# STUDIES ON ORGANOPHOSPHORUS COMPOUNDS. XXXVI.*
# SUBSTITUENT EFFECTS OF ALKYLPHOSPHONATES AND -PHOSPHINATES IN ALKALINE HYDROLYSIS

CHENGYE YUAN,† SHUSEN LI AND XIUGAO LIAO

*Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Linling Lu, Shanghai 200032, China*

*ABSTRACT* Alkaline hydrolysis of diethyl alkylphosphonates and alkyl diethylphosphinates was studied in aqueous dimethyl sulphoxide. The behaviour of these acyclic phosphorus esters is very similar to that of some cyclic phosphorus esters. Rate constants were measured at three temperatures over a 30 °C range, and the activation functions of the reaction were estimated. The basic hydrolytic process was proved to be a bimolecular AE reaction. Multiple regression analyses involving rate constants and substituent parameters gave, as a rule, poor results using steric constants derived from carbon compounds. However, the substituent steric effect on the rate of hydrolysis of phosphonates and phosphinates studied correlated very well with $\Delta\Delta E$, representing the difference in steric energy calculated by molecular mechanics. It is attributed to the various degrees of susceptibility of carbon and phosphorus atoms to the steric hindrance of the substituents. Moreover, Newman's rule of six for the hydrolytic reaction of carboxylates was completely eliminated in phosphorus ester hydrolysis.

## INTRODUCTION

Investigation of the substituent effect of organophosphorus esters provides a basis for quantitative structure–activity relationship (QSAR) studies of this biologically important class of compounds and can contribute to progress in phosphorus chemistry in general.[1,2] The hydrolytic reaction of phosphorus-based esters has been the subject of many previous investigations,[3-5] but the QSAR examination of these compounds was hindered by insufficient structural parameters of groups directly bonded to phosphorus. As shown previously, the structure of exocyclic alkyl groups has a remarkable influence on the rate constant ($k$) of alkaline hydrolysis of some cyclic esters of alkylphosphonic acids.[6-8] However, regression analyses demonstrated that log $k$ did not correlate with commonly used steric parameters, including Taft's $E_s$ and Charton's $v$. In the meantime, the energy difference between the most stable conformation of the penta-coordinated transition-state and the ground-state phosphorus esters during the basic hydrolysis as represented by $\Delta\Delta E$ seems to reflect the contribution of the primary steric effect of substituents in this process. The term $\Delta\Delta E$ was therefore suggested by us as a substituent steric parameter in the alkaline hydrolysis of the

cyclic esters of alkylphosphonic acids.[9] In this paper, we report the characteristic behaviour of diethyl alkylphosphonates (1) and alkyl diethylphosphinates (2) in alkaline hydrolysis and to examine the accept-



1: $R^1 = CH_3, C_2H_5, n\text{-}C_3H_7, iso\text{-}C_3H_7, n\text{-}C_4H_9,$
    $iso\text{-}C_4H_9, sec\text{-}C_4H_9, n\text{-}C_6H_{13}, n\text{-}C_8H_{17},$
    $n\text{-}C_{12}H_{25}$

2: $R^2 = CH_3, C_2H_5, iso\text{-}C_3H_7, n\text{-}C_4H_9, iso\text{-}C_4H_9,$
    $sec\text{-}C_4H_9, n\text{-}C_6H_{13}, n\text{-}C_8H_{17}, n\text{-}C_{12}H_{25}$

ability of this substituent steric parameter in correlation analysis. Based on these data, the difference in hydrolytic behaviour among 1,2,2-alkyl-2-oxo-1,3,2-dioxaphosphorinanes (3) and -phosphepanes (4) was examined and the various susceptibilities of the central atom to the steric hindrance of the substituents in the alkaline hydrolysis of these phosphorus esters and carboxylates (5) are illustrated.
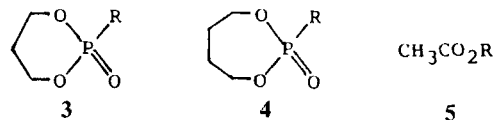
## RESULTS AND DISCUSSION

The alkaline hydrolysis of diethyl alkylphosphonates (1) and alkyl diethylphosphinates (2) was carried out in aqueous dimethyl sulphoxide solution of sodium hydroxide at different temperatures over a 30 °C range. The saponification rate was found to be second order, i.e. $v = k$ [ester] [OH$^-$] and the rate constants ($k$) were calculated by the least-squares method as indicated in Table 1.

