# Dependence of Transition-state Structure on Nucleophile in the Reaction of Aryl Oxide Anions with Aryl Diphenylphosphate Esters

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Second-order rate constants have been measured for reaction of aryl oxide anions with substituted phenyl diphenylphosphate esters in aqueous media at 25 °C. The rate constants obey good Brønsted type correlations with the p$K_a$ of either the leaving group or nucleophile. Both $\beta_{nuc}$ and $\beta_{lg}$ values vary substantially with basicity of leaving group and nucleophile, respectively, providing evidence for coupling between bond fission and formation.

Attack of phenolate ions on 2,4-dinitrophenyl diphenylphosphate has a $\beta_{nuc}$ value of 0.12 giving a Kreevoy's tightness parameter value, $\tau$, of 0.18 which is consistent with an 'exploded' transition state for the identity reaction involving 2,4-dinitrophenolate ion as the nucleophile. Transfer of the diphenylphosphinoyl group between 2,4-dinitrophenolate ion nucleophiles has a $\tau$ value of 0.28, consistent with an 'exploded' transition state for this reaction also.

The identity reaction involving transfer of the diphenylphosphoryl group between phenolate ions has a $\tau$ value of 1.20, indicating an almost synchronous process. The data for transfer of the diphenylphosphinoyl and diethylphosphoryl groups between phenolate ion nucleophiles indicates that the identity reaction for the parent phenol has an almost synchronous mechanism for the former phosphinoyl species ($\tau$ = 0.92) whereas the latter ($\tau$ = 1.45) is almost associative.

There is much evidence to indicate that the transfer of neutral phosphoryl groups between basic nucleophiles can involve mechanisms with single transition states[1] as well as with discrete pentacoordinate and tricoordinate intermediates.[1d,2] Variation of transition state structure has been noted in reactions of phosphodianions,[3] of the diphenylphosphinate esters[1b] and of neutral phosphate esters.[4,5] Observation of a linear Brønsted type plot indicates that the electronic component of the transition state structure being 'reported' by the effect of the substituent change is constant in the range of substituents studied.[6]

We have recently shown that the reaction of aryl oxide ion with 4-nitrophenyl diphenylphosphate proceeds through a mechanism involving a single transition state.[1a] The aim of the present work is to consider the variation of the structure of the transition state as a function of the basicity of the leaving group and nucleophile [eqn. (1)], *i.e.* to define the boundary conditions of basicity of the 'ligands' where discrete dissociative and associative pathways should take place. As a result of this study we are also able to estimate $\beta_{eq}$ for transfer of the diphenylphosphoryl group between nucleophiles and aryl oxide ions.

$$ArO^- + (PhO)_2PO{-}OAr' \longrightarrow (PhO)_2PO{-}OAr + {}^-O{-}Ar' \quad (1)$$

## Experimental

Substituted phenyl diphenylphosphates were prepared from the chlorodiphenylphosphate by methods previously described[1a] and the physical and analytical data are recorded as supplementary data [sup. no. 56848 (2 pp.)]; m.p.s are recorded in Table 1. Other materials were obtained as before and methods employed are as described in the earlier work.[1a] Liquid nitrophenyl esters (supplementary data and Table 1) were not distilled owing to their propensity to explode; purity was checked by TLC and by elemental analysis (supplementary data).

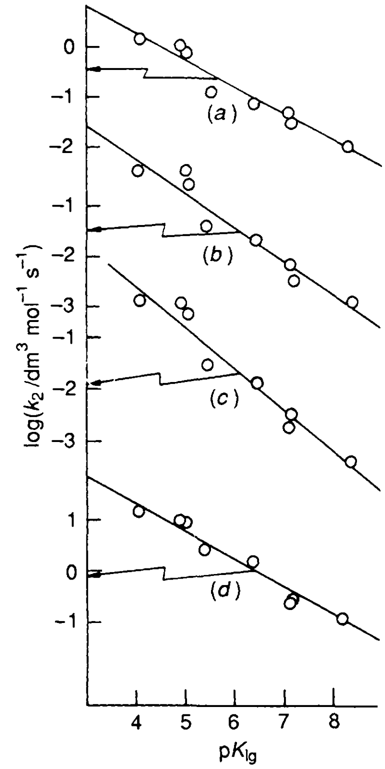

**Fig. 1** Dependence of log $k_2$ on the p$K_a$ of the leaving group for attack on aryl diphenylphosphate esters of (*a*) phenolate ion; (*b*) 4-acetylphenolate ion; (*c*) 4-formylphenolate ion; (*d*) hydroxide ion. Conditions and data are from Table 1 and the lines are calculated from the equations given in Table 2. Identity of the points in increasing order of p$K_a$: 2,4-$(NO_2)_2$; 2,3-$(NO_2)_2$; 2,5-$(NO_2)_2$; 2-Cl-4-$NO_2$; 2-$NO_2$-4-Cl; 4-$NO_2$; 2-$NO_2$; 3-$NO_2$.

## Results

Reactions of substituted phenyl diphenylphosphates in buffers containing substituted phenolate ions exhibited excellent

