Evidence for an Open Transition State in the Transfer of a Carbonyl Acyl Group between Phenolate Anions

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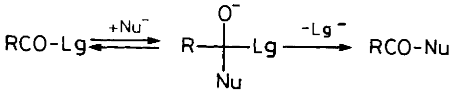
Rate constants for transesterification between 2,4-dinitrophenyl 4-methoxy-2,6-dimethylbenzoate and thirteen substituted phenolate anions obey a Brønsted equation with β_{nuc} 0.19; the bond making and breaking parameter for the completely symmetrical reaction of the ester with 2,4-dinitrophenolate anion indicates significant benzoylium ion character in the transition state of the concerted displacement reaction.

Classical work supports stepwise associative (equation 1)[1] and dissociative (equation 2)[2] paths for displacement reactions by nucleophiles at carbonyl centres. Contemporary work[3a—d] has provided evidence for *concerted*† displacements at carbonyl centres; the systems so far studied have transition states where the bond fission and formation parameters are consistent with strongly coupled processes.

Studies of the reaction of aryl oxide anions with aryl acetates[3b] indicate that decreasing the nucleophilicity of the aryl oxide leaving anions will reduce the coupling between bond formation and fission in the transition state. However, Waring found[4] that reaction of aryl oxide ions with 2,4-dinitrophenyl acetate has a β_{nuc} value of 0.58 which gives a Leffler index[5] of 0.34 (when β_{nuc} is combined with a β_{eq} value of 1.7 for equilibrium transfer of the acetyl group between aryloxide ions). The observed Leffler index, on a scale of 0—1, indicates that there is significant coupling in the transition state of the symmetrical transfer of acetyl between 2,4-dinitrophenolate anions. Oxyanion entering and leaving nucleophiles much weaker than the 2,4-dinitrophenolate ion would be required to reduce the 'coupling' in the transition state in order for acetylium ion character to predominate. Such systems would not be subject to verification in a simple kinetic study because of competition by hydrolysis of the acetate ester rendered highly reactive by the leaving group.

Different extents of coupling between bond formation and fission may be represented on a reaction map as shown in Figure 1. Increasing the stability of the putative acylium ion (bottom right corner of the reaction map, Figure 1) could induce acylium ion character in the transition state. We chose to study displacements at the 4-methoxy-2,6-dimethylbenzoyl centre where the benzoylium ion would be stabilised by electron donation and by steric means. An oxyanion substituent in the 4-position stabilises a benzoylium ion so that it can form a kinetically observable intermediate;[6] even non-anionic electron donating groups can favour the formation of an intermediate (equation 2), provided entering and leaving nucleophiles are weak enough.[2,7]

 (1)

$$\mathrm{RCO{-}Lg} \overset{+\mathrm{Nu}^-}{\rightleftharpoons} \mathrm{R}{-}\overset{\mathrm{O}^-}{\underset{\mathrm{Nu}}{+}}{-}\mathrm{Lg} \xrightarrow{-\mathrm{Lg}^-} \mathrm{RCO{-}Nu} \quad (1)$$

$$\mathrm{RCO{-}Lg} \overset{-\mathrm{Lg}^-}{\rightleftharpoons} \mathrm{RCO}^+ \xrightarrow{+\mathrm{Nu}^-} \mathrm{RCO{-}Nu} \quad (2)$$

$$\log k_{\mathrm{ArO}} = 0.19 \pm 0.06\, \mathrm{p}K_a^{\mathrm{ArOH}} - 4.7 \pm 0.49 \quad (3)$$

Lg = leaving group

Second order rate constants for reaction of thirteen substituted phenolate ions with 2,4-dinitrophenyl 4-methoxy-2,6-dimethylbenzoate obey equation (3) over a range of $\mathrm{p}K_a^{\mathrm{ArOH}}$ from 5.49 to 10.2. The conditions are 25° and 40% (v/v) dioxan/water with ionic strength maintained at 0.1 M with KCl.‡ Nucleophiles with high steric requirements are excluded from the investigation. Recent studies[3b] indicate that the displacement of 4-nitrophenolate ion from 4-nitrophenyl acetate by aryl oxide ions has a single transition state. It is reasonable to assume that the reaction under investigation here is also concerted; the steric requirements of the orthomethyl groups and electron donation from the 4-methoxy substituent also mitigate against a stepwise process with a tetrahedral intermediate. The transition state for

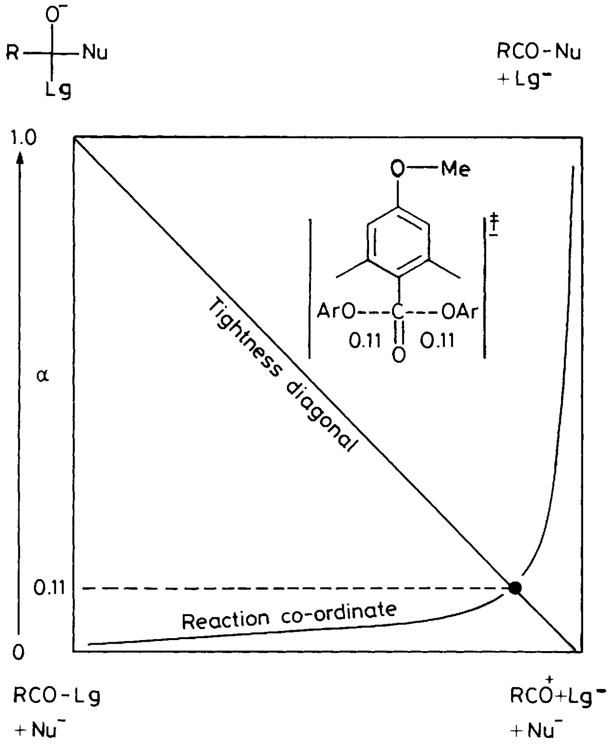


Figure 1. A reaction map for the attack of aryl oxide ions (Nu⁻) on aryl benzoates (RCO–L); ● indicates the structure of the transition state for the symmetrical displacement reaction of 2,4-dinitrophenyl-4-methoxy-2,6-dimethylbenzoate. The inset indicates the transition state structure for the symmetrical transfer of the benzoyl group between 2,4-dinitrophenolate ions.

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† A concerted mechanism is one where there is only a *single* transition state between reactant and product states.

‡ The product of the reaction is the corresponding aryl ester. So far all carbonyl transfer equilibria between oxyanions have β_{eq} values close to 1.7 except where there are gross electrostatic effects from atoms α to the carbonyl group.[5]

identical entering and leaving nucleophiles will lie on the tightness diagonal in the diagram and its position for the transfer between 2,4-dinitrophenolate anions may be computed from the Leffler value for bond formation assuming reasonably that equation (3) holds for the pK_a of this phenol. The β_{nuc} for attack of aryloxide ions (0.19) coupled with the β_{eq} for the equilibrium transfer of the acyl function between phenolate ions gives a Leffler value of 0.11, which indicates that the transition state has substantial benzoylium ion character. The value of α is close to that found in classical systems of sulphuryl and phosphoryl group transfer exhibiting 'exploded' transition states.§

As the bonds become weaker to the acylium ion residue in the transition state, solvation effects will begin to dominate the value of α. The extent that the present α value represents steps other than bonding changes will be discussed later. The stereochemistry of the transition state is presumably close to square planar.

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§ Phosphoryl group transfer between pyridines has an α value of 0.145[5] and sulphuryl group transfer between pyridines has an α value of 0.25[5] for bond formation in the symmetrical reaction.

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