DEPENDENCE OF TRANSITION-STATE STRUCTURE ON:
NUCLEOPHILE IN THE REACTION OF ARYL OXIDE ANIONS WITH
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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-degrees-C.
The rate constants obey good Bronsted type correlations with
the pK(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.

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