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Kinetics and Reaction Mechanism for Alkaline Hydrolysis of Y-Substituted-Phenyl Diphenylphosphinates

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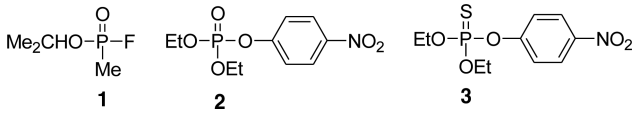
The second-order rate constants (k_{OH^-}) for the reactions of Y-substituted-phenyl diphenylphosphinates (**4a-4i**) with OH^- in H_2O at 25.0 ± 0.1 °C have been measured spectrophotometrically. Comparison of k_{OH^-} with k_{EtO^-} (the second-order rate constants for the corresponding reactions with EtO^- in ethanol) has revealed that EtO^- is less reactive than OH^- although the former is *ca*. 3.4 pK_a units more basic than the latter, indicating that the reactivity of these nucleophiles is not governed by their basicity alone. The Brønsted-type plot for the reactions of **4a-4i** with OH^- is linear with $\beta_{lg} = -0.36$. The Hammett plot correlated with σ^- constants results in a slightly better correlation than that correlated with σ^o constants but exhibits many scattered points. In contrast, the Yukawa-Tsuno plot for the same reactions exhibits an excellent linear correlation with $\rho = 0.95$ and $r = 0.55$. The r value of 0.55 implies that a negative charge develops partially on the O atom of the leaving group. Thus, the reactions of **4a-4i** with OH^- have been concluded to proceed through a concerted mechanism.

Key Words : Brønsted-type plot, Hammett plot, Yukawa-Tsuno plot, Rate-determining step, Concerted mechanism

Introduction

Nucleophilic substitution reactions of phosphorus centered esters are of prime importance in biological systems, *e.g*., the transfer of a phosphoryl group between ATP and ADP is the fundamental mechanism for energy transfer. Furthermore, certain organophosphorus compounds (*e.g*., sarin **1**, paraoxon **2** and parathion **3**) are known to possess mammalian toxicity and insecticidal properties.[1-4] Accordingly, numerous studies have been performed to breakdown these toxic compounds under mild conditions.[5-12] It has been reported that α-nucleophiles such as HOO^-, *o*-iodosylbenzoate and various oximate anions are highly effective in destruction of such toxic materials under mild conditions.[5-9] Besides, various metal ions (*e.g*., La^{3+}, Eu^{3+}, Co^{3+}, Zn^{2+}, Mn^{2+}, K^+, Na^+, Li^+, *etc*.) have been used as Lewis acid catalysts in reactions of various organophosphorus compounds.[10-12]



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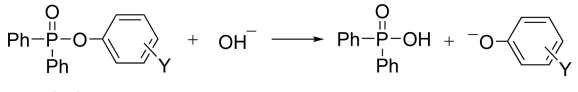
However, mechanistic studies have much less been investigated. Accordingly, the reaction mechanisms have not been completely understood but remain controversial (*i.e*., a concerted mechanism *vs*. a stepwise pathway).[13-19] It has been reported that nucleophilic substitution reactions of 4-nitrophenyl dimethylphosphinothioate with a series of aryloxides result in a linear Brønsted-type plot over 4.6 pK_a units with $\beta_{nuc} = 0.47$.[13a] Besides, alkaline hydrolysis of aryl dimethylphosphinothioates has been reported to exhibit a much better Hammett correlation with σ^- constants (R^2 = 0.991) than with σ^o (R^2 = 0.933) or σ constants (R^2 = 0.926).[13a] Thus, these reactions have been concluded to proceed through a concerted mechanism.[13a]

On the contrary, alkaline hydrolysis of aryl diphenylphosphinates has been reported to proceed through a stepwise mechanism on the basis of the result that σ^o constants exhibit a better Hammett correlation than σ^- constants.[15] Similar results have been reported for alkaline hydrolysis of *O*-aryl dimethylphosphinothioates,[16] imidazole catalyzed hydrolysis of aryl diphenylphosphinates[17] and alkaline ethanolysis of aryl dimethylphosphinates.[10a] Thus, these reactions have been concluded to proceed through a stepwise mechanism, in which departure of the leaving group occurs after the rate-determining step (RDS).[10a,15-17]