The experimental data in Table 1 demonstrate that an increase in number of carbon atoms in the $n$-alkyl substituent in the phosphonates and phosphinates had no significant influence on rate constant of hydrolysis, especially when the carbon number of the ester alkyl group exceeded four. However, a considerable decrease in the rate constant was observed when the bulkiness of the alkyl substituents was increased. Thus, the rate constants for the basic hydrolysis of 1 and 2 decrease in the order methyl > ethyl > $n$-propyl > $n$-butyl > $n$-hexyl > $n$-octyl > $n$-dodecyl > isobutyl > isopropyl > $sec$-butyl. This order is in good agreement with the decreasing trend in the alkaline hydrolysis of some cyclic esters of alkylphosphonic acids.[6] The results revealed that there is a similar influence of steric effects of substituents on

the rate constants of the hydrolytic reaction for phosphonates and phosphinates.

It was found that neither Charton's $v$[10,11] nor Taft's $E_s$[12] parameter fitted the data for the alkaline hydrolysis of 1, as shown by very poor result in regression analyses [equation (1)]. However, correlation analysis involving log $k$ for compounds 1 with Charton's $v'$ value[13] provided better result [equation (2)].

$$\log k(1) = -2 \cdot 24v + 3 \cdot 28 \qquad (1)$$
$$r = 0 \cdot 706,\ n = 10,\ CL = 95\%$$

$$\log k(1) = -4 \cdot 41v' + 3 \cdot 70 \qquad (2)$$
$$r = 0 \cdot 916,\ n = 10,\ CL = 99 \cdot 9\%$$

where $v'$ is Charton's substituent constant of an alkyl group for pentacoordinated transition species, $k$ is the reaction constant, $r$ is the correlation coefficient, $n$ is the number of points and $CL$ is the confidence level.

On the other hand, log $k$ for compounds 2 correlated very well with Charton's $v$ value:

$$\log k(2) = -4 \cdot 176v + 3 \cdot 84 \qquad (3)$$
$$r = 0 \cdot 990,\ n = 9,\ CL = 99 \cdot 9\%$$

where the rate constant (log $k$) was determined at 60 °C, and the fact that the $r$ and $CL$ values are 0·990 and 99·9%, respectively, indicate satisfactory results in correlation analysis. However, in multiple regression analysis with log $k(1)$ and Taft's $\sigma^*$ and $E_s$ no radical improvement could be found:

$$\log k(1) = 4 \cdot 77\sigma^* + 0 \cdot 423E_s + 3.17 \qquad (4)$$
$$r = 0 \cdot 906,\ S_\rho = 2 \cdot 63,\ S_\delta = 0 \cdot 323,\ S_c = 0 \cdot 421,$$
$$T_\rho = 1 \cdot 82,\ T_\delta = 1 \cdot 31,\ T_c = 7 \cdot 52,\ n = 10,\ CL = 99 \cdot 9\%$$

where $S$ is the standard deviation and $T$ is the $T$-test from regression analysis. It is interesting that, in contrast with the unsatisfactory result of multiple regression analysis involving log $k(1)$ and Taft's $\sigma^*$ and $E_s$, a significant improvement was achieved in correlating log $k(2)$ with Kabachnik's $\sigma^p$[14-16] and Charton's $v$

$$\log k(2) = -0 \cdot 614\sigma^p - 0 \cdot 479v + 3 \cdot 96 \qquad (5)$$
$$r = 0 \cdot 992,\ S_\rho = 0 \cdot 468,\ S_\delta = 0 \cdot 549,\ S_c = 0 \cdot 167,$$
$$T_\rho = -1 \cdot 26,\ T_\delta = -8 \cdot 72,\ T_c = 23.7,\ n = 9,$$
$$CL = 99 \cdot 9\%$$