**Table 1** Reactions of nucleophiles with substituted phenolate anions with substituted phenyl diphenylphosphate esters[a]

| Substituent | p$K_a$[n] | pH[b] | $\lambda_{max}$/nm[c] | $N$[d] | $k_{obs}/10^{-2}$ s$^{-1}$[e] | $k_2/10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$[f] | [Nuc]/10$^{-2}$ mol dm$^3$[g] |
|---|---|---|---|---|---|---|---|
| Phenolate ion nucleophile with substituted phenyl diphenylphosphate esters | | | | | | | |
| 2,4-N$_2$[k] | 4.11 | 10.45 | 400 | 6 | 0.90–4.70 | 135 | 0.1–5.0 |
| 2,3-N$_2$[m] | 4.96 | 10.45 | 420 | 6 | 0.90–3.50 | 101 | 0.1–3.6 |
| 2,5-N$_2$[h] | 5.04 | 10.45 | 400 | 6 | 0.54–4.04 | 74 | 0.1–6.6 |
| 2-C–4-N[h] | 5.45 | 10.45 | 400 | 6 | 0.19–0.63 | 11 | 0.1–6.6 |
| 2-N–4-C[h] | 6.46 | 10.45 | 420 | 6 | 0.04–0.20 | 6.9 | 0.1–3.3 |
| 4N[i] | 7.14 | 11.25 | 400 | 5 | 0.01–0.05 | 4.3 | 0.1–10.4 |
| 2-N[h] | 7.21 | 10.65 | 420 | 5 | 0.08–0.20 | 2.6 | 0.9–4.5 |
| 4-Acetylphenolate ion nucleophile with substituted phenyl diphenylphosphate esters | | | | | | | |
| 2,4-N$_2$ | 4.11 | 8.66 | 400 | 6 | 0.80–4.00 | 49 | 0.1–8.6 |
| 2,3-N$_2$ | 4.96 | 8.50 | 420 | 6 | 0.17–2.80 | 51 | 0.1–6.9 |
| 2,5-N$_2$ | 5.04 | 8.50 | 400 | 6 | 0.18–1.58 | 28 | 0.1–6.9 |
| 2-C–4-N | 5.45 | 8.40 | 400 | 5 | 0.70–2.60 | 3.9 | 1.8–8.8 |
| 2-N–4-C | 6.46 | 9.27 | 420 | 5 | 0.02–0.29 | 1.9 | 0.01–9.3 |
| 4-N | 7.14 | 9.00 | 400 | 5 | 0.01–0.04 | 0.60 | 1.2–6.2 |
| 2-N | 7.21 | 8.44 | 400 | 5 | 0.01–0.03 | 0.29 | 1.8–8.8 |
| 3-N | 8.38 | 8.40 | 400 | 4 | 0.006–0.012 | 0.13 | 3.5–8.8 |
| 4-Formylphenolate ion nucleophile with substituted phenyl diphenylphosphate esters | | | | | | | |
| 2,4-N$_2$ | 4.11 | 8.84 | 400 | 6 | 0.36–2.60 | 55 | 0.1–4.0 |
| 2,3-N$_2$ | 4.96 | 8.85 | 420 | 6 | 0.03–2.10 | 50 | 0.01–4.0 |
| 2,5-N$_2$ | 4.96 | 8.85 | 420 | 6 | 0.20–0.87 | 31 | 0.01–2.27 |
| 2-C–4-N | 5.45 | 8.49 | 410 | 6 | 0.09–0.25 | 3.0 | 0.01–8.5 |
| 2-N–4-C | 6.46 | 9.13 | 420 | 6 | 0.02–0.19 | 1.1 | 0.1–7.7 |
| 4-N | 7.14 | 9.6 | 400 | 4 | 0.03–0.04 | 0.17 | 3.5–8.8 |
| 2-N | 7.21 | 8.86 | 400 | 4 | 0.009–0.031 | 0.31 | 0.01–8.5 |
| 3-N | 8.38 | 8.86 | 400 | 3 | 0.006–0.008 | 0.038 | 2.7–6.7 |
| Alkaline hydrolysis of substituted phenyl diphenylphosphate esters | | | | | | | |
| 2,4-N$_2$ | 4.11 | | 400 | 4 | 0.50–3.70 | 1700 | 0.012–0.214 |
| 2,3-N$_2$ | 4.96 | | 420 | 4 | 0.50–2.56 | 1000 | 0.012–0.214 |
| 2,5-N$_2$ | 5.04 | | 420 | 4 | 0.72–1.68 | 1000 | 0.011–0.331 |
| 2-C–4-N | 5.45 | | 420 | 4 | 0.10–0.77 | 250 | 0.041–0.331 |
| 2-N–4-C | 6.46 | | 420 | 4 | 0.01–0.56 | 156 | 0.041–0.331 |
| 4-N | 7.14 | | | | | 26[p] | |
| 2-N | 7.21 | | 400 | 4 | 2.30–8.70 | 29 | 8–32 |
| 3-N | 8.38 | | 400 | 5 | 1.60–6.60 | 13 | 8–32 |
| Reaction of substituted phenolate ions with 2,4-dinitrophenyl diphenylphosphate ester[j] | | | | | | | |
| 4-CN | 7.96 | 8.70 | | 5 | 0.07–2.10 | 78 | 0.6–2.6 |
| 4-C | 9.38 | 9.59 | | 5 | 0.69–1.35 | 60 | 0.4–2.2 |
| 3-C | 9.02 | 9.68 | | 3 | 0.56–1.67 | 140 | 0.4–1.3 |
| 4-CHO[q] | 7.66 | 8.84 | | 5 | 1.00–3.40 | 120 | 0.5–2.5 |
| 4-CH$_3$CO[q] | 8.05 | 9.00 | | 4 | 0.71–1.92 | 76 | 0.4–2.2 |
| 2-C | 8.48 | 9.31 | | 5 | 0.64–1.02 | 33 | 0.3–1.4 |
| 4-EtO$_2$C | 8.50 | 8.94 | | 3 | 0.57–1.09 | 55 | 0.6–1.9 |
| 3-EtO$_2$C | 8.90 | 9.41 | | 5 | 0.85–1.57 | 63 | 0.3–1.8 |
| 4-F | 9.95 | 9.64 | | 6 | 0.60–0.80 | 73 | 0.1–3.8 |
| F$_5$ | 5.49 | 8.87 | | 5 | 0.60–0.80 | 8.5 | 0.4–2.1 |
| 4-CH$_3$ | 10.2 | 8.94 | | 3 | 0.60–0.80 | 84 | 0.6–2.3 |
| 2,3,5-C$_3$ | 6.43 | 8.73 | | 5 | 0.90–1.90 | 53 | 0.4–2.3 |
| 2,3,5,6-F$_4$ | 5.53 | 8.75 | | 5 | 0.80–1.30 | 25 | 0.5–2.3 |
| 2,4,5-C$_3$ | 6.72 | 8.94 | | 5 | 0.80–2.00 | 79 | 0.4–1.9 |
| 2,3-C$_2$ | 7.85 | 8.94 | | 5 | 0.80–1.70 | 47 | 0.5–2.6 |
| 4-CH$_3$O | 10.2 | 9.95 | | 5 | 1.00–2.00 | 90 | 0.9–4.3 |
| 2,3,4-C$_3$ | 7.23 | 9.09 | | 5 | 0.90–1.50 | 31 | 0.4–1.8 |

