Combined dual substituent constant and activation parameter analysis assigns a concerted mechanism to alkaline ethanolysis at phosphorus of Y-substituted phenyl diphenylphosphinates†

Ik-Hwan Um,* Jee Eun Park and Young-Hee Shin

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Second-order rate constants have been measured for reactions of Y-substituted phenyl diphenylphosphinates (**1a–h**) with EtO^-K^+ in anhydrous ethanol. A linear Brønsted-type plot is obtained with $\beta_{Lg} = -0.54$, a typical β_{Lg} value for reactions which proceed through a concerted mechanism. The Hammett plots correlated with σ^o and σ^- constants are linear but exhibit many scattered points, while the corresponding Yukawa–Tsuno plot results in excellent linear correlation with $r = 0.41$. The r value of 0.41 indicates that the leaving group departs at the rate-determining step (RDS) whether the reactions proceed through either a concerted or a stepwise mechanism. However, a stepwise mechanism in which departure of the leaving group occurs at the RDS is excluded since the incoming EtO^- ion is much more basic and a poorer leaving group than the leaving aryloxide. The $\Delta H^\ddagger$ values determined in the current reactions are strongly dependent on the nature of the substituent Y, while the $\Delta S^\ddagger$ values remain constant on changing the substituent Y in the leaving group, *i.e.*, from Y = H to Y = 4-NO_2 and Y = 3,4-$(NO_2)_2$. These $\Delta H^\ddagger$ and $\Delta S^\ddagger$ trends also support a concerted mechanism.

Introduction

Certain organophosphorus compounds are widely used as pesticides, neurotoxins and other biologically active substances. Thus, there has been considerable recent and continuing interest in phosphoryl transfer and related reactions due to their importance in the environment, as well as in biological processes.[1–14] Numerous studies have been performed to enhance the rate of decomposition of toxic organophosphorus compounds.[2–10] Accordingly, a range of methods have been developed, from use of metal ions as Lewis acid catalysts[2–5] to use of highly reactive α-nucleophiles.[6–10] Various metal ions including alkali metal ions engender significant catalytic effects in dephosphorylations of neurotoxin simulants.[2–5] The α-nucleophiles (*e.g.*, oximates, HOO^- and *o*-iodosylbenzoate) have also exhibited highly enhanced nucleophilicity under mild conditions.[6–10]

However, systematic kinetic studies have been pursued much less intensively. Therefore, mechanisms for phosphoryl transfer and related reactions have not been completely elucidated but remain controversial (*i.e.*, a concerted *versus* a stepwise mechanism).[1,2,11,12] In a series of important studies by Williams *et al.*, reactions of 4-nitrophenyl diphenylphosphinate with aryloxides have been concluded to proceed through a concerted mechanism.[11] The evidence consisted mainly of the absence of a break (or curvature) in the Brønsted-type plot obtained for the reactions with a series of aryloxides whose pK_a values straddle the basicity of the leaving 4-nitrophenoxide.[11] Similarly, Hengge *et al.* found that reactions of 4-nitrophenyl dimethylphosphinothioate with aryloxides also result in a linear Brønsted-type plot with $\beta_{nuc} = 0.47$, while those of aryl dimethylphosphinothioates with phenoxide exhibit much better Hammett correlation with σ^- than σ^o constants.[1e] Their LFER study has led them to conclude that the reaction proceeds through a concerted mechanism. This conclusion has been further supported by studies of the primary ^{18}O and secondary ^{15}N kinetic isotope effects.[1e]

On the contrary, Buncel and coworkers have shown that σ^o constants result in much better Hammett correlation than σ^- constants for alkaline ethanolysis of aryl dimethylphosphinates.[2a] A similar result has been reported for alkaline hydrolysis of aryl diphenylphosphinates and imidazole catalyzed hydrolysis of aryl diphenylphosphinates.[12] Thus, these reactions have been concluded to proceed through a stepwise mechanism with a pentacoordinate intermediate, in which formation of the intermediate is the rate-determining step (RDS).[2a,12]

We have recently shown that aminolysis of Y-substituted phenyl diphenylphosphinates and diphenylphosphinothioates results in better Hammett correlation with σ^o constants than with σ^- constants.[13] Traditionally, such a result has been interpreted as evidence of a stepwise mechanism.[14–17] However, in this case, we concluded that the reaction proceeds through a concerted mechanism.[13] This was because the Yukawa–Tsuno plots for the same reactions exhibit significantly better correlation than the Hammett plots correlated with σ^o constants alone.[13]

We have extended our kinetic study to reactions of Y-substituted phenyl diphenylphosphinates (**1a–h**) with ethoxide anion in anhydrous ethanol at various temperatures (Scheme 1). The kinetic data have been analyzed using the dual-parameter Yukawa–Tsuno equation together with the activation parameters (*i.e.*, $\Delta H^\ddagger$ and $\Delta S^\ddagger$) associated with the reactions. Application of this combined approach permits unambiguous assignment of the reaction mechanism here.