Equation (5), in which both $\rho$ ($-0 \cdot 614$) and $\delta$ ($-0 \cdot 479$) are negative, shows the increasing trend of the influence of polar effects of the substituent in the hydrolytic reaction of compounds 2. This structural effect is in contradiction with the experimental data. It is therefore reasonable to conclude that substituents parameters, $E_s$ and $\sigma^*$, derived from the hydrolytic reaction of carboxylates are not suitable in correlation analysis with the phosphorus-based esters investigated. This can probably be attributed to the difference in the conformation change from substrate to products via different transition states in the process of alkaline hydrolysis of 1 and

Table 1. Rate constants for alkaline hydrolysis of acyclic phosphorus esters at various temperatures

| R | 1, (C$_2$H$_5$O)$_2$P(O)R | | 2, (C$_2$H$_5$)$_2$P(O)R | |
|---|---|---|---|---|
| | Temp. (°C) | $k$ (l mol$^{-1}$) | Temp. (°C) | $k$ (l mol$^{-1}$) |
| CH$_3$ | 50 | 30·4 | 40 | 63·4 |
| | 60 | 59·6 | 50 | 129·3 |
| | 70 | 108·1 | 60 | 234·1 |
| C$_2$H$_5$ | 70 | 23·5 | 60 | 48·0 |
| | 80 | 47·4 | 70 | 95·5 |
| | 90 | 83·7 | 80 | 177·2 |
| $n$-C$_3$H$_7$ | 70 | 18·5 | — | — |
| | 80 | 37·8 | — | — |
| | 90 | 61·1 | — | — |
| $iso$-C$_3$H$_7$ | 70 | 1·88 | 60 | 4·41 |
| | 80 | 3·25 | 70 | 10·5 |
| | 90 | 6·23 | 80 | 21·0 |
| $n$-C$_4$H$_9$ | 70 | 18·7 | 60 | 27·6 |
| | 80 | 35·7 | 70 | 64·2 |
| | 90 | 59·3 | 80 | 125·5 |
| $iso$-C$_4$H$_9$ | 70 | 12·3 | 60 | 18·3 |
| | 80 | 23·3 | 70 | 43·8 |
| | 90 | 44·3 | 80 | 88·8 |
| $sec$ C$_4$H$_9$ | 90 | 6·63 | 60 | 2·61 |
| $n$-C$_6$H$_{13}$ | 70 | 16·6 | 60 | 26·7 |
| | 80 | 35·0 | 70 | 62·2 |
| | 90 | 57·6 | 80 | 122·7 |
| $n$-C$_8$H$_{17}$ | 90 | 54·7 | 60 | 22·2 |
| | — | — | 70 | 57·2 |
| | — | — | 80 | 110·0 |
| $n$-C$_{12}$H$_{25}$ | 90 | 49·0 | 60 | 20·9 |

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Table 2. Activation parameters of alkaline hydrolysis of compounds **1** and **2**[a]

