

Kinetics and mechanism of the aminolysis of phenyl substituted phenyl chlorophosphates with anilines in acetonitrile

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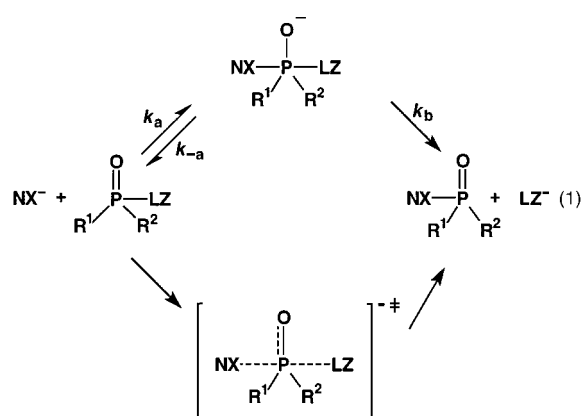
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The kinetics and mechanism of the aminolysis of phenyl substituted phenyl chlorophosphates with anilines are investigated in acetonitrile at 55.0 °C. Very sensitive variation of ρ_Y ($\delta\rho_Y \gg 0$) with the change of substituent on the nucleophile ($\delta\sigma_X$) leads to a large negative cross-interaction constant, $\rho_{XY} = (\delta\rho_Y)/(\delta\sigma_X) = -1.31$. The secondary kinetic isotope effects observed with deuterated aniline nucleophiles are of the inverse type ($k_H/k_D = 0.61-0.87$), and small ΔH^\ddagger (1.6–9.7 kcal mol⁻¹) and large negative ΔS^\ddagger (–43 to –65 e.u.) values are obtained. These results are consistent with a concerted process with a late, product-like transition state in which both bond making and leaving group departure are extensive.

Introduction

Nucleophilic substitution at neutral phosphoryl species has been considered to proceed either stepwise through a pentacoordinate intermediate,¹ upper route, or concertedly through a single transition state (TS),² lower route, eqn. (1). Williams and



co-workers have provided examples of the concerted phosphoryl transfer process. The aminolyses of phosphoropyridines with substituted pyridines have been shown to occur by a concerted process in aqueous solution.^{2b} The reactions of aryl diphenylphosphinate,^{2c} dimethylphosphinate^{2e} and diphenyl phosphate^{2d} with phenolate ions are also known to proceed through a concerted pathway in aqueous solution. The stepwise mechanism involving a pentacoordinate intermediate should undergo a change in rate-limiting step yielding a nonlinear Brønsted plot with a break point at a nucleophile with $pK_a = pK_a^0$ where $k_{-a} = k_b$, i.e., the nucleophile (NX^-) with pK_a^0 has the same leaving ability from the intermediates as the leaving group of the substrate (LZ^-).³ For the concerted path a linear plot without such a break point is obtained, providing evidence for a single TS.

We report here an examination of the aminolysis of phenyl substituted phenyl chlorophosphates [$R^1 = OC_6H_5$, $R^2 = OC_6H_4Y$ and $LZ = Cl$ in eqn. (1)] with a series of anilines ($NX = XC_6H_4NH_2$) in acetonitrile at 55.0 °C. We have varied substituents in both nucleophile ($X = p-OCH_3$, $p-CH_3$, H and $p-Cl$) and substrate ($Y = p-OCH_3$, $p-CH_3$, H, $p-Cl$ and $p-CN$) so that the cross-interaction constant, ρ_{XY} in eqn. (2), can be determined.