We have recently shown that σ^o constants result in a better Hammett correlation than with σ^- constants for alkaline ethanolysis of Y-substituted-phenyl diphenylphosphinates (**4a-4i**).[18,19] Traditionally, such result has been taken as evidence for a stepwise mechanism, in which departure of the leaving group occurs after the RDS.[10a,15-17] However, we have concluded that the reaction proceeds through a



4a-i

Y = 3,4-$(NO_2)_2$ (**4a**), 4-NO_2 (**4b**), 4-CHO (**4c**), 4-CN (**4d**), 4-COMe (**4e**), 3-Cl (**4f**), 3-COMe (**4g**), 4-Cl (**4h**), H (**4i**).

Scheme 1

Table 1. Summary of Second-Order Rate Constants for the Reactions of Y-Substituted-Phenyl Diphenylphosphinates (**4a-4i**) with OH^- in H_2O and with EtO^- in Anhydrous Ethanol at 25.0 ± 0.1 °C[a]

Entry	Y	k_{OH^-}/$M^{-1}s^{-1}$	k_{EtO^-}/$M^{-1}s^{-1}$
4a	3,4-$(NO_2)_2$	89.7	21.4
4b	4-NO_2	22.1	1.09
4c	4-CHO	12.6	0.265
4d	4-CN	15.1	0.563
4e	4-COMe	8.84	0.170
4f	3-Cl	5.12	-
4g	3-COMe	5.44	0.0641
4h	4-Cl	3.79	0.0419
4i	H	1.61	0.00751

[a]The k_{EtO^-} values were taken from ref 18.

concerted mechanism, since the Yukawa-Tsuno plots for the same reactions exhibit a significantly better correlation than the Hammett plots correlated with σ° constants.[18,19] We have now extended our study to alkaline hydrolysis of **4a-4i** (Scheme 1) to obtain further information on the reaction mechanism through analysis of various LFERs (*e.g.*, Brønsted, Hammett and Yukawa-Tsuno equations).

Results and Discussion

All of the reactions in this study obeyed pseudo-first-order kinetics. Pseudo-first-order rate constants (k_{obsd}) were calculated from the equation, $\ln (A_\infty - A_t) = -k_{obsd}t + C$. The plots of k_{obsd} *vs*. [OH^-] were linear and passed through the origin, indicating that the contribution of H_2O to k_{obsd} is negligible. Thus, the second-order rate constants (k_{OH^-}) were calculated from the slope of the linear plots of k_{obsd} *vs*. [OH^-]. The correlation coefficient for the linear regression was always higher than 0.9995. The uncertainty in the k_{OH^-} values is estimated to be less than 3% from replicate runs. The k_{OH^-} values calculated in this way are summarized in Table 1 together with the reported k_{EtO^-} values (the second-order rate constants for the corresponding reactions with EtO^- in anhydrous ethanol) for comparison.

Effect of Leaving-Group Substituent on Reactivity and Mechanism. As shown in Table 1, k_{OH^-} decreases as the substituent Y in the leaving-group becomes a weaker electron-withdrawing group (EWG), *e.g.*, it decreases from 89.7 $M^{-1}s^{-1}$ to 8.84 and 1.61 $M^{-1}s^{-1}$ as Y changes from 3,4-$(NO_2)_2$ to 4-COMe and H, in turn. A similar reactivity trend is demonstrated for the reactions with EtO^-. It is also noted that EtO^- is much less reactive than OH^-, although the former in ethanol is *ca.* 3.4 pK_a units more basic than the latter in water (pK_a = 19.18 for EtOH in ethanol and pK_a = 15.74 for H_2O in water).[20] This demonstrates convincingly that the reactivity of these nucleophiles is not governed by their basicity alone.

