An 'Open' Transition State in the Transfer Reaction of a Neutral Phosphoryl Group between Phenolate Anions

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A Brønsted exponent (β_{nuc}) of 0.12 has been obtained for reaction of seventeen substituted phenolate ions with 2,4-dinitrophenyl diphenyl phosphate in methanol/water solution. The Leffler α value for P–O bond formation (0.09) indicates that the transition-state of the symmetrical concerted reaction of 2,4-dinitro phenolate ion with the ester has 91% of the character of the putative phosphorylium ion intermediate state.

It has generally been thought that nucleophilic displacement reactions of derivatives of acids (acyl group transfer)† occur in a stepwise rather than a concerted manner. Indeed Bender showed that carbonyl group transfer between strong nucleophiles involves an associative mechanism.[1] A concerted mechanism involves a single transition state and its reaction co-ordinate lies between those for the two extremes of association–elimination and the elimination–association pathways on the reaction map (inset to Figure 1).

An important factor in understanding the mechanism of a reaction is knowledge of the charge change on individual

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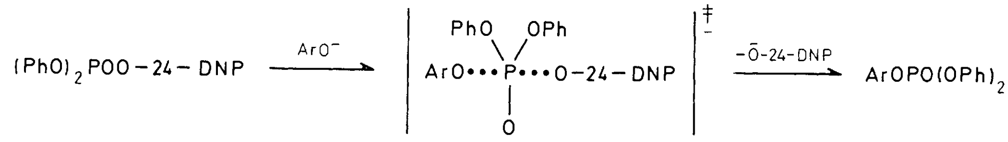
† The term 'acyl' is taken to mean the general electrophilic component (A–) of any acid (A–OH) such as carboxylic (RCO–OH), phosphoric [$(RO)_2PO$–OH], and sulphonic [RSO_2–OH)].



(1)

(HO-24-DNP = 2,4-dinitrophenol)

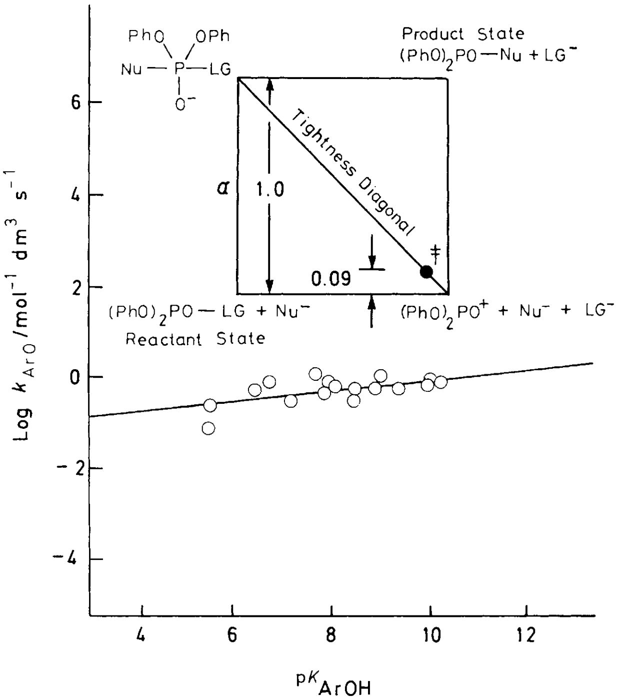


Figure 1. Brønsted dependence for attack of substituted phenolate ions on 2,4-dinitrophenyl diphenyl phosphate in $MeOH/H_2O$ (43% v/v) at 25 °C and ionic strength made up to 0.1 M with KCl. The line is drawn from the equation in the text. The identities of phenolate ions are, in increasing order of pK_a: F_5; 2,3,5,6-F_4; 2,3,5-Cl_3; 2,4,5-Cl_3; 2,3,4-Cl_3; 4-CHO; 2,4-Cl_2; 4-CN; 4-COMe; 2-Cl; 4-CO_2Et; 3-CO_2Et; 3-Cl; 4-Cl; 4-F; 4-OMe; 4-Me. (Nu = nucleophile, LG = leaving group).

Inset: reaction map showing the transition state for the concerted reaction of 2,4-dinitrophenolate ion with 2,4-dinitrophenyl diphenylphosphate. The discrete pathways involving association–elimination and elimination–association go through the top left corner and bottom right corner of the reaction map, respectively.

atoms. It is possible to measure change in 'effective' charge by the use of substituent effects determined against a standard equilibrium directly related to the reaction in question.[2] Leffler[3] first proposed a description of the transition state in terms of the known structures of the reactant and product states. The effects of modifiers on the rate constant are compared with their effects on the overall equilibrium constant of the reaction. The most convenient modifier to employ is a polar substituent which will cause variation in rate or equilibrium by electrostatic interaction with charge, or dipole at the reaction centre. Leffler's index (α) is a measure of bond change at the reaction site as a function of that 'bond' in the two extreme states of reaction and product. It can be represented as $\alpha = \beta_f/\beta_{eq}$ where β_f is the Brønsted exponent for the forward reaction rate constant and β_{eq} is the exponent for the equilibrium constant of the reaction where the substituent senses charge change in the bond in question. The Brønsted plot of the reaction of substituted phenolate ions with 4-nitrophenyl diphenyl phosphate is linear over a substantial pK_a range encompassing the pK_a where a 'break' would occur in a putative stepwise process;[4] it is consistent with a single transition state mechanism. In the present study kinetics were measured for reaction of seventeen substituted phenolate ions with 2,4-dinitrophenyl diphenyl phosphate [equation (1)] and the Brønsted plot (Figure 1) is linear [equation (2)].

$$\log k_{ArO} = 0.12 \pm 0.04\, pK_{ArOH} - 1.23 \pm 0.32 \qquad (2)$$

The value of α (0.09) is obtained by division of 0.12 by the value of β_{eq}.[4] Thus bond formation is 9% of its full bond in the final product over the range of phenolate ions studied. It is reasonable to assume[4] that equation (2) holds down to the pK_{ArOH} corresponding to 2,4-dinitrophenolate ion acting as nucleophile. The symmetrical reaction is reasonably assumed from previous work[4] to be a concerted process [equation (1)]. The single transition state for reaction of 2,4-dinitrophenolate anion with the ester must therefore lie on the 'tightness' diagonal[5] (inset to Figure 1) and is very close to the structure of the phosphorylium ion state rather than to that of the penta-co-ordinate intermediate state. The extent of bond fission in the symmetrical reaction will be the same as that of bond formation in reverse, namely 91% of full bond fission. This is the first reported quantitative evidence of an 'open' transition state in the transfer of a neutral phosphoryl group. These results have a bearing on sulphuryl and phosphoryl group transfer where the 'open' transition states involve participation of anionic oxygen atoms attached to the phosphorus or sulphur atoms.

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