[a] General conditions: 25 °C; 0.5 mol dm$^{-3}$ ionic strength maintained with KCl; tris(hydroxymethylamino)methane buffer (0.1 mol dm$^{-3}$); 32% methanol–water, v/v; see Table 2, footnote *h* for abbreviations. [b] Average pH for all the runs. [c] Wavelength for kinetic runs. [d] Number of data points not including duplicate runs. [e] Range of observed rate constants. [f] Error range not more than 10% of quoted figure. [g] Concentration range of the total nucleophilic species. [h] Liquid; isolated by extraction from the reaction mixture after washing with mild base and acid. [i] M.p. 48–49 °C (lit.,[21] 48–49 °C). [j] For this series of reactions the methanol concentration was 43% MeOH–water, v/v, and the ionic strength was maintained at 0.1 mol dm$^{-3}$ with KCl. [k] M.p. 108–113 °C. [m] M.p. 109–110 °C. [n] This is the p$K_a$ of the phenol corresponding to the substituent of either nucleophile or leaving group. [p] Data from reference 1(*a*). [q] Values for these points are repeats of those quoted elsewhere in the Table for a slightly different composition of the medium.

pseudo first-order kinetics up to *ca.* 90% of the total release of the leaving group. The rate constants are linear in total phenol concentration in the buffer and we assume from previous work that the rate enhancement is due to a second-order rate law involving the ester and base form of the phenol, eqn. (2), where

$$dk_{obs}/d[\text{phenol}]_{tot} = k_2 \cdot \text{FB} \qquad (2)$$

FB is the fraction of total phenol present in the base form. The derived second-order rate constants ($k_2$) are recorded in Table 1 for attack of phenolate ion, 4-acetylphenolate ion and

**Table 2** Brønsted dependences for reactions of substituted phenolate anions with substituted phenyl diphenylphosphate esters[g]

| Nu[a] | Lg[b] | $\beta$[c] | Intercept | $r$ | $\tau$[e] | $\log k_{ii}$[d] | $pK_i$[f] | $\beta_{nuc}$(calc.)[m] |
|---|---|---|---|---|---|---|---|---|
| Parent | $ArO^-$ | −0.52 ± 0.07[n] | 2.3 ± 0.41 | 0.955 | 1.20 | −2.89 | 9.99 | 0.78 |
| $4\text{-}CH_3CO$ | $ArO^-$ | −0.68 ± 0.08[n] | 2.68 ± 0.49 | 0.963 | 0.95 | −2.81 | 8.05 | 0.62 |
| 4-CHO | $ArO^-$ | −0.81 ± 0.09[n] | 3.30 ± 0.52 | 0.968 | 0.75 | −2.90 | 7.66 | 0.49 |
| $ArO^-$ | $24N_2$[h] | 0.12 ± 0.04[k] | −1.23 ± 0.32 | 0.628 | 0.18 | −0.74 | 4.11 | |
| $ArO^-$ | 4-N | 0.53 ± 0.05[k] | −0.60 ± 0.40 | 0.930 | 0.82 | −2.82 | 7.14 | |
| $OH^-$ | $ArO^-$ | −0.55 ± 0.05[n] | 3.61 ± 0.33 | 0.996 | | | | |
| 'Three-point' Brønsted dependences[j] | | | | | | | | |
| $ArO^-$ | 3-N | 0.60 ± 0.12[k] | −7.86 ± 1.0 | 0.980 | 0.92 | −2.83 | 8.38 | |
| $ArO^-$ | 2-N | 0.43 ± 0.08[k] | −5.86 ± 0.69 | 0.983 | 0.66 | −2.76 | 7.21 | |
| $ArO^-$ | 4-N | 0.55 ± 0.14[k] | −6.82 ± 1.2 | 0.970 | 0.85 | −2.88 | 7.14 | |
| $ArO^-$ | 2N4C[h] | 0.32 ± 0.06[k] | −4.39 ± 0.43 | 0.988 | 0.49 | −2.32 | 6.46 | |
| $ArO^-$ | 2C4N[h] | 0.23 ± 0.01[k] | −3.30 ± 0.07 | 0.999 | 0.35 | −2.05 | 5.45 | |
| $ArO^-$ | $25N_2$[h] | 0.18 ± 0.05[k] | −1.94 ± 0.39 | 0.971 | 0.28 | −1.03 | 5.04 | |
| $ArO^-$ | $23N_2$[h] | 0.14 ± 0.02[k] | −1.38 ± 0.15 | 0.992 | 0.22 | −0.69 | 4.96 | |
| $ArO^-$ | $24N_2$ | 0.19 ± 0.05[k] | −1.74 ± 0.43 | 0.966 | 0.29 | −0.96 | 4.11 | |