The effect of the leaving-group basicity on reactivity of OH^- toward **4a-4i** is illustrated in Figure 1. The Brønsted-type plot for the reactions of **4a-4i** with OH^- is linear with β_{lg} = –0.36, indicating that the reactions proceed without

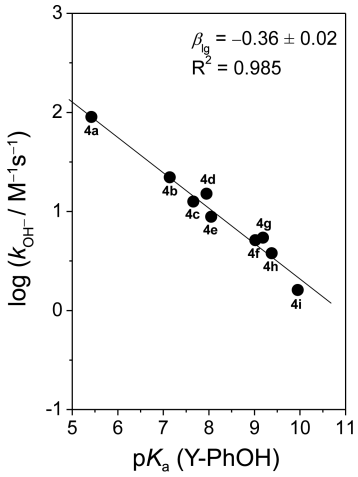
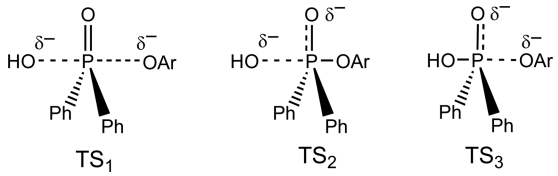


Figure 1. Brønsted-type plot for the reactions of Y-substituted-phenyl diphenylphosphinates (**4a-4i**) with OH^- in H_2O at 25.0 ± 0.1 °C. The identity of the points is given in Table 1.

changing the mechanism (or the RDS) upon changing the leaving-group basicity over 4.5 pK_a units. Besides, the β_{lg} value of –0.36 obtained for the reactions with OH^- is much smaller than the β_{lg} value of –0.54 reported for the corresponding reactions with EtO^- in anhydrous ethanol, which was concluded to proceed through a concerted mechanism.[18] Thus, one might suggest that the reactions of **4a-4i** with OH^- proceed through a stepwise mechanism, in which the departure of the leaving group occurs after the RDS, on the basis of the small β_{lg} value.

However, one cannot exclude a possibility that the reactions proceed through a concerted mechanism because a β_{lg} value of –0.36 can be taken as a lower limit for a concerted mechanism. Thus, more conclusive information is necessary to deduce whether the reactions of **4a-4i** with OH^- proceed through a concerted mechanism or via a stepwise pathway, in which formation of an intermediate is the RDS.

Deduction of Reaction Mechanism. The reactions of **4a-4i** would proceed through a concerted mechanism with a transition state (TS) structure similar to TS_1, in which the HO–P bond formation and the P–OAr bond rupture occur simultaneously, or through a stepwise mechanism with TS_2 or TS_3 depending on the RDS.



If the reactions proceed through a stepwise mechanism, the leaving-group departure would occur after the RDS. This is because the incoming OH^- is significantly more basic and a poorer nucleofuge than the leaving aryloxides. Accordingly, if the reactions proceed through a stepwise mechanism, the TS structure should be similar to TS_2, in which the P–OAr bond rupture is not advanced in the RDS. On the contrary, if the reactions proceed through a concerted

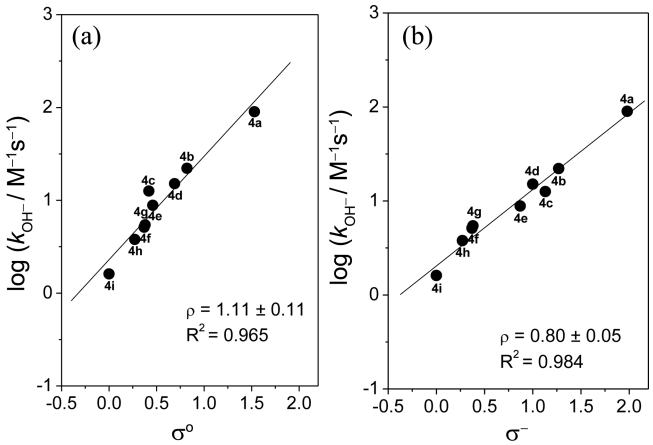


Figure 2. Hammett plots correlated with σ° (a) and σ⁻ constants (b) for the reactions of Y-substituted-phenyl diphenylphosphinates (**4a-4i**) with OH^- in H_2O at 25.0 ± 0.1 °C. The identity of the points is given in Table 1.

