtO	5.12	1.01–1.10	2.75	0.98	—	—	This work
	6:	YPhO	EtO	2.80	1.06–1.27	3.15–3.33	1.11–1.17	0.75–0.95	0.19	[22]
	8:	YPhO	PhO	1.01	1.11–1.33	3.81–4.01	1.34–1.41	0.67–0.73	0.22	[19]

^{a} X = Y = H.

phosphinates yields $\delta = 1.32$ $(r = 0.954)$, which leads to the conclusion that the sequence of reactivity for the phosphinates is determined mainly by steric factors.[34–37] Large steric effects on the ethanolysis of the phosphinates can be rationalized by the *backside* nucleophilic attack towards the 4-NO$_2$PhO leaving group since large steric effects on the reaction rates cannot be substantiated by frontside nucleophilic attack regardless of ap(Nu)-eq(Lg) or eq(Nu)-ap(Lg) positions in the TS. The smaller magnitudes of δ values in the present work compared to that of the phosphinates may be ascribed to the intervening oxygen atoms in the phosphates which render more available space to attacking nucleophiles.

Selectivity parameters and deuterium KIEs for the anilinolysis of **1**–**8** in acetonitrile at 55.0 °C are summarized in Table 5. The magnitudes of both Hammett ρ_X (ρ_{nuc}) and Brönsted β_X (β_{nuc}) values of **1**–**4** are large, suggesting extensive bond formation in the TS. However, these values are somewhat smaller than those of **5**–**8**, indicating a lesser degree of bond formation in the anilinolyses of **1**–**4** than in those of **5**–**8**.

In our previous work on the anilinolysis of **7**,[23] a backside nucleophilic attack concerted mechanism with a late, product-like TS was proposed on the basis of large ρ_X (and β_X), large negative cross-interaction constant,[38–40] $\rho_{XY} = -1.31$ and the secondary inverse KIEs, $k_H/k_D = 0.61$–0.87, with deuterated aniline nucleophile. However, in the anilinolysis of **5**,[22] **6**[22] and **8**,[19] a partial frontside nucleophilic attack concerted mechanism through a hydrogen-bonded four-centre type TS I was suggested for several reasons, mainly based on the primary KIEs, $k_H/k_D = 1.07$–1.80, 1.06–1.27 and 1.11–1.33, respectively.

TS I   TS II
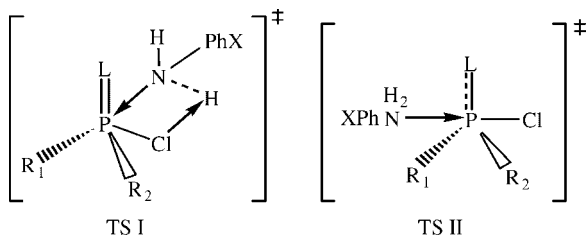
In the present work on the anilinolysis of **1** and **3**, the KIEs are less than unity, $k_H/k_D = 0.798$–0.979 and 0.714–0.919, respectively. In the anilinolysis of **2**, the KIEs gradually change from less than unity to greater than unity, $k_H/k_D = 0.945$–1.06, as the nucleophiles change from less basic to more basic. In the anilinolysis of **4**, the KIEs are greater than unity, $k_H/k_D = 1.01$–1.10. In an S$_N$2 mechanism, the secondary inverse KIE, $k_H/k_D < 1$, is ascribed to the increment of vibrational frequencies of N—H(D) in the TS II due to an increase in steric crowding in the bond-making process.[41,42] In contrast, the primary normal KIE, $k_H/k_D > 1$, indicates that partial deprotonation of the aniline nucleophile occurs in the rate-limiting step by hydrogen bonding.[43] Therefore, the KIEs in **2**, $k_H/k_D = 0.945$–1.06, imply that steric congestion in TS II is dominant for less basic nucleophiles, X = 3-Cl—H $(k_H/k_D = 0.945$–$0.991)$, while partial deprotonation in TS I is dominant for more basic nucleophiles, X = 4-MeO—3-Me $(k_H/k_D = 1.06$–$1.03)$. These results can be rationalized in that backside attack (TS II) is dominant for less basic nucleophiles, while frontside attack (TS I) involving hydrogen bond between the Cl leaving group and the hydrogen (deuterium) atom of the N—H(D) moiety in aniline is dominant for more basic nucleophiles. We can also suggest that backside attack (TS II) is dominant for the anilinolyses of **1** $(k_H/$