It has been shown that the sign and magnitude of ρ_{XY} provide important information:⁴

$$\log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \quad (2)$$

(1) The sign of ρ_{XY} is negative in a concerted nucleophilic substitution (S_N2) reaction, whereas it is positive for a stepwise reaction with rate-limiting leaving group departure from the intermediate.⁵ (2) The magnitude of ρ_{XY} is inversely related to the distance between the two substituents (X and Y) through the reaction center (P); the greater the magnitude, the tighter is the bond formation in the TS.^{4,6}

Phenyl substituted phenyl chlorophosphates are readily obtained and react at relatively fast rates with anilines. Since chloride is a much better leaving group than anilines or phenoxides ($k_b \gg k_{-a}$), stability of the pentacoordinate intermediate should be very low and hence it is unlikely that the aminolysis of phenyl substituted phenyl chlorophosphates will proceed through a stepwise pathway involving such an intermediate (for which $k_{-a} \geq k_b$).

Results and discussion

The rate law obeyed in the present reactions is given by eqn. (3),

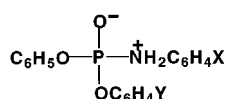
$$k_{obs} = k_0 + k_2[N] \quad (3)$$

where k_0 is the rate constant in the absence of aniline ($k_0 = 0$) and $[N]$ is the aniline concentration. The second-order rate constants, k_2 , obtained as the slope of plot of k_{obs} vs. $[N]$ are summarized in Table 1. In general, the rate is greater with a stronger nucleophile ($X = p-OMe$) and also with a stronger electron-withdrawing substituent in the substrate ($Y = p-CN$) as expected from a typical nucleophilic substitution reaction with negative charge development at the reaction center (P) in the transition state (TS). We note in Table 1 that the rate is very sensitive to changes in the nucleophile [e.g., for $Y = H$, $k_2(p-OMe)/k_2(p-Cl) \cong 80$], especially for the substrate with a strong acceptor substituent [for $Y = p-CN$, $k_2(p-OMe)/k_2(p-Cl) \cong 230$]. These behaviors suggest that the bond formation step is important in the TS of the present reactions. Since k_{obs} values are proportional to aniline concentration then the deprotonation step is not rate controlling. Thus the reaction being measured is the formation of the conjugate acid, form I.

Table 1 Second order rate constants ($k_2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), Hammett reaction constants, Brønsted constants and cross interaction constant for the reactions of phenyl substituted Y-phenyl chlorophosphates with substituted X-anilines in acetonitrile at 55 °C

X	Y					ρ_X^a
	<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -CN	
<i>p</i> -OMe	62.4	79.4	107	178	410	0.87 ± 0.01^b (0.999) ^c
<i>p</i> -Me	21.6	25.1	31.5	50.1	109	0.77 ± 0.02 (0.999)
H	6.50	7.30	8.91	12.0	20.6	0.54 ± 0.01 (0.999)
<i>p</i> -Cl	1.12	1.20	1.30	1.45	1.80	0.22 ± 0.01 (0.999)
ρ_X^d	-3.42 ± 0.17 (0.997)	-3.55 ± 0.20 (0.997)	-3.74 ± 0.21 (0.997)	-4.09 ± 0.19 (0.998)	-4.63 ± 0.14 (0.999)	$\rho_{XY} = -1.31 \pm 0.20$ (0.998)
β_X^e	1.24 ± 0.08 (0.995)	1.29 ± 0.09 (0.995)	1.36 ± 0.01 (0.995)	1.48 ± 0.09 (0.996)	1.68 ± 0.08 (0.998)	

^{a,d} Sigma values were taken from: C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165. ^b Standard deviation. ^c Correlation coefficient. ^e p*K*_a values were taken from: *Introduction to Organic Chemistry*, A. Streitwiser, Jr. and C. H. Heathcock, Third Edition, 1989, p. 693, Macmillan Publishing Co., New York.