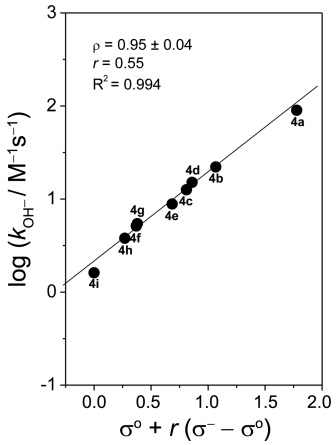


Figure 3. Yukawa-Tsuno plot for the reactions of Y-substituted-phenyl diphenylphosphinates (**4a-4i**) with OH^- in H_2O at 25.0 ± 0.1 °C. The identity of the points is given in Table 1.

mechanism, a negative charge would develop partially on the O atom of the leaving aryloxide as shown in TS_1. Since such a negative charge can be delocalized to the substituent Y through resonance interactions, σ⁻ constants should result in a better Hammett correlation than σ° constants. However, if the reactions proceed through a stepwise mechanism, no negative charge would develop on the O atom of the leaving aryloxide, since the P–OAr bond rupture would occur after the RDS as mentioned above. In this case, σ° constants would give a better Hammett correlation than σ⁻ constants. In fact, Haake *et al*. have concluded that alkaline hydrolysis of Y-substituted-phenyl diphenylphosphinates (Y = 4-COMe, 4-Br, 4-Cl, H, 3-Me, and 4-Me) proceeds through a stepwise mechanism with a TS structure similar to TS_2 on the basis of the results that σ° constants exhibit a better Hammett correlation than σ⁻ constants.[15]

Thus, Hammett plots for the reactions of **4a-4i** have been constructed using σ° and σ⁻ constants to deduce the reaction mechanism. As shown in Figure 2, the Hammett plot correlated with σ⁻ constants results in a better linear correlation than that correlated with σ° constants, although the difference in the correlation coefficient is not significant (*e.g.*, R^2 = 0.965 for σ° constants and R^2 = 0.984 for σ⁻ constants). However, this is in contrast to the report by Haake *et al*. that alkaline hydrolysis of Y-substituted-phenyl diphenylphosphinates (Y = 4-COMe, 4-Br, 4-Cl, H, 3-Me, and 4-Me) results in a better Hammett correlation with σ° constants than with σ⁻ constants.[15] We suggest that the discrepancies are due to the limited numbers of substituents which were taken to construct the Hammett plot with σ⁻ constants. This is because only 4-COMe has a σ⁻ constant among the six substituents studied by Haake *et al*.[15]

To get more conclusive information on the reaction mechanism, we have employed the Yukawa-Tsuno equation (1). Eq. (1) was originally derived to account for the kinetic data obtained from solvolysis of benzylic systems, in which a partial positive charge develops.[21] We have shown that Eq. (1) is highly effective to elucidate ambiguities in reaction mechanisms for various nucleophilic substitution reactions, *e.g.*, aminolyses of 4-pyridyl X-substituted-benzoates,[22a] Y-substituted-phenyl 2-methoxybenzoates,[22b] 2,4-dinitrophenyl X-substituted-benzoates,[22c] Y-substituted-phenyl diphenyl phosphinates,[22d] *O*-aryl thionobenzoates,[22e] and alkaline ethanolysis of aryl benzenesulfonates[22f] and phenyl Y-substituted-phenyl carbonates,[22g] and Michael-type reactions of activated acetylenes with amines.[22h]

$$\log k^Y/k^H = \rho[\sigma^o + r(\sigma^- - \sigma^o)] \quad (1)$$

Thus, a Yukawa-Tsuno plot has been constructed in Figure 3. One can see that the Yukawa-Tsuno plot exhibits an excellent linear correlation (R^2 = 0.994) with ρ = 0.95 and *r* = 0.55. The *r* value in Eq. (1) represents the resonance demand of the reaction center or the extent of resonance contribution.[21] The *r* value of 0.55 clearly indicates that a negative charge develops partially on the O atom of the leaving group, which can be delocalized to the substituent Y through resonance interactions. This is possible only when the P–OAr bond rupture occurs in the RDS. Thus, one can conclude that the reactions of **4a-4i** with OH^- proceed through a concerted mechanism and the β_{lg} value of –0.36 shown in Figure 1 represents a lower limit for a concerted mechanism.