| Compound | R | $\Delta G^{+}$ (kcal mol$^{-1}$) | $\Delta H^{+}$ (kcal mol$^{-1}$) | $\Delta S^{+}$ (e.u.) |
|---|---|---|---|---|
| **1a** | $CH_3$ | 23·0 | 14·2 | −25·6 |
| **1b** | $C_2H_5$ | 26·0 | 16·5 | −27·8 |
| **1c** | $n$-$C_3H_7$ | 25·0 | 15·7 | −27·0 |
| **1d** | $iso$-$C_3H_7$ | 26·2 | 16·0 | −29·7 |
| **1e** | $n$-$C_4H_9$ | 26·8 | 16·9 | −28·8 |
| **1f** | $iso$-$C_4H_9$ | 29·7 | 18·8 | −31·8 |
| **1h** | $n$-$C_6H_{13}$ | 26·3 | 16·6 | −28·4 |
| **2a** | $CH_3$ | 22·2 | 13·9 | −25·0 |
| **2b** | $C_2H_5$ | 24·7 | 15·8 | −26·8 |
| **2c** | $iso$-$C_3H_7$ | 25·8 | 16·0 | −29·3 |
| **2d** | $n$-$C_4H_9$ | 28·6 | 18·3 | −30·9 |
| **2e** | $iso$-$C_4H_9$ | 29·9 | 19·1 | −32·5 |
| **2g** | $n$-$C_4H_{13}$ | 28·8 | 18·4 | −31·1 |
| **2h** | $n$-$C_8H_{17}$ | 30·3 | 19·4 | −32·6 |

[a] Activation parameters were determined at three temperatures over a 30 °C range according to data in Table 1.

5, since the alkaline hydrolysis of phosphorus-based esters proceeds from a tetracoordinated substrate through a pentacoordinated species to the final products. However, the saponification of the carboxylates occurs from a planar tricoordinated substrate to the final product through a tetracoordinated transition state. Therefore, the contribution of the variation of the structure of alkyl or alkoxy groups to the rate constants of hydrolysis of **1** and **2** is significantly larger than that for **5**.

A series of thermodynamic functions of alkaline hydrolysis for compounds **1** and **2** were evaluated, based on the measurement of rate constants of alkaline hydrolysis at different temperatures. Corresponding activation parameters $\Delta G^{+}$, $\Delta H^{+}$ and $\Delta S^{+}$ were obtained, as given in Table 2.

The magnitude of the $\Delta S^{+}$ values (−25 to −32·6 e.u.) indicated that the hydrolytic reaction proceeded via the typical bimolecular AE mechanism. The results were very similar to those for the hydrolytic reactions of **3** and **4** studied previously.[6] Therefore, the influence of alkyl and alkoxy groups on the hydrolysis rate may vary from **3** and **4** to **1** and **2**. However, a similar substituent effect in the alkaline hydrolysis of **1**, **3** and **4** was observed by plotting log $k(1)$ versus log $k(3)$ (Figure 1). A better result of correlation analysis
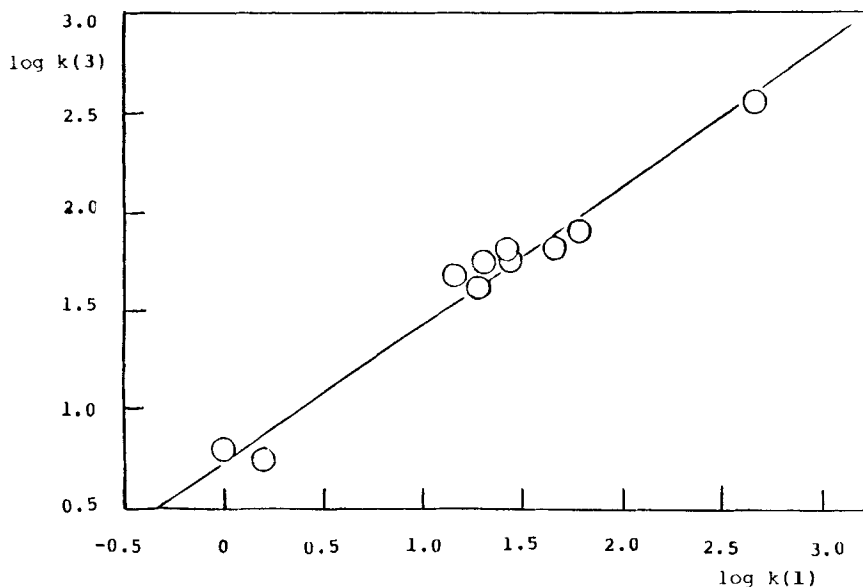