[a] Nucleophile (substituted phenolate ion or hydroxide ion). [b] Leaving group (substituted phenolate ion). [c] Brønsted $\beta$ value (for leaving group or nucleophile) for the equation $\log k_2 = \beta pK_a + \text{intercept}$. [d] Value of $k_{ii}/dm^3\ mol^{-1}\ s^{-1}$ calculated from the Brønsted equation using $pK_i$. [e] Value of $\tau$ obtained from $\alpha$ as explained in the text using $\beta_{eq} = 1.30$. [f] Value of the $pK_a$ of the nucleophile for the identity reaction. [g] Data calculated from the rate constants given in Table 1. [h] The abbreviations employed here for the substituents are: C = Cl and N = $NO_2$. [i] The Brønsted equation from the three-point correlation for the 4-nitrophenyl ester agrees well with that for the more extensive correlation. [j] The three-point Brønsted correlations involve 4-acetylphenolate, 4-formylphenolate and phenolate ion as nucleophiles. [k] $\beta_{nuc}$. [m] Calculated from $\beta_{eq}$ (=1.30) and $\beta_{lg}$ (experimental) as indicated in the results section. [n] $\beta_{lg}$.

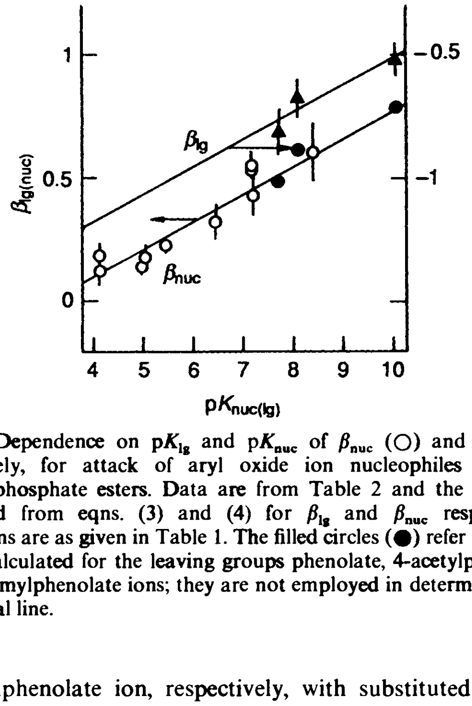

**Fig. 2** Dependence on $pK_{lg}$ and $pK_{nuc}$ of $\beta_{nuc}$ (○) and $\beta_{lg}$ (▲), respectively, for attack of aryl oxide ion nucleophiles on aryl diphenylphosphate esters. Data are from Table 2 and the lines are calculated from eqns. (3) and (4) for $\beta_{lg}$ and $\beta_{nuc}$ respectively. Conditions are as given in Table 1. The filled circles (●) refer to values of $\beta_{nuc}$ calculated for the leaving groups phenolate, 4-acetylphenolate and 4-formylphenolate ions; they are not employed in determining the theoretical line.

4-formylphenolate ion, respectively, with substituted phenyl diphenylphosphate esters. Table 1 also records data for attack of hydroxide ion on aryl diphenylphosphates in aqueous solution and the data for attack of substituted phenolate ions on 2,4-dinitrophenyl diphenylphosphate. Data for various reactions of nucleophile with substituted phenyl diphenylphosphate esters obey good Brønsted dependences and the equations for these lines are collected in Table 2. 'Three point' Brønsted correlations to give eight values of $\beta_{nuc}$ may be determined for attack of phenolate ion, 4-acetylphenolate ion and 4-formylphenolate ion on diphenylphosphate esters with different leaving groups; the data for these are also given in Table 2. Fig. 1 illustrates the correlations; the correlation of the data for reaction of phenolate ions with 2,4-dinitrophenyl diphenylphosphate has been recorded in a preliminary report.[7]

Values of $\beta_{lg}$ and $\beta_{nuc}$ are fitted to linear functions in $pK_{nuc}$ and $pK_{lg}$, respectively, and these are given in eqns. (3) and (4). The correlations are illustrated in Fig. 2. The linear equation (3) for $\beta_{lg}$ with only three points is less certain than

$$\beta_{lg} = (0.112 \pm 0.034)\,pK_{nuc} - (1.63 \pm 0.29) \qquad (3)$$

$$\beta_{nuc} = (0.118 \pm 0.014)\,pK_{lg} - (0.381 \pm 0.088) \qquad (4)$$

that for $\beta_{nuc}$ with ten points [eqn. (4), which includes duplicates for the 4-nitro and 2,4-dinitro substituents]. The variation of both $\beta_{lg}$ and $\beta_{nuc}$ over the range of $pK_a$ is well outside the confidence limits represented by the error bars in Fig. 2.

The Brønsted equations from Table 2 may be used to extrapolate values of identity rate constants ($k_{ii}$) where a phenolate ion expels an identical leaving group. The identity rate constants (from the first five Brønsted equations of Table 2) may be fitted to the theoretical equation (5).[8,*]

$$\log k_{ii} = p_{xy} \cdot pK_i^2 + BpK_i + C \qquad (5)$$

The parameters $p_{xy}$ and $B$ in the theoretical equation (5) may be calculated from eqns. (3) and (4) by applying the relationships $\beta_{eq} = \beta_{nuc} - \beta_{lg}$[10] and $\beta_{ii} = \beta_{nuc} + \beta_{lg}$[11] and $d\log k_{ii}/dpK_i = \beta_{ii}$. The values of $p_{xy}$ and $B$ are thus 0.115 [(0.112 + 0.118)/2 from eqns. (3) and (4)] and −2.01 [−1.63–0.381 from eqns. (3) and (4)]. The data for $\log k_{ii}$ (from the five good Brønsted correlations in Table 2 but excluding those from the three-point correlations) may be fitted to eqn. (5) with the calculated values of $p_{xy}$ and $B$ to give a best value of $C$ at 5.70.* The data for $\log k_{ii}$ from the three-point correlations fit the line calculated using the above parameters (see Fig. 3).