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The Hammett ρ_X and ρ_Y values are shown in Table 1. Although the rates are determined in acetonitrile, the Brønsted β_X (β_{nuc}) values are obtained using the p*K*_a values in water as shown in Table 1. It has been shown that the $\Delta\text{p}K_a = \text{p}K_a(\text{MeCN}) - \text{p}K_a(\text{H}_2\text{O})$ values for structurally similar amines are nearly constant so that determination of β_X by plotting $\log k_2(\text{MeCN})$ vs. $\text{p}K_a(\text{water})$ is probably justified.⁷ We note that the magnitudes of ρ_X (-3.4 – -4.6) and β_X (1.2 – 1.7) are both large suggesting extensive bond formation in the transition state. The β_X values are greater than those reported for a stepwise acyl transfer process with rate limiting formation of the intermediate in water, $\beta_X = 0$ – 0.3 .⁸ The values are also greater than those found for a concerted acyl transfer ($\beta_X = 0.4$ – 1.0)^{2,9} as well as for the stepwise mechanism in which the rate-determining step is expulsion of the leaving group in aqueous solution ($\beta_X = 0.8$ – 1.0).^{8a-c,10} In aqueous solution a relatively loose, 'open', TS for the identical phosphoryl ($-\text{PO}_3^-$) transfer reaction gave $\beta_X = 0.53$.¹¹ In dipolar aprotic solvents larger β_X values ($\beta_X = 1.3$ and 1.6) which are close to the values obtained in the present work are found for the concerted reactions of acyl transfer with phenoxide nucleophiles.¹²

These experimental β_X values demonstrate that the magnitude of β_X (which is large, ranging from 1.2 to 1.7) alone can not provide conclusive evidence for a definite mechanism, which has been pointed out by Floriàn *et al.* recently using high level theoretical calculations in aqueous solution at the MP2/6-31 + G** + LD and MP2/6-31 + G** + PCM levels.¹³

The intermediate should be destabilized by the strong electron donating ability of the attached groups.¹⁴ The MO theoretical (RHF/6-31G*) structure (Fig. 1) shows that the three oxygens and chlorine in the diphenyl chlorophosphate have a near tetrahedral geometry with the phosphorus atom at the center. But neither of the two phenoxy groups is coplanar with the P=O group so that the following type of delocalized (or stabilized), form II, is not possible in the putative pentacoordinate intermediate as well as in the substrate. The phenoxy group is a relatively strong inductive electron withdrawing group ($\sigma_I = 0.40$, which is intermediate between CN: $\sigma_I = 0.59$ and OCH₃: $\sigma_I = 0.30$) so that the two phenoxy groups present in the phenyl substituted phenyl chlorophosphate will increase the

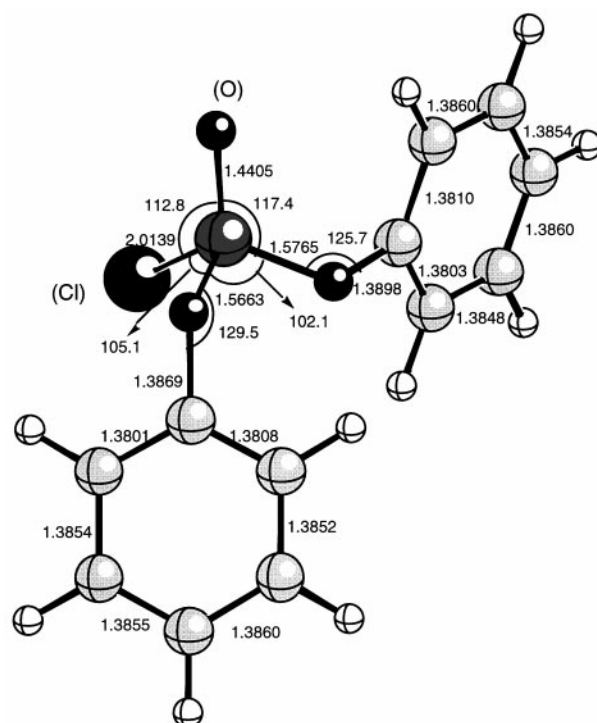
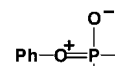


Fig. 1 The RHF/6-31G* geometry of diphenyl chlorophosphate.