Division of Nano Sciences and Department of Chemistry, Ewha Womans University, Seoul, 120-750, Korea. E-mail: ihum@ewha.ac.kr; Fax: +82-2-3277-2844; Tel: +82-2-3277-2349

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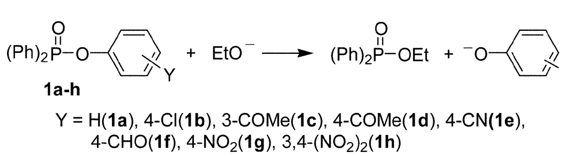


Scheme 1

Results and discussion

All reactions in this study obeyed pseudo-first-order kinetics. Pseudo-first-order rate constants (k_{obsd}) were determined from the equation $\ln(A_\infty - A_t) = -k_{obsd}t + C$. The plots of k_{obsd} *vs.* [EtO^-K^+] were linear passing through the origin, indicating that the contribution of EtOH to k_{obsd} is negligible. Thus, the rate law is given by eqn 1. The second-order rate constants (k_{EtO^-}) were determined from the slopes of the linear plots of k_{obsd} *vs.* [EtO^-K^+] and summarized in Tables 1 and 2. The uncertainty in the k_{EtO^-} is estimated to be less than 3% from replicate runs. Kinetic conditions and results are detailed in the electronic supplementary information (ESI)†.

$$\text{Rate} = k_{obsd}[\text{Sub}], \text{ where } k_{obsd} = k_{EtO^-}[EtO^-K^+] \qquad (1)$$

Effect of leaving group basicity on reactivity

As shown in Table 1, the second-order rate constant increases as the leaving group becomes less basic, *i.e.*, it increases from 7.51×10^{-3} M^{-1} s^{-1} to 0.170 and 21.4 M^{-1} s^{-1} as the pK_a of the conjugate acid of the leaving aryloxide decreases from 15.76 to 13.26 and 9.75, respectively. The effect of leaving group basicity on reactivity is illustrated in Fig. 1. The Brønsted-type plot is linear with $\beta_{Lg} = -0.54$.

Table 1 Summary of second-order rate constants for reactions of Y-substituted phenyl diphenylphosphinates (**1a–h**) with EtO^-K^+ in the presence of 18-crown-6-ether (18C6) in anhydrous EtOH at 25.0 ± 0.1 °C. [18C6]/[EtO^-K^+] = 5.0

Entry	Y	pK_a (Y–PhOH)[a]	k_{EtO^-}/M^{-1} s^{-1}
1a	H	15.76	0.00751
1b	4-Cl	14.90	0.0419
1c	3-COMe	14.64	0.0641
1d	4-COMe	13.26	0.170
1e	4-CN	13.04	0.563
1f	4-CHO	12.66[b]	0.265
1g	4-NO_2	11.98[b]	1.09
1h	3,4-$(NO_2)_2$	9.75[b]	21.4

[a] pK_a data in anhydrous ethanol were taken from ref. 18. [b] pK_a values were calculated from the relationship, pK_a (in EtOH) = 1.30pK_a (in H_2O) + 2.70. (see ref. 18).

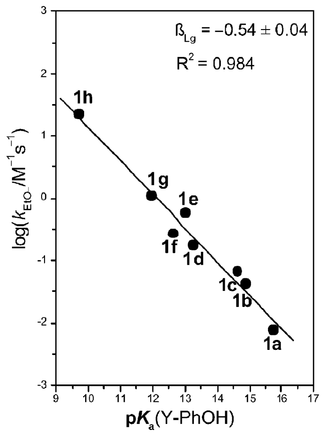


Fig. 1 Brønsted-type plot for reactions of Y-substituted phenyl diphenylphosphinates (**1a–h**) with EtO^-K^+ in the presence of 18-crown-6-ether (18C6) in anhydrous EtOH at 25.0 ± 0.1 °C. [18C6]/[EtO^-K^+] = 5.0.