The above idea (*i.e.*, a concerted mechanism) accounts for the result shown in Table 1 that EtO^- in ethanol is much less reactive than OH^- in H_2O although the former is *ca*. 3.4 pK_a units more basic than the latter. The fact that the more basic EtO^- is less reactive than the less basic OH^- implies that the reaction rate is not governed by the basicity alone but is influenced also by nucleofugality of the leaving group, if the leaving-group departure occurs at the RDS. Aryloxides have been reported to be over 5 pK_a units more basic in ethanol than in H_2O, indicating that Y-substituted phenoxide in **4a-4i** becomes a significantly poorer nucleofuge upon the medium change from H_2O to ethanol. It is apparent that the decreased nucleofugality would cause a decrease in reactivity of a concerted reaction or a stepwise reaction in which leaving-

group departure occurs in the RDS. As mentioned earlier, leaving-group departure should occur after the RDS if the current reactions proceed through a stepwise mechanism. Thus, the fact that **4a-4i** are less reactive in ethanol than in H_2O indicates that the reaction proceeds through a concerted mechanism and the decreased nucleofugality of the aryloxides in **4a-4i** upon the medium change from H_2O to ethanol is mainly responsible for the decreased reactivity shown by EtO^-.

Conclusions

The current study has allowed us to conclude the following: (1) The Brønsted-type plot for the reactions of **4a-4i** with OH^- is linear with $\beta_{lg} = -0.36$. (2) The Hammett plot correlated with σ^- constants results in a slightly better correlation than that correlated with σ^o constants (*e.g.*, $R^2 = 0.984$ for σ^- constants and $R^2 = 0.965$ for σ^o constants) but exhibits many scattered points. (3) In contrast, the Yukawa-Tsuno plot exhibits an excellent linear correlation ($R^2 = 0.994$) with $\rho = 0.95$ and $r = 0.55$, indicating that a negative charge develops partially on the O atom of the leaving group in the RDS. (4) The reactions of **4a-4i** with OH^- proceed through a concerted mechanism. (5) The β_{lg} value of –0.36 shown in the Brønsted-type plot for the reactions of **4a-4i** represents a lower limit for a concerted mechanism.

Experimental Section

Materials. Y-Substituted-phenyl diphenylphosphinates (**4a-4i**) were readily prepared from the reaction of diphenylphosphinyl chloride with Y-substituted phenol in anhydrous ether under the presence of triethylamine as reported previously.[23] NaOH and other chemicals were of the highest quality available. Doubly glass distilled water was further boiled and cooled under nitrogen just before use.

Kinetics. The kinetic study was performed using a UV-Vis-spectrophotometer equipped with a constant temperature circulating bath to maintain the reaction mixture at 25.0 ± 0.1 °C. The reactions were followed by monitoring the appearance of Y-substituted phenoxide. All the reactions were carried out under pseudo-first-order conditions. All solutions were transferred by gas-tight syringes. Generally, the OH^- concentration was varied over the range (5–100) × 10^{-3} M, while the substrate concentration was *ca.* 2×10^{-5} M. Pseudo-first-order rate constants (k_{obsd}) were calculated from the equation, $\ln (A_\infty - A_t) = -k_{obsd}t + C$. The plots of $\ln (A_\infty - A_t)$ *vs*. time were linear over 90% of the total reaction. Usually, five different OH^- concentrations were employed and replicate values of k_{obsd} were determined to obtain the second-order rate constants (k_{OH^-}) from the slope of linear plots of k_{obsd} *vs*. OH^- concentrations.

Products Analysis. Y-Substituted phenoxide was liberated quantitatively and identified as one of the products in the reaction of **4a-4i** by comparison of the UV-vis spectrum after completion of the reaction with that of authentic sample under the same reaction condition.

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