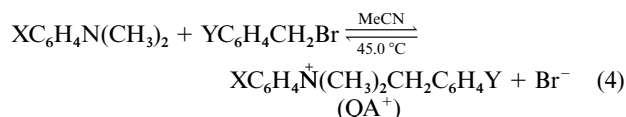


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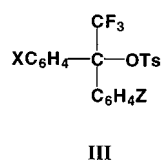
stability of the putative pentacoordinate intermediate.¹⁴ This will lead to more associative mechanisms, either concerted ones if the leaving group is good (like Cl) with more nucleophilic participation in the TS, or stepwise mechanisms with rate-limiting expulsion of the leaving group from the pentacoordinate intermediate.¹⁵ The superior leaving ability of Cl should make the intermediate kinetically unstable. For example, the p*K*_a value of the conjugate acid is -5.7 for Cl⁻,¹⁶ which is extremely low compared to 3.98–5.34 for the anilines used in this study, 3.45 for F⁻,¹⁶ 7.14, 4.07 and 4.02 for 4-nitro-, 2,4-dinitro- and 2,4,6-trinitrophenoxide, respectively. In view of the superior nucleofugacity of Cl together with the presence of two

electron withdrawing phenoxy groups in the putative penta-coordinate intermediate the aminolysis of phenyl substituted phenyl chlorophosphates is very likely to occur through an associative but concerted process. The large magnitude of ρ_X and β_X indeed suggests that bond formation has progressed to a large extent in the TS. This is supported by relatively large changes in ρ_Y values (0.22–0.87) as the basicity of nucleophiles (amines) is varied less than 1.5 pK_a unit, or $\Delta\sigma_X \cong 0.5$. The large sensitivity of ρ_Y to change in pK_a or σ_X of the nucleophile indicates that the effect of the substituent on the nucleophile is transmitted efficiently; *i.e.*, the reaction center, P, is close to the substituent X in the TS due to the extensive bond making. In fact this sensitive change of ρ_Y with σ_X [or pK_a(X)] can be represented by a cross-interaction constant, ρ_{XY} , which is defined by eqn. (2). A similar coefficient is given by Jencks *et al.*,¹⁷ p_{xy} [$= (\partial\beta_X/\partial\sigma_Y) = (\partial\rho_Y/\partial\Delta pK_a(X))$]. The two, ρ_{XY} and p_{xy} , have opposite signs and magnitude is related by $\rho_X = \beta_X\rho_e^X$ where $\Delta pK_X = \rho_e^X\sigma_X^4$; thus for the anilines ($\rho_e^X = -4.2$), the two are related by $\rho_{XY} = -4.2 p_{xy}$. The ρ_{XY} value (-1.31) obtained in the present work is large and negative. The negative ρ_{XY} constant (positive p_{xy}) is characteristic of concerted nucleophilic substitution of benzyl, benzoyl and benzenesulfonyl chlorides and arenesulfonates ($\rho_{XY} = -0.6$ – -0.8).⁴ The aminolysis of *N*-methyl-*N*-phenylcarbamoyl chlorides with benzylamines in acetonitrile has been shown to proceed by a concerted mechanism¹⁸ for which the ρ_{XY} values obtained was -0.14 . This value will correspond to *ca.* -0.8 – -0.9 if we correct for the fall-off factor of *ca.* 2.5 for each intervening group $-NCH_3-$ and $-CH_2-$ in substrate and nucleophile, respectively.⁴ In contrast, a positive ρ_{XY} value has been obtained for the stepwise acyl transfer process with rate limiting breakdown of the intermediate.⁵ As has been discussed above, the large magnitude of ρ_{XY} is an indication of very extensive bond formation in the TS. For the associative S_N2 reactions of benzyl fluorides with anilines in methanol at 55.0 °C, the larger magnitude of $\rho_{XY} = -1.67$ in MeOH was obtained,¹⁶ which was ascribed to extensive bond formation in the TS.¹⁹