The magnitude of the Brønsted coefficients β_{nuc} and β_{Lg} has been used as a measure of reaction mechanisms including transition-state structures of various types of reactions.[15–17] It has often been reported that β_{nuc} (or $-\beta_{Lg}$) changes from 0.9 ± 0.1 to 0.3 ± 0.1 for reactions which proceed through a stepwise mechanism with a change in the RDS. Hupe and Jencks found curved Brønsted-type plots for reactions of aryl acetates with thiolate nucleophiles (*i.e.*, β_{Lg} = *ca.* −0.9 for strongly basic leaving group but $\beta_{Lg} = -0.33$ for weakly basic leaving group).[19] A change in the RDS has been suggested to be responsible for the curved Brønsted-type plots.[19] The linear Brønsted-type plot with a β_{Lg} value of −0.54 obtained in the present system is typical for reactions which proceed through a concerted mechanism (*e.g.*, $\beta_{Lg} = -0.52$ for reactions of aryl dimethylphosphinothioates with phenoxide[1e] and $\beta_{Lg} = -0.66$ for reactions of aryl diphenylphosphinate with piperidine[13a]). Thus, one might suggest that the current reactions of **1a–h** with EtO^- proceed through a concerted mechanism.

Hammett *versus* Yukawa–Tsuno plots

To get more conclusive information on the reaction mechanism, Hammett plots have been constructed using σ^o and σ^- constants in Fig. 2A and 2B, respectively. One might expect that σ^- constants would result in a better Hammett correlation than σ^o constants if the P–OAr bond rupture is involved in the RDS. On the contrary, σ^o constants would exhibit a better correlation than σ^- constants if the P–OAr bond rupture occurs after the RDS. In fact, as shown in Fig. 2, σ^o constants result in only slightly better Hammett correlation than σ^- constants (*i.e.*, $R^2 = 0.981$ for σ^o and $R^2 = 0.979$ for σ^- constants). Thus, one cannot obtain any conclusive information on the reaction mechanism from these Hammett plots.

Table 2 Summary of kinetic results for reactions of phenyl diphenylphosphinates (**1a**), 4-nitrophenyl diphenylphosphinates (**1g**) and 3,4-dinitrophenyl diphenylphosphinates (**1h**) with EtO^-K^+ in the presence of 18-crown-6-ether in anhydrous EtOH at 5 different temperatures. [18C6]/[EtO^-K^+] = 5.0

	10^2 k_{EtO^-}/M^{-1} s^{-1}						
	15.0 °C	20.0 °C	25.0 °C	35.0 °C	45.0 °C	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal mol^{-1} K^{-1}
1a	0.378	0.580	0.751	1.41	2.85	11.3 ± 0.2	−30 ± 1
1g	59.1	84.1	109	169	273	8.4 ± 0.4	−30 ± 1
1h	1480	1760	2140	3280	4680	6.5 ± 0.2	−30 ± 1

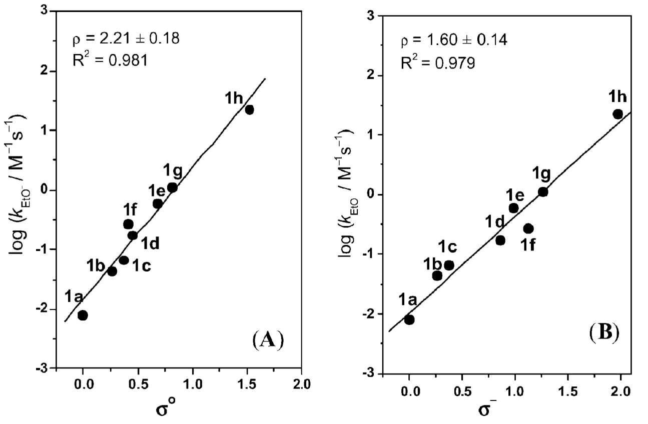


Fig. 2 Correlation of log k_{EtO^-} with σ^o (A) and σ^- (B) for reactions of Y-substituted phenyl diphenylphosphinates (**1a–h**) with EtO^-K^+ in the presence of 18-crown-6-ether in anhydrous EtOH at 25.0 ± 0.1 °C. $[18C6]/[EtO^-K^+] = 5.0$. The σ^o and σ^- values were taken from ref. 20.