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* The parameters of eqn. (5) may also be obtained by freely fitting the $\log k_{ii}$ data (first five values in Table 2) by use of the ENZFITTER program; the values of $p_{xy}$ (0.104 ± 0.01), $B$ (−1.81 ± 0.16) and $C$ (4.95 ± 0.53) thus obtained are in good agreement with those determined from eqns. (3) and (4). The data for $k_{ii}$ from the 'three-point' Brønsted equations (Table 2) are not used in the correlations to fit to eqn. (5) because the range of extrapolation required to obtain the identity rate constants from so few points gives poor values for $k_{ii}$ (see Table 2).

**Table 3** Brønsted dependences for reactions of substituted phenolate anions with substituted phenyl diphenylphosphinate esters[g]

| Nu[a] | Lg[b] | $\beta$[c] | Intercept | $r$ | $\tau$[e] | $\log k_{ii}$[d] | $pK_i$[f] |
|---|---|---|---|---|---|---|---|
| Parent | $ArO^-$ | −0.66 ± 0.06 | 4.72 ± 0.37 | 0.968 | 0.92 | −1.87 | 9.99 |
| $4\text{-}CH_2CO$ | $ArO^-$ | −0.72 ± 0.11 | 4.50 ± 0.63 | 0.940 | 0.82 | −1.32 | 8.05 |
| 4-CHO | $ArO^-$ | −0.77 ± 0.12 | 4.58 ± 0.70 | 0.940 | 0.74 | −1.38 | 7.66 |
| $ArO^-$ | $4\text{-}NO_2$ | 0.46 ± 0.03 | −4.73 ± 0.25 | 0.953 | 0.75 | −1.45 | 7.14 |
| 'Three-point' Brønsted dependences[j] | | | | | | | |
| $ArO^-$ | $24N_2$[h] | 0.17 ± 0.03 | −0.02 ± 0.28 | 0.979 | 0.28 | 0.69 | 4.11 |
| $ArO^-$ | $23N_2$[h] | 0.14 ± 0.02 | 0.031 ± 0.2 | 0.988 | 0.23 | 0.73 | 4.96 |
| $ArO^-$ | $25N_2$[h] | 0.25 ± 0.05 | −0.87 ± 0.41 | 0.980 | 0.41 | 0.41 | 5.04 |
| $ArO^-$ | $34N_2$[h] | 0.25 ± 0.03 | −1.44 ± 0.28 | 0.992 | 0.41 | −0.09 | 5.42 |
| $ArO^-$ | 2C4N[h] | 0.71 ± 0.02 | −5.59 ± 0.17 | 0.999 | 1.16 | −1.72 | 5.45 |
| $ArO^-$ | 2N4C[h] | 0.31 ± 0.03 | −2.48 ± 0.31 | 0.994 | 0.51 | −0.48 | 6.46 |
| $ArO^-$ | $4\text{-}NO_2$[i] | 0.47 ± 0.06 | −4.95 ± 0.54 | 0.991 | 0.77 | −1.58 | 7.14 |
| $ArO^-$ | $2\text{-}NO_2$ | 0.39 ± 0.02 | −3.68 ± 0.17 | 0.999 | 0.64 | −0.87 | 7.21 |

[a] Nucleophile (substituted phenolate ion or hydroxide ion). [b] Leaving group (substituted phenolate ion). [c] Brønsted $\beta$ value for the equation $\log k_2 = \beta pK_a$ + intercept. [d] Value of $k_{ii}/dm^3\ mol^{-1}\ s^{-1}$ calculated from the Brønsted equation using $pK_i$. [e] Value of $\tau$ obtained from $\alpha$ as explained in the text using $\beta_{eq} = 1.22 \pm 0.09$. [f] Value of the $pK_a$ of the nucleophile for the identity reaction. [g] Data taken from Bourne *et al.*[1b] The values of $\beta_{nuc}$ obey the equation: $\beta_{nuc} = (0.096 \pm 0.016)\ pK_{lg} - (0.269 \pm 0.095)$ ($r = 0.929$); the point for the 2-chloro-4-nitrophenyl ester is omitted from the correlation. [h] The abbreviations employed here for the substituents are: C = Cl and N = $NO_2$. [i] The Brønsted equation from the three-point correlation for the 4-nitrophenyl ester agrees well with that for the more extensive correlation. [j] The three-point Brønsted correlations involve 4-acetylphenolate, 4-formylphenolate and phenolate ion as nucleophiles.

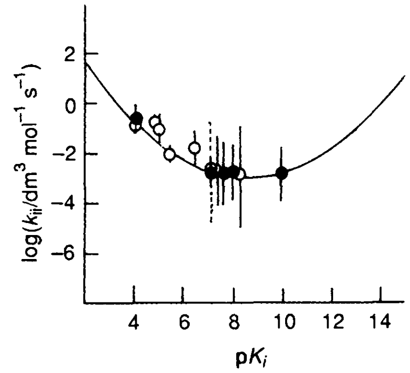

**Fig. 3** Dependence on $pK_i$ of $\log k_{ii}$ for identity reactions of aryl oxide ion nucleophiles with aryl diphenylphosphate esters. Data are from Table 2 and conditions are given in Table 1. The filled circles (●) correspond to $\log k_{ii}$ values obtained from the first five Brønsted lines in Table 2. [The open circles (○) are from $\log k_{ii}$ values from 'three-point' Brønsted lines and are not employed to fit the line (see Results section)]. The line is from eqn. (5) employing the calculated values of the parameters $p_{xy}$ and $B$ and a fitted value for $C$.