Figure 1. Plot of log $k(1)$ versus log $k(3)$

Table 3. Relative rate constants for basic hydrolysis of alkylphosphonates and carboxylates

| Ester | Solvent | Temperature (°C) | $k_{rel}$ R = CH$_3$ | R = C$_2$H$_5$ | R = iso-C$_3$H$_7$ | R = iso-C$_4$H$_9$ | Ref. |
|-------|---------|------------------|-----|-----|-----|-----|------|
| 1 | 83·3% DMSO | 70 | 58 | 13 | 1 | 7 | This work |
| 3 | 50% dioxane | 29·5 | — | 38 | 1 | 11 | 6 |
|   | 50% DMSO | 19·5 | — | 38 | 1 | 11 | 7 |
| 4 | 50% dioxane | 90 | — | 21 | 1 | 5 | 6 |
|   | 50% DMSO | 90 | — | 19 | 1 | 5 | 7 |
| RCO$_2$Et | 70% acetone | 35 | — | 4 | 1 | 0·5 | 17 |
|   | 85% ethanol | 50 | 7 | 4 | 1 | 0·6 | 18 |
| RCO$_2$Me | 40% dioxane | 35 | 4 | 3 | 1 | 0·4 | 19 |
| RCO$_2$Et | 70% acetone | 25 | 8 | 4 | 1 | 0·4 | 17 |

($r = 0·985$ for compounds 1) was obtained. Figure 1, of log $k(1)$ vs log $k(3)$, exhibited an identical substituent effect in hydrolytic behaviour among compounds 1, 3 and 4, illustrating a similar transition state in the basic hydrolysis of acyclic and cyclic phosphonates.
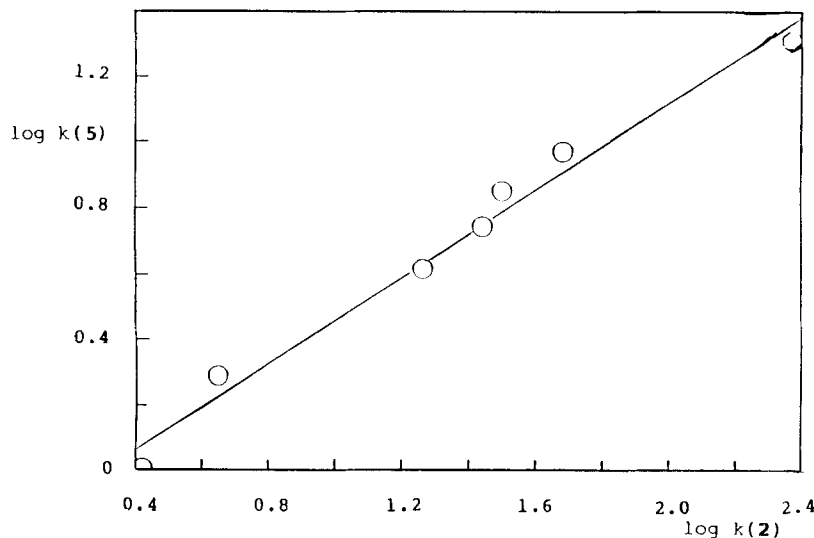
In order to examine the influence of substituent effects on the base hydrolysis of phosphonates, phosphinates and carboxylates, the relative rate constants ($k_{rel}$) for the hydrolytic reaction of various cyclic and acyclic alkylphosphonates and corresponding carboxylates in different mixed solvents were evaluated (Table 3).