We have recently shown that the dual-parameter Yukawa–Tsuno equation (eqn 2) is highly effective to elucidate ambiguities in reaction mechanisms of phosphinyl transfer and related reactions.[13,21] Thus, a Yukawa–Tsuno plot has been constructed for the reactions of **1a–h** with EtO^-. As shown in Fig. 3, the Yukawa–Tsuno plot now results in an excellent correlation (*i.e.*, $R^2 = 0.997$) with $\rho = 1.98$ and $r = 0.41$.

$$\log k^Y/k^H = \rho[\sigma^o + r(\sigma^- - \sigma^o)] \qquad (2)$$

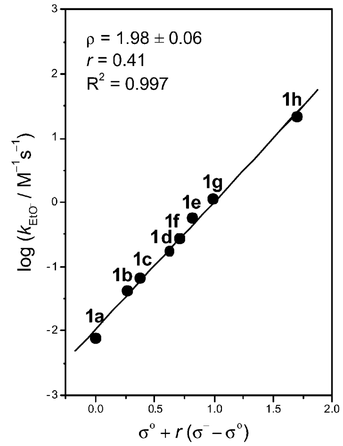
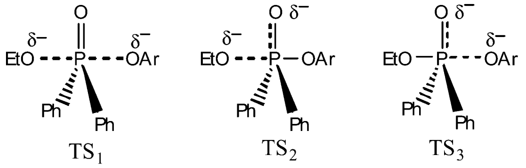


Fig. 3 Yukawa–Tsuno plot for reactions of Y-substituted phenyl diphenylphosphinates (**1a–h**) with EtO^-K^+ in the presence of 18-crown-6-ether in anhydrous EtOH at 25.0 ± 0.1 °C. $[18C6]/[EtO^-K^+] = 5.0$.

The *r* value in the Yukawa–Tsuno equation represents the resonance demand of the reaction center or the extent of resonance contribution.[22] Thus, the fact that $r = 0.41$ in the current reactions indicates that a partial negative charge develops on the O atom of the leaving aryloxide in the rate-determining transition state, which can be delocalized on the substituent Y through resonance interaction. Accordingly, one can suggest that the departure of the leaving group occurs definitely in the RDS in the present system whether the reactions proceed through a concerted mechanism with a transition-state structure similar to TS_1 or through a stepwise mechanism with a pentacoordinate intermediate. For the latter mechanism, two different transition-state structures are possible, *i.e.*, TS_2 represents the transition-state structures in the rate-determining formation of the intermediate and TS_3 applies to the rate-determining leaving group departure from the intermediate to yield the products.



Since leaving group departure is not advanced in TS_2, it does not bear a partial negative charge on the O atom of the leaving ArO moiety that the *r* value indicates. Accordingly, TS_2 is not likely to be the TS structure in this study. One can also exclude TS_3 on the basis of the fact that the incoming ethoxide is much more basic and a poorer leaving group than the leaving aryloxide. Thus, one can suggest that the current reactions proceed through a concerted mechanism with TS_1. This is consistent with the preceding argument on the basis of the linear Brønsted-type plot with $\beta_{Lg} = -0.54$.

Activation parameters and reaction mechanism

To further probe the above argument, activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) have been determined from rate constants measured at 5 different temperatures for the reactions of phenyl, 4-nitrophenyl, and 3,4-dinitrophenyl diphenylphosphinates (**1a**, **1g**, and **1h**, respectively) with ethoxide ion. The kinetic results are summarized in Table 2. The Arrhenius plots shown in Fig. 4 exhibit excellent linear correlations, indicating that the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values determined in this study are accurate and reliable.

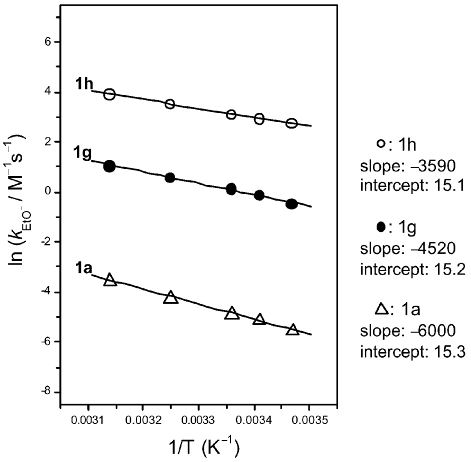


Fig. 4 Arrhenius plots for reactions of phenyl diphenylphosphinate (**1a**), 4-nitrophenyl diphenylphosphinate (**1g**) and 3,4-dinitrophenyl diphenylphosphinate (**1h**) with EtO^-K^+ in the presence of 18C6 in anhydrous EtOH. $[18C6]/[EtO^-K^+] = 5.0$.