The cross-interaction constants for an equilibrium process are in general large when in the product state the two fragments interacting are covalently bonded, and especially when a cationic reaction center is involved. An experimental example is the equilibrium cross-interaction constant determined for the nucleophilic substitution reactions of benzyl bromides with *N,N*-dimethylanilines (DMA) [eqn. (4)].²¹ In this case, the cross-



interaction constant ($\rho_{XY} = -1.45$) is that between X and Y within the quaternary ammonium ion (QA⁺) since the two reactants are non-interacting in the initial state. The two interacting fragments in QA⁺ are covalently bonded and the reaction center is positively charged so that the magnitude of the ρ_{XY} is large. Another example is found in the solvolysis of X,Z-disubstituted compounds III, in MeOH at 25 °C, for which $\rho_{XZ} = -6.03 \pm 0.05$ ($r = 0.973$) was obtained.²²



The magnitude is extremely large, in fact is the largest ever observed, since a very strong positive charge develops at the reaction center in the TS due to a strong electron acceptor, CF₃, attached to the reaction center, C_α. Although the ρ_{XZ} corre-

Table 2 Second order rate constant ($k \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and kinetic isotope effects, k_H/k_D , for the reactions of phenyl substituted Y-phenyl chlorophosphates with deuterated X-anilines in acetonitrile at 55 °C

X	Y	k	k_H/k_D
<i>p</i> -OMe	<i>p</i> -Me	$k_H = 79.4 \pm 2^a$ $k_D = 91.3 \pm 1$	0.87 ± 0.02^b
	H	$k_H = 107 \pm 5$ $k_D = 139 \pm 5$	0.77 ± 0.05
	<i>p</i> -Cl	$k_H = 178 \pm 3$ $k_D = 274 \pm 7$	0.65 ± 0.02
H	<i>p</i> -Me	$k_H = 7.30 \pm 0.07$ $k_D = 8.60 \pm 0.06$	0.85 ± 0.01
	H	$k_H = 8.91 \pm 0.04$ $k_D = 11.9 \pm 0.8$	0.75 ± 0.06
	<i>p</i> -Cl	$k_H = 12.0 \pm 0.6$ $k_D = 18.8 \pm 0.9$	0.64 ± 0.05
<i>p</i> -Cl	<i>p</i> -Me	$k_H = 1.20 \pm 0.01$ $k_D = 1.48 \pm 0.02$	0.81 ± 0.01
	H	$k_H = 1.30 \pm 0.02$ $k_D = 1.80 \pm 0.03$	0.71 ± 0.02
	<i>p</i> -Cl	$k_H = 1.45 \pm 0.03$ $k_D = 2.38 \pm 0.05$	0.61 ± 0.02

^{a,b} Standard deviation.

sponds in the case to an activation parameter, the development of positive charge is so strong that the interaction of the two substituents, X and Z, through the cationic center is the strongest ever observed. Thus it seems clear that in the S_N2 type reaction the sign of ρ_{XY} is negative and the magnitude is large when the two interacting fragments are close together (or covalently bonded) in the TS. We therefore conclude that the large negative ρ_{XY} value obtained in this work is consistent with a concerted mechanism with a TS in which bond formation is nearly complete.

This is supported by the secondary kinetic isotope effects observed with deuterated anilines, Table 2. The k_H/k_D values are much lower (0.61–0.87) than unity indicating that the N–H (D) vibrations on the aniline are severely hindered so that the frequencies increase substantially in the TS.^{4c} This is in line with the closer approach of aniline toward the reaction (P) in the TS. The steric hindrance during the bond formation should be relatively large since there are two phenoxy groups attached to the reaction center. For an electron-withdrawing substituent, Y = *p*-Cl, the k_H/k_D value (= 0.64) is smaller indicating a greater degree of bond making by the nucleophile, aniline, which is agreement with a greater magnitude of ρ_X (ρ_X values are -3.55 , -3.74 , -4.09 for Y = *p*-Me, H and *p*-Cl, respectively). The smaller k_H/k_D values for a weaker nucleophile (X = *p*-Cl) than for a stronger nucleophile (X = *p*-OCH₃) are also in line with a greater degree of bond cleavage as well as bond making for the weaker nucleophile since a smaller ρ_Y for X = *p*-Cl is an indication of a larger degree of bond cleavage.