The relative rate constants between ethyl- and isopropylphosphonates for 1, 3 and 4 in various mixed solvents are 13–38, compared with only 3–4 for the corresponding ethyl alkylcarboxylates. This proved that the influence of the steric effects of alkyl groups of alkylphosphonates was much larger than those of car-

boxylates in alkaline hydrolysis. The results can be rationalized by the different contributions of the substituent steric effects on the various configurations between the ground and transition states of phosphorus-based esters and carboxylates in such a process. However, the relative rate constants among isobutyl and isopropyl derivatives of 1, 3 and 4 in various aqueous solvents lay between 5 and 11, but were only 0·4 and 0·6 for the corresponding ethyl carboxylates (Table 3). The results in Table 3 demonstrate that Newman's rule of six,[22] which is well known in the solvolytic displacement of carboxylates, was completely eliminated in the hydrolysis of alkylphosphonates and alkylphosphinates. The configurational changes in the hydrolytic pathway of these phosphorus-based esters involves the conversion of tetrahedral to bipyramidal phosphorus. For the formation of hydrolysis products the leaving groups should be located at axial positions in the bipyramidal

Table 4. Relative rate constants for basic hydrolysis of alkyl dialkylphosphinates and carboxylates

| Ester | Solvent | Temperature (°C) | $k_{rel}$ R = CH$_3$ | R = C$_2$H$_5$ | R = iso-C$_3$H$_7$ | R = iso-C$_4$H$_9$ | Ref. |
|-------|---------|------------------|-----|-----|-----|-----|------|
| Ph$_2$P(O)OR | 33% dioxane | 50 | 320 | 27 | 1 | 5 | 5 |
| Et$_2$P(O)OR | 60% dimethyl glycol | 75 | 157 | 21 | 1 | — | 5 |
| (CH$_3$)$_2$CH—CH(C(CH$_3$)$_2$)P(O)OR | 65% dimethyl glycol | 75 | 40 | 10 | 1 | — | 5 |
| Et$_2$P(O)OR | 83·3% DMSO | 60 | 53 | 11 | 1 | 4 | This work |
| MeCO$_2$R | 40% dioxane | 35 | 11 | 5 | 1 | 2 | 20 |
| MeCO$_2$R | 70% acetone | 25 | 15 | 7 | 1 | 3 | 18 |
| EtCO$_2$R | 70% acetone | 25 | 22 | 8 | 1 | — | 18 |
| PhCO$_2$R | 60% dioxane | 35 | 19 | 6 | 1 | — | 21 |
| BuCO$_2$R | H$_2$O | 15 | 89 | 17 | 1 | — | 18 |

Figure 2. Plot of log $k(2)$ versus log $k(5)$

structure, whereas the variations in configuration in the hydrolytic pathways of ethyl carboxylates is concerned with a transformation from a planar trigonal to a tetrahedral configuration.

The data in Table 4 demonstrate that the influence of the structure of leaving alkoxy groups on the rate constants for the basic hydrolysis of phosphonates, phosphinates and carboxylates is identical. This is also evidenced by the excellent result in regression analysis involving log $k$ of 2 or 5 with Charton's $v$ parameter using equation (3). The plot of log $k(2)$ versus log $k(5)$ in dioxane–water (40 : 60, v/v) is shown in Figure 2. A better correlation coefficient of 0·990 was obtained.

In order to illustrate the difference in the structural influence of alkyl groups on the behaviour of the hydrolytic process of phosphorus-based esters and carboxylates, diethyl alkylphosphonates and alkyl diethylphosphinates were examined using molecular mechanics calculations (MM2), 1985 version).[23] The most stable conformation of each compound and corresponding intermediate state and its energy were selected for comparison with each other. In the alkaline hydrolytic reaction of phosphonates and phosphinates, the most stable intermediate state is usually considered to be a trigonal bipyramidal pentacoordinated species such as for diethyl alkylphosphonates (1).