Importantly, Table 2 shows that $\Delta H^\ddagger$ decreases significantly (*i.e.*, *ca.* 5 kcal mol^{-1}) on changing the substituent from H (**1a**) to $3,4\text{-}(NO_2)_2$ (**1h**) while $\Delta S^\ddagger$ remains constant. The effect of the substituent Y on $\Delta H^\ddagger$ is illustrated in Fig. 5. The correlation of $\Delta H^\ddagger$ with σ^- constants of the substituent Y exhibits an excellent linearity with a large slope, indicating that $\Delta H^\ddagger$ is strongly

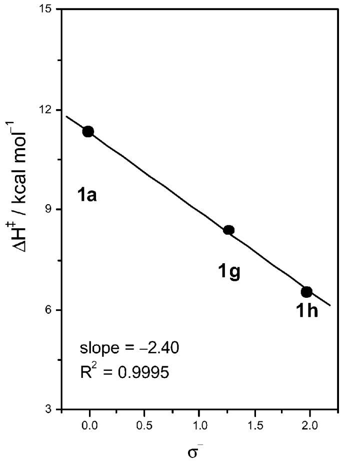


Fig. 5 Plot of $\Delta H^{\ddagger}$ *versus* σ^- constants for reactions of phenyl diphenylphosphinate (**1a**), 4-nitrophenyl diphenylphosphinate (**1g**), and 3,4-dinitrophenyl diphenylphosphinate (**1h**) with EtO^-K^+ in the presence of 18C6 in anhydrous EtOH at 25.0 ± 0.1 °C.

influenced by the electronic nature of the substituent Y. Such a strong dependence of $\Delta H^{\ddagger}$ on the substituent Y in the leaving group can be expected only for reactions in which the departure of the leaving group occurs in the RDS.[23]

The above argument is complemented by the $\Delta S^{\ddagger}$ values. One might expect that the transition state would become earlier as the substituent Y changes from H to 3,4-$(NO_2)_2$ on the basis of a normal Hammond effect.[15] If the current reaction proceeds through TS_2, in which the departure of the leaving group is not advanced, $\Delta S^{\ddagger}$ should be dependent mainly on the degree of bond formation between the incoming ethoxide and the P-electrophilic site. In this case, $\Delta S^{\ddagger}$ should be less negative for the reaction of **1h** (Y = 3,4-$(NO_2)_2$) than for that of **1a** (Y = H). However, as shown in Table 2, the $\Delta S^{\ddagger}$ value remains constant, indicating that the reactions do not proceed through TS_2 or a normal Hammond effect is not operative in the current system.

On the contrary, if the reaction proceeds through a concerted mechanism with a transition-state structure similar to TS_1, $\Delta S^{\ddagger}$ should be influenced by the degree of both bond formation and bond rupture. In this case, one might expect that $\Delta S^{\ddagger}$ would be independent of the electronic nature of the substituent Y. This is because the change in $\Delta S^{\ddagger}$ upon bond formation would be compensated by the change in $\Delta S^{\ddagger}$ upon bond rupture, whether the reactions proceed through an early or late transition state. In fact, Table 2 shows that $\Delta S^{\ddagger}$ remains constant upon changing the substituent Y. Besides, the current $\Delta S^{\ddagger}$ value of -30 ± 1 cal mol^{-1} K^{-1} is comparable to those reported for reactions which proceed through a concerted mechanism (*e.g.*, $\Delta S^{\ddagger} = -24.8$ and -36.6 cal mol^{-1} K^{-1} for hydrolysis of 4-nitrophenyl diethyl phosphate and ethyl phosphate, respectively,[1g] $\Delta S^{\ddagger} = -29.3$ and -34.3 cal mol^{-1} K^{-1} for aminolysis of 2,4-dinitrophenyl diphenylphosphinate and diphenylphosphinothioate, respectively in 80 mol% H_2O–20 mol% DMSO[13b] and $\Delta S^{\ddagger}$ = *ca.* −25 cal mol^{-1} K^{-1} for reactions of aryl *N*-phenyl thiocarbamates with benzylamines in CH_3CN[24a]). However, the current $\Delta S^{\ddagger}$ value is much less negative than those reported for reactions which proceed through a stepwise mechanism (*e.g.*, $\Delta S^{\ddagger}$ = *ca.* −60 cal mol^{-1} K^{-1} for pyridinolysis of aryl furan-2-carbodithioates[24b] and $\Delta S^{\ddagger}$ = *ca.* −50 cal mol^{-1} K^{-1} for aminolysis of phenyl cyclopropanecarboxylates in CH_3CN[24c]). Thus, one can suggest that the $\Delta S^{\ddagger}$ values determined in the present reactions also support a concerted mechanism.