Data from previous work[1b] on the reaction of substituted phenolate ions with substituted phenyl diphenylphosphinate esters enables $k_{ii}$ values to be extrapolated (Table 3) and the Brønsted type plot for these is illustrated in Fig. 4. Fitting the data (from Table 3 for $k_{ii}$ from the four good Brønsted relationships) to eqn. (5) would result in an extremely poor prediction for the extrapolated ranges above and below $pK_i$ values 10 and 7, respectively; the line illustrated in Fig. 4 employs $p_{xy}$ and $B$ (0.096 and −1.76, respectively) derived from $\beta_{eq}$ (1.22) and the dependence of $\beta_{nuc}$ on $pK_{lg}$. The value of $C$, obtained by fitting the data to the semi-empirical equation is +6.3. Data for $k_{ii}$ from 'three-point' Brønsted correlations (Table 3) derived from previous data[1b] are included in Fig. 4 but are not employed to fit eqn. (5) because of the inherent inaccuracy previously mentioned in such extrapolations to determine $k_{ii}$.

An average value of $\beta_{eq}$ (1.30 ± 0.04)† for transfer of the diphenylphosphoryl group from an aryl ester is obtained from $\beta_{nuc}$ values for attack of phenolate ions on the 4-acetylphenyl, phenyl and 4-formylphenyl esters extrapolated from eqn. (3) and using experimental values of $\beta_{lg}$ (Table 2). It is useful to demonstrate the goodness of fit by calculating $\beta_{nuc}$ for phenyl, 4-acetyl and 4-formyl esters from $\beta_{lg}$ [calculated from eqn. (3)] and $\beta_{eq}$ (1.30). These calculated values come close to the line calculated from the data for the measured $\beta_{nuc}$ values and this is illustrated in Fig. 2.

A similar approach using data from Table 3 gives $\beta_{eq}$ = 1.22 ± 0.09 for the diphenylphosphinoyl group.*

## Discussion

Evidence discussed previously[1a] indicates that the reaction map (Fig. 5) has a single transition state for nucleophilic attack by aryl oxide ions on aryl diphenylphosphates. Fig. 2 illustrates the dependence of $\beta_{nuc}$ and $\beta_{lg}$ on $pK_{lg}$ and $pK_{nuc}$, respectively, consistent with a change in transition-state structure consequent on 'ligand' basicity.† The observation of such a substantial $p_{xy}$ value is additional evidence for a concerted mechanism for the transfer reaction in question because the transition state of a rate-limiting step for the putative stepwise mechanism would lie along a coordinate of the reaction map (Fig. 5). The value of $p_{xy}$[9] (0.115) is larger than that estimated for the transfer of the diphenylphosphinoyl group between aryl oxide ions (0.096, see Table 3). The $p_{xy}$ value is also larger than those obtained by Khan and Kirby[5] and Rowell and Gorenstein[4] for reactions of the neutral phosphoryl groups with a variety of oxyanions; it is likely that the difference in this case resides in the accuracy of $p_{xy}$ obtained from studies on anions of mixed structure. The value of $p_{xy}$ obtained here is smaller than that for transfer of the acetyl group between phenolate ions (0.17).[8] The parameter $p_{xy}$ measures the susceptibility of the transition state to change in electronic structure as a function of the basicity of the ligand oxyanions. The parameter $\tau$ is a measure of the position of

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* There seems to be no reason why this dependence should be linear except that the change in energy of nucleophile or leaving group is over a small range; the slope of the plots of $\beta$ *vs.* $pK_a$ ($p_{xy}$) must be identical at each $pK_a$.[9]

† Previous work[1a,7] has taken $\beta_{eq}$ to be 1.4 for the transfer of the diphenylphosphoryl group to phenolate ion nucleophiles; a small change is also noted for $\beta_{eq}$ for diphenylphosphinoyl group transfer from that previously quoted;[1b] the differences are not, however, significant to the discussions here.

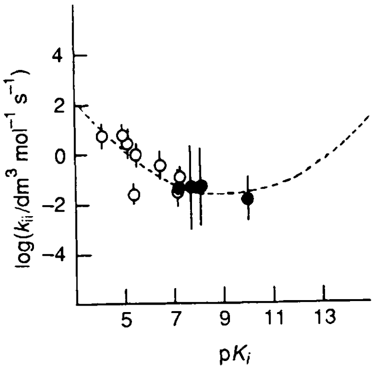

**Fig. 4** Dependence on $pK_i$ of $\log k_{ii}$ for identity reactions of aryl oxide ion nucleophiles with aryl diphenylphosphinate esters. Data are from Table 3 and the conditions are quoted therein. The line is calculated from eqn. (5) with parameters $p_{xy}$ and $B$ calculated as shown in the text for the points represented by the closed circles (●). [The open circles (○) refer to $\log k_{ii}$ values from 'three-point' Brønsted correlations and are not used to fit the line in the Figure]

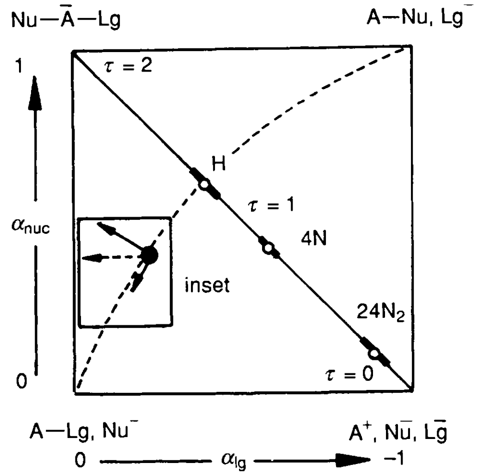

**Fig. 5** Reaction map for transfer of a general acyl group ($A^-$) between anionic nucleophiles. The open circles (○) refer to the transition states of the identity reactions involving transfer of diphenylphosphoryl between phenolate (H), 4-nitrophenolate (4-$NO_2$) and 2,4-dinitrophenolate (2,4-$NO_2$) ions. The values of $\tau$ are from Table 2 and the errors are given by the heavy lines in the Figure. The inset describes the change in transition state structure as a function of increasing nucleophile strength as described in the text.