OH
|
C₂H₅O⟍ |
       P—R₁
C₂H₅O⟋ |
       |
       OH

1a

OH
|
C₂H₅⟍ |
      P—OR
C₂H₅⟋ |
      |
      OH

2a
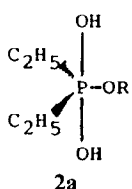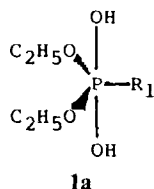
The most stable conformations of 1 and 2 are the corresponding pentacoordinated intermediate species 1a and 2a, respectively. On the basis of the assumption that the attack of OH⁻ on a phosphorus atom to form the pentacoordinated trigonal bipyramidal intermediate state is the rate-determining step in the basic hydrolytic reaction of 1, the difference in the steric energy $(\Delta E)$ between 1a and 1 can be used as a measure of the steric effect of an alkyl group for compound 1, $\Delta E_R = E_{1a} - E_1$. If $CH_3$ is taken as a reference group, $\Delta\Delta E_R$ can be obtained from the equation $\Delta\Delta E_R = \Delta E_R - \Delta E_{CH_3}$.

The alkaline hydrolytic reaction of compounds 2 was studied in a similar manner. Consequently, the most stable conformation of the intermediate state of 2 is 2a, in which two ethyl groups are located in equatorial positions.

The $\Delta E_R$ and $\Delta\Delta E_R$ can thus be obtained from the steric energies of 2 and 2a calculated by the molecular mechanics method as shown in Table 5:

$$\Delta E_R = E_2 - E_{2a}; \quad \Delta\Delta E_R = \Delta E_R - \Delta E_{CH_3}$$

Charton's $v$ in equations (1) and (3) was replaced with $\Delta\Delta E_R$ estimated by molecular mechanics calculation, and the results of the regression analysis are given in Tables 6 and 7.

However, when Taft's $E_s$ in equation (4) and Charton's $v$ in equation (5) were replaced with $\Delta\Delta E_R$, a better regression analysis result was obtained by equations (6) and (7).

$$\log k(1) = \delta\Delta\Delta E_R + \rho\sigma^* + c \quad (6)$$

$$\log k(2) = \delta\Delta\Delta E_R + \rho\sigma^p + c \quad (7)$$

The parameters of these correlation analyses are given

Table 5. Log $k$ and $\Delta\Delta E_R$ values of 1 and 2 (energy unit kcal mol$^{-1}$)

| Compound | Parameter | Temperature (°C) | R group | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Me | Et | n-Pr | i-Pr | n-Bu | i-Bu | s-Bu | n-Hex | n-Oct | n-Dod |
| 1 | $\Delta\Delta E_R$ | | 0·0 | 0·226 | 0·223 | 1·96 | 0·222 | 0·643 | 1·85 | 0·223 | 0·223 | 0·223 |
| | Log $k$ | 70 | 2·53 | 1·92 | 1·79 | 0·794 | 1·77 | 1·65 | 0·822 | 1·76 | 1·74 | 1·69 |
| | | 80 | 2·28 | 1·68 | 1·58 | 0·572 | 1·55 | 1·37 | — | 1·55 | 1·54 | — |
| | | 90 | 2·03 | 1·39 | 1·26 | 0·274 | 1·25 | 1·09 | — | 1·22 | 1·21 | — |
| 2 | $\Delta\Delta E_R$ | | 0·0 | 0·0 | — | 0·413 | 0·0 | 0·0 | 0·476 | 0·0 | 0·0 | 0·0 |
| | Log $k$ | 60 | — | 2·25 | — | 1·32 | 2·10 | 1·95 | — | 2·09 | 2·04 | — |
| | | 70 | — | 1·98 | — | 1·02 | 1·81 | 1·64 | — | 1·79 | 1·76 | — |
| | | 80 | 2·37 | 1·68 | — | 0·644 | 1·44 | 1·26 | 0·417 | 1·43 | 1·35 | 1·32 |