$k_D = 0.798$–$0.979)$ and **3** $(k_H/k_D = 0.714$–$0.919)$ and that front side attack (TS I) is dominant for the anilinolysis of **4** $(k_H/k_D = 1.01$–$1.10)$.

Another plausible TS structure with $k_H/k_D > 1$ could be TS III where there is a hydrogen bond between the oxygen (or sulphur) atom in P=O(S) and the hydrogen (deuterium) of the N—H(D) moiety in aniline. A four-membered TS IV was proposed in the ethanolysis of the phosphinates, paraxon and parathion with alkali metal ions by Buncel[44,45] and Um.[46]

TS III   TS IV
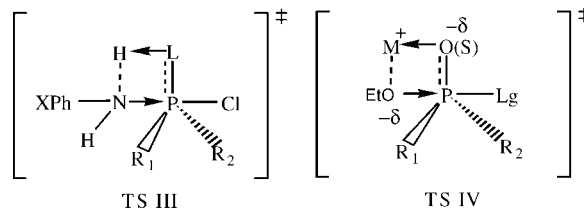
However, positive charge development on the hydrogen (deuterium) of the N—H(D) moiety in the TS would be much smaller than that on M$^+$ ions, so a hydrogen bond involving the acceptor P=O(S), as in TS III, is not feasible. In addition, the difference between the secondary inverse KIEs in **1**, **3** and **7**[23] and the primary normal KIE in **5**[22] cannot be substantiated by TS III. Moreover, the KIEs, $k_H/k_D = 0.945$–1.06, in **2** cannot be rationalized by TS III at all. So we can neglect TS III with $k_H/k_D > 1$.

CONCLUSIONS

The reactions of dimethyl chlorophosphate (**1**), dimethyl chlorothionophosphate (**2**), diethyl chlorophosphate (**3**) and diethyl chlorothionophosphate (**4**) with substituted anilines and deuterated anilines (XC$_6$H$_4$NH$_2$ and XC$_6$H$_4$ND$_2$) are studied kinetically in acetonitrile at 55.0 °C. By comparing the kinetics and mechanism of these reactions with those of similar reactions, we reached the following conclusions: (i) **1** and **3** react with anilines through a concerted mechanism involving dominant backside nucleophilic attack in the TS; (ii) a concerted mechanism involving a partial frontside attack through a hydrogen-bonded four-centre-type TS is proposed for the reaction of **2**; (iii) **4** reacts with anilines through a concerted mechanism involving dominant frontside nucleophilic attack in the TS and (iv) steric effect is the major factor that determines the reactivities of the studied phosphate and thionophosphate systems.

EXPERIMENTAL

Materials

Aldrich GR grade dimethyl chlorophosphate (96%), diethyl chlorophosphate (97%), dimethyl chlorothionophosphate (97%) and diethyl chlorothionophosphate (97%) were used without further purification. The other materials are the same as previously described.[19]

Kinetics procedure

Rates were measured conductometrically as described previously.[19,23] [**1** and **3**] = 2×10^{-3} M; [An] = 0.1–0.3 M and [**2** and

4] $= 1 \times 10^{-3}$ M; [An] $= 0.3$–0.15 M were used for the present work.