Conclusion

We conclude that the current reactions of **1a–h** proceed through a concerted mechanism with a transition-state structure similar to TS_1 on the basis of the following arguments:

(1) The linear Brønsted-type plot with $\beta_{Lg} = -0.54$ observed for reactions of **1a–h** with EtO^- is typical for reactions which proceed through a concerted mechanism.

(2) The Yukawa–Tsuno plot for reactions of **1a–h** with EtO^- exhibits an excellent correlation with $r = 0.41$, indicating that the departure of the leaving group occurs in the RDS.

(3) The $\Delta H^{\ddagger}$ values are strongly dependent on the nature of substituent Y in the leaving group, which is only possible when the leaving group departure is involved in the RDS.

(4) The $\Delta S^{\ddagger}$ values are *ca.* −30 cal mol^{-1} K^{-1} regardless of the substituent Y, which also support a concerted mechanism.

Experimental

Materials

Y-substituted phenyl diphenylphosphinates (**1a–h**) were synthesized by modification of literature reported previously.[12b,25] EtO^-K^+ stock solution was prepared by dissolving potassium metal in anhydrous ethanol under nitrogen and was stored in the refrigerator. The concentration of EtO^-K^+ stock solution was determined by titration with standard HCl solution. 18-Crown-6-ether (18C6) was recrystallized from acetonitrile and dried over P_2O_5 *in vacuo*. The anhydrous ethanol used was further dried over magnesium and distilled under N_2.

Kinetics

Kinetic studies were performed with a Scinco S-3100 UV–vis spectrophotometer for slow reactions ($t_{1/2} \geq 10$ s) or with an Applied Photophysics DX-17 MV stopped-flow spectrophotometer for fast reactions ($t_{1/2} < 10$ s) equipped with a constant temperature circulating bath. The reactions were followed by monitoring the appearance of the leaving aryloxide at a fixed wavelength corresponding to the maximum absorbance (λ_{max}) of Y–$C_6H_4O^-$.

All the reactions were carried out under pseudo-first-order conditions in the presence of a complexing agent, 18C6 to sequester K^+ and avoid possible catalysis by K^+ ion (*i.e.*, $[18C6]/[EtO^-K^+] = 5.0$). Typically, the reaction was initiated by adding 5 μL of a 0.02 M substrate solution in MeCN by a 10 μL gastight syringe to a 10 mm quartz UV cell containing 2.50 mL of the thermostated reaction mixture made up of anhydrous ethanol and an aliquot of EtO^-K^+ stock solution. All the solutions were transferred by Hamilton gastight syringes under nitrogen. Generally, the concentration of EtO^-K^+ was varied over the range $1–100 \times 10^{-3}$ M, while the substrate concentration was $2–4 \times 10^{-5}$ M. Usually 5 different concentrations of EtO^-K^+ solution were used to determine the k_{EtO^-} value from the slope of the linear plot of k_{obsd} *vs.* EtO^-K^+ concentration.

Products analysis

Y-substituted phenoxide was liberated quantitatively and identified as one of the reaction products by comparison of the UV–vis spectra after the completion of the reactions with those of the authentic samples under the same reaction conditions.

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23 A referee suggested an alternative explanation for the dependence of $\Delta H^{\ddagger}$ on the substituent Y, *i.e.*, "the electron withdrawing nature of the ester group (which is reflected in the magnitude of σ^- constant) affects the electrophilicity of the phosphorus atom, and thus destabilizes the reactant ground state." We thank the referee for calling our attention to this alternative explanation.

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