Table 6. Linear regression analysis of log $k$ with $\Delta\Delta E_R$ (log $k = \delta\Delta\Delta E_R + c$)

| No. | Compound | Temperature (°C) | $\delta$ | $c$ | $\gamma$ | $n$ | CL (%) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 70 | −0·653 | 2·03 | 0·922 | 10 | 99·9 |
| 2 | 1 | 80 | −0·707 | 1·84 | 0·917 | 8 | 99·9 |
| 3 | 1 | 90 | −0·675 | 1·53 | 0·880 | 8 | 99·0 |
| 4 | 2 | 60 | −1·85 | 2·09 | 0·955 | 6 | 99·0 |
| 5 | 2 | 70 | −1·88 | 1·80 | 0·945 | 6 | 99·0 |
| 6 | 2 | 80 | −2·33 | 1·55 | 0·804 | 9 | 99·0 |

Table 7. Results of correlation analysis with equations (6) and (7)

| No. | $\rho$ | $\delta$ | $c$ | $S_\rho$ | $S_\delta$ | $S_c$ | $T_\rho$ | $T_\delta$ | $T_c$ | $r$ | $n$ | $R$ | CL (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4·27 | −0·429 | 2·47 | 0·448 | 0·0365 | 0·0350 | 9·53 | −11·8 | 46·7 | 0·995 | 10 | 0·0499 | 99·9 |
| 2 | 3·94 | −0·500 | 2·22 | 0·550 | 0·0501 | 0·0620 | 7·16 | −9·98 | 35·9 | 0·993 | 8 | 0·0538 | 99·9 |
| 3 | 4·52 | −0·437 | 1·97 | 0·565 | 0·0515 | 0·0636 | 8·01 | −8·49 | 31·0 | 0·992 | 8 | 0·0552 | 99·9 |
| 4 | 1·07 | −1·72 | 2·54 | 0·391 | 0·187 | 0·169 | 2·72 | −9·19 | 15·0 | 0·987 | 6 | 0·0479 | 99·9 |
| 5 | 1·18 | −1·73 | 2·30 | 0·452 | 0·216 | 0·196 | 2·60 | −8·00 | 11·7 | 0·984 | 6 | 0·0553 | 99·9 |
| 6 | 2·40 | −1·43 | 2·48 | 0·288 | 0·222 | 0·119 | 8·34 | −6·46 | 20·9 | 0·986 | 9 | 0·0889 | 99·9 |

in Table 6. The experimental data in Table 6 showed that all the correlation coefficients exceed 0·98. The $T$-test, $T_\rho$ and $T_\delta$ values, indicated that substituent and solvation effects are very important for log $k$. For sets 1, 2, 3 and 6 the weight of $\sigma^*$ or $\sigma^P$ is almost the same as the weight of $\delta\Delta\Delta E_R$, but for sets 4 and 5 $\delta\Delta\Delta E_R$ has a much greater contribution than $\sigma$.

## EXPERIMENTAL

IR spectra were obtained on a Shimadzu 440 spectrometer, the sample being prepared as a liquid film. $^1$H NMR spectra were recorded on a Varian EM-360L spectrometer, using carbon tetrachloride as solvent and TMS as internal standard. $^{31}$P NMR spectra were obtained on a JEOL FX-90Q spectrometer using CDCl$_3$ as solvent and 85% H$_3$PO$_4$ as external standard. Mass spectra were measured on a Finnigan 4021 apparatus. Titrations were performed on a Methohm Model 636 Titroprocesser.

*Determination of rate constant.* A dimethyl sulphoxide–water (83·3 : 16·7, v/v) solution containing 0·015 mol diethyl alkylphosphonates or alkyl diethylphosphinates and sodium hydroxide was prepared at room temperature by shaking the flask thoroughly in a Jubblo constant-temperature bath (precision + 0·01 C). At appropriate time intervals, aliquots were removed and followed by addition of standard hydrochloric acid solution to retard the hydrolytic reaction. The residual acid was then back-titrated with standard sodium hydroxide solution and the concentration of phosphorus ester was thus calculated. The second rate constants at various temperature were obtained both by graphical analysis and by calculation utilizing the least-squares method.

Diethyl alkylphosphonates and alkyl diethylphosphinates were synthesized by standard models.[5,24,25]

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