The activation parameters, ΔH^\ddagger and ΔS^\ddagger , based on the k_2 values at three temperatures in Table 3 are consistent with our proposed mechanism. The small positive ΔH^\ddagger values and large negative ΔS^\ddagger values are characteristic of a relatively late TS with a large degree of bond making and leaving group departure. Since the Cl is a strong nucleofuge, the large negative values are characteristic of a relatively late TS with a large bond cleavage which will not require much energy. On the other hand a large degree of bond making will provide partial bond energy in the TS. The large negative ΔS^\ddagger values may result from a large degree of bond cleavage and also a strong steric hindrance in the bond making of the aniline.

In summary, the aminolysis mechanism of phenyl substituted phenyl chlorophosphates with anilines in acetonitrile at 55.0 °C is consistent with a concerted process with a late TS in which

Table 3 Activation parameters^a for the reactions of phenyl substituted Y-phenyl chlorophosphates with substituted X-anilines in acetonitrile at 55 °C

Y	X	Temp./ °C	$k_2 \times 10^4 /$ $\text{m}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger / \text{kcal}$ mol^{-1}	$-\Delta S^\ddagger / \text{cal}$ $\text{mol}^{-1} \text{K}^{-1}$
H	<i>p</i> -Me	45	28.3		
		55	31.5	1.7 ± 0.1^b	65 ± 1^c
		65	35.2		
	H	45	5.40		
		55	8.91	9.7 ± 0.3	43 ± 1
		65	14.2		
	<i>p</i> -Cl	45	1.00		
		55	1.30	5.4 ± 0.2	60 ± 1
		65	1.74		
<i>p</i> -Cl	<i>p</i> -Me	45	45.2		
		55	50.1	1.6 ± 0.1	64 ± 1
		65	55.5		
	H	45	9.50		
		55	12.0	4.2 ± 0.1	59 ± 1
		65	15.0		
	<i>p</i> -Cl	45	1.10		
		55	1.45	5.0 ± 0.2	61 ± 1
		65	1.84		

^a Calculated by Eyring equation. ^{b,c} Standard deviation.

the extent of bond making as well as bond breaking is large. This proposal was based on (1) the large negative ρ_{XY} value, (2) the inverse secondary kinetic isotope effects ($k_H/k_D < 1.0$) and (3) small ΔH^\ddagger with large negative ΔS^\ddagger values. The existence of a pentacoordinate intermediate is safely ruled out in view of these (1–3) and the extremely strong nucleofuge, Cl, attached to the reaction center, P.

Experimental

Materials

Fisher Scientific (USA) HPLC grade acetonitrile was used for kinetic studies without further purification. Anilines were redistilled or recrystallized before use as described previously.²³ Deuterated anilines were prepared by refluxing anilines with D₂O at 120 °C for 36 h. The analysis by ¹H-NMR spectroscopy of deuterated anilines showed more than 99% deuterium content, so no corrections to kinetic isotope effects for a complete deuteration were made. The substrate, diphenyl chlorophosphate (Y = H) was Aldrich G. R. purchased, and was used without further purification. Phenyl substituted phenyl chlorophosphates (Y = *p*-OCH₃, *p*-CH₃, *p*-Cl and *p*-CN) were prepared by reacting phenyl dichlorophosphate with phenols in the presence of triethylamine in acetonitrile on an ice bath.²⁴ Triethylamine hydrochloride salt was separated by filtration. The remaining product in acetonitrile was treated with water and ether for work up. After work-up anhydrous MgSO₄ was added and the solvent was evaporated under reduced pressure after filtration. The substrates were identified by TLC, IR, ¹H-NMR and GC-MS analysis. The physical constants after column chromatography (silica gel/ethyl acetate + *n*-hexane) were:

Phenyl *p*-methoxyphenyl chlorophosphate. Liquid, δ_H (CDCl₃), 7.2–7.4 (Ph-H, 5H, m), 6.9 (*p*-OCH₃-Ph-H, 4H, m), 3.7–3.8 (OCH₃, 3H, s); ν_{max} (neat) 3076 (C-H, aromatic), 2947 (C-H, aliphatic), 1593, 1507 and 1195 (P-O-C₆H₅, 1303 (P=O); *m/z*, 298 (M⁺).

Phenyl *p*-methylphenyl chlorophosphate. Liquid, δ_H (CDCl₃), 7.3–7.4 (Ph-H, 5H, m), 7.2–7.3 (*p*-CH₃-Ph-H, 4H, m), 2.4 (CH₃, 3H, s); ν_{max} (neat), 3078 (C-H, aromatic), 2926 (C-H, aliphatic), 1598, 1511, 1194 and 1158 (P-O-C₆H₅), 1306 (P=O); *m/z*, 282 (M⁺).

Phenyl *p*-chlorophenyl chlorophosphate. Liquid, δ_H (CDCl₃), 7.1–7.4 (Ph-H + *p*-Cl-C₆H₄-H, 9H, s); ν_{max} (neat), 3040 (C-H, aromatic), 1485 and 1190 (P-O-C₆H₅), 1313 (P=O); *m/z*, 302 (M⁺).

Phenyl *p*-cyanophenyl chlorophosphate. Liquid, δ_H (CDCl₃), 7.2–7.4 (Ph-H, 5H, s), 7.4–7.7 (*p*-CN-C₆H₄-H, 4H, s); ν_{max} (neat), 3103 (C-H, aromatic), 2227 (C≡N), 1598, 1496, 1200 and 1173 (P-O-C₆H₅), 1292 (P=O); *m/z*, 293 (M⁺).

Kinetic procedure

Rates were measured conductometrically at 55.0 ± 0.05 °C using a computer-controlled conductivity bridge constructed in the Department of Chemistry. Pseudo-first-order rate constants, k_{obs} , were determined for the release of chloride ion by the Guggenheim method²⁵ with a large excess of aniline, [Phenyl substituted phenyl chlorophosphates] $\cong 3.0 \times 10^{-3}$ mol dm⁻³ and [Anilines] = 0.1–0.5 mol dm⁻³. Second-order rate constants, k_2 , values were obtained from the slope of a plot of k_{obs} vs. [Anilines] with more than four concentrations of anilines. The values of k_{obs} were taken as the averages of more than three runs and were reproducible to within $\pm 3\%$.

Product analysis

Phenyl *p*-methoxyphenyl chlorophosphate was treated with double molar quantity of *p*-methylaniline with stirring for more than 15 half-lives at 55.0 °C in acetonitrile. The aniline hydrochloride salt was separated by filtration. The remaining product was isolated with ether by a work-up process and dried over anhydrous MgSO₄. The product was isolated by evaporating the solvent under reduced pressure after filtration. The physical constants after column chromatography (silica gel/ethyl acetate + *n*-hexane) were:

(PhO)(*p*-OCH₃-C₆H₄O)P(=O)NH-C₆H₄-*p*-CH₃, Liquid δ_H (CDCl₃), 7.2–7.3 (Ph-H, 5H, s), 6.9–7.0 (*p*-CH₃-C₆H₄-H, 4H, s), 6.6–6.8 (*p*-OCH₃-C₆H₄-H, 4H, s), 5.3 (N-H, 1H, w), 3.8 (OCH₃, 3H, s), 2.1–2.3 (CH₃, 3H, s); ν_{max} (neat), 3361 (N-H), 3221 (C-H, aromatic), 2926 (C-H, aliphatic), 1507 and 1179 (P-O-C₆H₅), 1297 (P=O).

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