the transition state structure for the identity reaction on the 'tightness diagonal' (Fig. 5) and is defined by Kreevoy and Lee.[12b] Simple arguments yield eqn. (6) and thus the ratio

$$A = d\tau/dpK_i = 2p_{xy}/\beta_{eq} \qquad (6)$$

$2p_{xy}/\beta_{eq}$ (A) directly controls the extent of movement of the transition state for unit change in ligand basicity. The transition state for the diphenylphosphoryl group thus has approximately the same susceptibility to ligand basicity to movement along the tightness diagonal ($A = 0.177$) as that of the diphenylphosphinoyl species ($A = 0.157$) and that of the acetyl group ($A = 0.21$).*

The absolute value of $\tau$ will depend on the parameter $B$ as well as on $p_{xy}$, $pK_i$ and $\beta_{eq}$ [eqn. (7)].

$$\tau = 1 + \beta_{ii}/\beta_{eq} = 1 + 2(p_{xy}pK_i + B)/\beta_{eq} \qquad (7)$$

Inserting $\tau$ values of 2, 1 and 0 into eqn. (7) indicates that the $pK_i$ values of 14.39, 8.74 and 3.09, respectively, correspond to associative, synchronous and dissociative pathways for transfer of the diphenyl phosphoryl group between phenolate ions. The values for $\tau$ of 2 and 0 are outside the experimental limits and are therefore subject to errors such as those induced by edge effects. The corresponding values of $pK_i$ for $\tau = 2$, 1 and 0 for the diphenylphosphinoyl group transfer between phenoxide ion ligands are 15.52, 9.17 and 2.81, respectively.

The measured value of Leffler's index, $\alpha$[12b] for attack of phenolate ions on 2,4-dinitrophenyl diphenylphosphate is 0.092 corresponding to a $\tau$ value of $0.18 \pm 0.06$ which agrees well with the value (0.18) calculated for $pK_i$ of 4.11 from eqn. (7). Transfers of the diphenylphosphinoyl group between weakly basic nucleophiles also have 'exploded' transition states as judged from the low observed $\tau$ values (Table 3). Similar low values of $\tau$ have been observed for identity reactions involving attack of pyridines on pyridine phosphonates[3] and on pyridine sulphonates.[13] The inclusion of nucleophilic atoms $\alpha$ to the acyl function such as $-N^--$, $-CH^--$ or $-O^--$ has been considered to be one of the factors favouring the dissociative pathway in acyl group transfer because they tend to stabilise the putative acylium ion ($-CO^+$, $-SO_2^+$ or $-PO^+$).[14] It was assumed also that lowering the basicity of the ligands in the transition state would also increase the propensity of the reaction to take a dissociative pathway. Fig. 5 illustrates the structures of the transition states for the identity reactions involving phenolate ion, 4-nitrophenolate ion and 2,4-dinitrophenolate ion ligands. This represents a smooth change in transition-state structure compared with the abrupt changes seen with attack of nucleophiles on hippurate esters[15] and other species[14] which can undergo an $El_cB$ mechanism.

When low values of $\beta$ are being considered it is necessary to introduce the possibility that there is a significant contribution from desolvation of the nucleophile. Studies for both aqueous and non-aqueous media indicate a relatively low $\beta$ value for hydrogen bonding between substituted phenoxide ions and amines[3b,16] and various substituted bases and 4-fluorophenol and other hydrogen-bonding equilibria.[16] These values of $\beta$ indicate that if desolvation of the nucleophile is significant in the transition state then $\beta_{nuc}$ could be larger than is apparent and could markedly contribute to a reaction with a low observed $\beta$ value.

The question of the meaning of reaction maps of the type illustrated by Fig. 5 should be addressed because of the similarity between these diagrams representing experimental results and theoretical potential energy diagrams involving single molecules. So far the only reasonable experimental way of estimating transition state structure in condensed systems has been through comparison of an experimental parameter relating to assemblies of molecules (*e.g.* a Brønsted $\beta$ value) for the difference in ground and transition state with that for the difference between ground and product state. The transition state structure is thus definable on a scale of states between ground and product and the structure will thus not correspond to that of a single molecule as is usually represented in mechanistic schemes. Moreover, the 'structure' should include solvent as this part of the state. We have been using the idea[17] that the coordinates of the reaction map are the experimental parameters which could be normalised and defined as Leffler indices ($\alpha$) or they could be some other parameters such as an isotope effect so long as it is normalised. There is no easy connection between the Leffler type index as a coordinate and the distance parameters often used in theoretical discussions of reaction maps because of the 'state' definition in the former case and the 'molecular' definition in the latter.

It will be some time before the two approaches can be reconciled; in the meantime the experimental Brønsted-type

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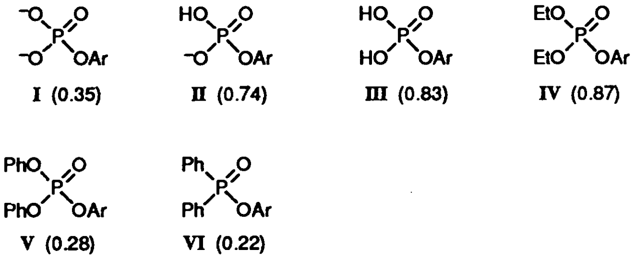
* Values of $p_{xy}$ for diphenylphosphoryl, diphenylphosphinoyl and acetyl are taken as, respectively, 0.114, 0.096 and 0.18.

approach should be recognised as not necessarily conforming with a model based on theoretical potential energy surfaces for reactions of single molecules.[18]