Product analysis

Dimethyl chlorophosphate, dimethyl chlorothionophosphate, diethyl chlorophosphate and diethyl chlorothionophosphate were reacted with excess 4-chloroaniline, aniline and 4-methylaniline, respectively, for more than 15 half-lives at 55.0 °C in acetonitrile as described previously.[19] Analysis data of the products gave the following results:

(CH₃O)₂P(=O)NHC₆H₄-4-Cl
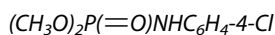
Brown, gummy solid, ^{1}H NMR (400 MHz, CDCl₃) δ 3.76 (3H, s, OCH₃), 3.79 (3H, s, OCH₃), 5.457 (1H, d, $J = 7.6$ Hz, NH), 6.91 (2H, d, $J = 8.8$ Hz, phenyl), 7.20 (2H, d, $J = 8.8$ Hz phenyl); ^{13}C NMR (100 MHz, CDCl₃) δ 53.37 (OCH₃), 114.17, 118.59, 126.99, 129.21, 137.85 (C=C, aromatic); ^{31}P NMR (162 MHz, CDCl₃) δ 9.83 (s, 1P, P=O); MS m/z, 235 (M+); (found: C 41.2, H 5.0, N 6.1; C₈H₁₁NO₃PCl requires C 40.8, H 4.7, N 6.0%).

(CH₃O)₂P(=S)NHC₆H₅
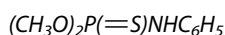
Brown liquid, ^{1}H NMR (400 MHz, CDCl₃) δ 3.73–3.77 (6H, d, $J = 16$ Hz, OCH₃), 5.34–5.38 (1H, d, $J = 16$ Hz, NH), 6.96–7.01 (3H, m, phenyl), 7.23–7.27 (2H, m, phenyl); ^{13}C NMR (100 MHz, CDCl₃) δ 53.52–53.55 (d, $J = 3$ Hz, OCH₃), 117.59, 117.565, 122.30, 129.32, 138.95,138.99 (C=C, aromatic); ^{31}P NMR (162 MHz, CDCl₃) δ 74.79 (s, 1P, P=O); MS m/z, 217 (M+); (found: C 44.2, H 5.7, N 6.9, S 14.3; C₈H₁₂NO₂PS requires C 44.2, H 5.6, N 6.5, S 14.7%).

(C₂H₅O)₂P(=O)NHC₆H₅
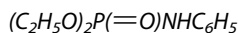
Brown solid, m.p. 92–94 °C, ^{1}H NMR (400 MHz, CDCl₃) δ 1.29–1.33 (6H, m, CH₃), 4.08–4.17 (4H, m, CH₂), 5.42 (1H, d, $J = 8.8$ Hz, NH), 6.96–6.98 (2H, d, $J = 7.6$ Hz, phenyl), 7.22–7.26 (3H, t, $J = 7.6$ Hz phenyl); ^{13}C NMR (100 MHz, CDCl₃) δ 16.2 (CH₃), 62.9 (CH₂), 117.2, 121.6, 129.2, 129.21, 139.4 (C=C, aromatic); ^{31}P NMR (162 MHz, CDCl₃) δ 7.24 (s, 1P, P=O); MS m/z, 229 (M+); (found: C 52.8, H 7.4, N 6.1; C₁₀H₁₁NO₃PCl requires C 52.4, H 7.0, N 6.1%).

(C₂H₅O)₂P(=S)NHC₆H₄-4-CH₃
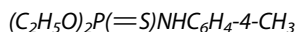
Pink liquid, ^{1}H NMR (400 MHz, CDCl₃) δ 1.29–1.33 (6H, m, CH₃), 4.08–4.17 (4H, m, CH₂), 5.377 (1H, d, $J = 14.8$ Hz, NH), 6.88–6.90 (2H, q, phenyl), 7.03–7.05 (2H, d, $J = 8$ Hz phenyl); ^{13}C NMR (100 MHz, CDCl₃) δ 15.77–15.86 (CH₃, d, $J = 8.4$ Hz), 20.6 (CH₃), 63.09–63.14 (CH₂, d, $J = 4.5$ Hz), 117.6, 117.7, 129.6, 131.4, 136.6, 136.7 (C=C, aromatic); ^{31}P NMR (162 MHz, CDCl₃) δ 70.36 (s, 1P, P=S); MS m/z, 259 (M+); (found: C 51.0, H 7.0, N 5.8, S 12.2; C₁₁H₁₈NO₂PS requires C 50.9, H 7.2, N 6.2, S 11.8%).

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