Linearity of Brønsted type plots as observed here is explained by a compensation of movement of the transition state in the reaction map. In the case of the map discussed here the transition state as defined by the Brønsted slopes exhibits compensation. When the nucleophile Nu increases its basicity the effect at the transition state position parallel to the reaction coordinate (Hammond effect) reduces the 'strength' of A ··· Nu and augments the A ··· Lg bond; the effect of an increase in Nu basicity perpendicular to the reaction coordinate (anti-Hammond effect) is to make the transition state 'tighter' *i.e.* to augment both Lg ··· A and A ··· Nu 'bonding'. The overall effect is that the Lg ··· A 'bonding' is augmented and that of A ··· Nu stays approximately the same (see Fig. 5). Of course, this is just another way of stating the canonical definitions of the Bema Hapothle.[16b]

The data on the variation of $\beta_{lg}$ and $\beta_{nuc}$ obtained here enable us to compute $\beta_{eq}$ for the transfer of the diphenylphosphoryl group between substituted phenolate ions and a standard nucleophile. The value of 1.30 is a lower $\beta_{eq}$ value than that determined for neutral phosphoryl [$(HO)_2PO$–Ar] and diethylphosphoryl group [$(EtO)_2PO$–Ar] transfer. It should be noted that the errors obtained in the present method (whereby one of the kinetic $\beta$ values is computed from a linear regression) must be larger than is expected from the technique involving explicit measurement of $\beta_{nuc}$ and $\beta_{lg}$. Such errors were noted in the present method when employed for measuring $\beta_{eq}$ for acetyl group transfer ($CH_3CO$–OAr).[8] Values of $\beta_{eq}$ for transfer of the phosphyl group to aryl oxide ions may be expressed in terms of effective charge on the ether oxygen in the ester state; these values are collected in Scheme 1. In view of the above discussion it would be premature to comment on the differences between effective charges for the various esters. It is possible that the low positive values in **V** and **VI** compared with those in **III** and **IV** could be due to a lack of hydrogen bonding in the former pair with the solvent.


**I** (0.35) **II** (0.74) **III** (0.83) **IV** (0.87)

**V** (0.28) **VI** (0.22)

**Scheme 1** Values of 'effective' charge on the ether oxygen for acyl group transfer in aqueous solution

The application of identity rate methodology is most useful for a reaction with a single transition state, since a single Brønsted dependence can identity the electronic structure owing to the requirement that the transition state lies on the tightness diagonal. Thus the transition state for the identity transfer between phenolate ions can be obtained simply from $\beta_{lg}$ for phenolate ion attack on the aryl esters (provided $\beta_{eq}$ is known). The $\tau$ values for diphenylphosphinoyl, diphenylphosphoryl and diethylphosphoryl group transfer between phenolate ions are 0.92 (Table 3), 1.20 (Table 2) and 1.45.[19] Thus the diphenylphosphinoyl and diphenylphosphoryl group transfers are almost synchronous and the diethylphosphoryl group transfer is the most associative-like for the phenolate ion nucleophile.

Attack of hydroxide ion on the diphenylphosphate esters has a $\beta_{lg}$ value of $-0.55$ (Leffler's $\alpha = 0.42 \pm 0.02$) which compares with values of $\alpha$ of 0.24[20] for the diethylphosphate and 0.55[21] for the diphenylphosphinate. These values are consistent with relatively little bond fission in the case of the diethylphosphate.

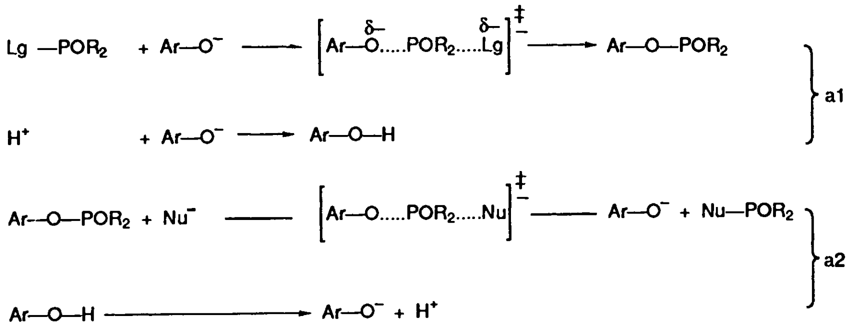
The diphenylphosphinate and diphenylphosphate esters, however, show more bond fission in the transition state than in the diethyl case consistent with a concerted process for hydroxide ion attack.

## Appendix

*Confidence Limits.*—Data for attack of phenolate ions on phenyl esters (Fig. 1) deviate from the least-squares lines, presumably due to microscopic medium effects. Scrutiny of Fig. 1 indicates a regularity of the deviations which is not consistent with experimental error. In the case of phenolate ion attack of ester with constant leaving group the variations arise from the slight specific differences between the phenolate oxygen in the transition state and in the non-ionised state in the standard reaction [eqn. (a1)]. In the case of attack of a constant phenolate ion on ester with varying phenolate ion leaving group the variation comes from the small differences between the phenolate oxygen in the four states illustrated in eqn. (a2).

Sufficient data must therefore be collected to give reasonable confidence in the Brønsted line and the data must therefore be well spaced over as wide a range of $pK_a$ values as is possible. The confidence limits on the 'three-point' Brønsted plots are especially emphasised in Tables 2 and 3 because reliance on the $\beta$ values from these relationships is less than that on $\beta$ values from Brønsted plots with more substantial numbers of points over wider $pK_a$ ranges. It is noted in Table 2 that the 2,4-dinitrophenyl and 4-nitrophenyl lines for the three point plots agree with those for the more extensive data; the same applies to the 4-nitrophenyl lines in Table 3.

The data for log $k_{ii}$ are NOT employed to define curvature in the plots of Figs. 3 and 4. The curved plot [eqn. (5)] is theoretically predicted from the equation $\beta_{ii} = \beta_{nuc} + \beta_{lg}$ and the log $k_{ii}$ data is fitted to this. Work to be submitted from this laboratory[22] for the attack of phenolate ions on aryl



acetates indeed shows a Lewis–Kreevoy plot (like Figs. 3 and 4) with points on both up and down slopes.

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