

Alkali Metal Ion Catalysis in Nucleophilic Displacement by Alkoxide Ion in *p*-Nitrophenyl Diphenylphosphinate. Rate Retardation by Crown Ether and Cryptand Complexing Agents

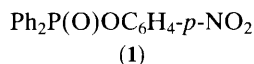
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Nucleophilic displacement by ethoxide on the title compound is subject to catalysis by lithium and potassium cations.

We report here on a striking instance of catalysis by alkali metal cations in nucleophilic displacement by alkoxide ion at a phosphinoyl centre in protic media. Though catalysis by divalent cations (Mg^{2+} , Zn^{2+} , Co^{2+} , etc.) has been observed for a variety of substrates containing specific co-ordination sites,¹⁻³ including some with phosphorus functionalities,⁴⁻⁶ catalysis by monovalent cations is of much rarer occurrence.⁷⁻⁹ The possible role of cations in nucleophilic displacement at tetra-co-ordinate phosphorus has been examined in only few studies⁹⁻¹² and to our knowledge there has been no kinetic study reported on catalysis by alkali metal cations.†



We present here the results of a study of nucleophilic displacement on *p*-nitrophenyl diphenylphosphinate [$\text{Ph}_2\text{P}(\text{O})\text{OC}_6\text{H}_4\text{-}p\text{-NO}_2$, (1)] which gives kinetic evidence of such catalysis. Reaction of (1) with lithium or potassium ethoxide (excess) in ethanol leads to quantitative liberation of *p*-nitrophenoxide ion and follows clean first order kinetics. In Figure 1 are plotted the pseudo first order rate constants as a function of base concentration in the absence, and in the presence, of macrocyclic crown ether and cryptand complexing agents. The latter series of runs were performed with the complexing agent in excess of alkoxide, under conditions where separate experiments showed that a minimum in rate had been attained.

The increasing slopes of the plots with increasing alkoxide concentration, in the absence of complexing agents (Figure 1), are consistent with a greater reactivity of undissociated EtO^-Li^+ and EtO^-K^+ species compared with free ethoxide ions. The opposite type of behaviour, *i.e.* a downward curvature in k vs. $[\text{Nu}]$ plots, has been observed in a variety of S_N2 processes at saturated carbon centres, which was interpreted as arising from decreased reactivity of ion-paired species compared with the dissociated anions.¹³ The results of a study of the effect of cations on isotopic exchange between chloride ion and *O,O*-diphenylphosphorochlorodithionate in acetonitrile were similarly interpreted on the basis that reaction occurred *via* the dissociated salts.¹¹

Thus, in the present system, the greater reactivity of lithium ethoxide compared to potassium ethoxide, the upward curvature in the k_{obs} vs. $[\text{EtOM}]$ plots in the absence of complexing agents, and the rate-retarding effects of the latter, all point to participation by the alkali metal cation in the transition state of the rate-determining step for the overall displacement process. This participation could occur in several possible ways. (1) The ion-paired RO^-M^+ species would attack

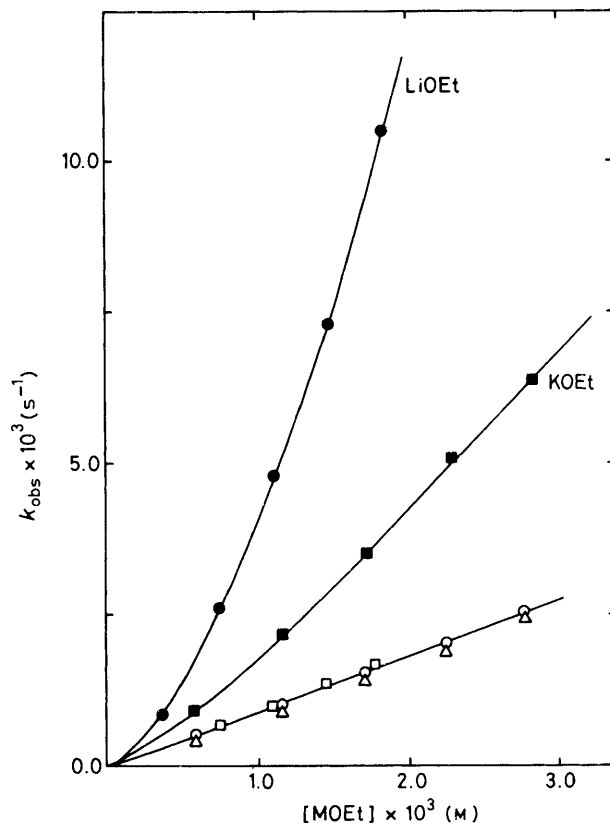


Figure 1. Kinetic data for the reaction of (1) in ethanol at 25 °C with LiOEt (●), KOEt (■), LiOEt + [2.1.1]cryptand (□), KOEt + dicyclohexano-18-crown-6 (○), or KOEt + [2.2.2]cryptand (△).

simultaneously at the phosphorus and oxygen centres of the $\text{P}=\text{O}$ bond *via* a four-centred transition state, giving rise to a pentacovalent intermediate¹⁴⁻¹⁷ from which the aryloxide ion would be ejected in a subsequent fast step. (2) Pre-equilibrium association of M^+ with the oxygen of $\text{P}=\text{O}$ would be followed by rate-determining attack of RO^- on phosphorus to give a pentacovalent species, followed by its breakdown as above. (3) The metal ion could act as an electrophilic catalyst through co-ordination at the phenoxy oxygen thereby enhancing its leaving group ability from the pentacovalent intermediate. (4) Reaction could occur by one of the pathways as above but a discrete intermediate would not be formed.‡ Future work will be directed at differentiating between these mechanisms and

† In the course of studies of the stereochemistry of nucleophilic displacement reactions of various organophosphorus esters with sodium alkoxide/phenoxide, it was found that addition of lithium perchlorate resulted in a decrease in reaction rate but no kinetic data were reported (refs. 9, 12).

‡ Although evidence has been presented (ref. 16) that hydrolysis of aryl diphenylphosphinates occurs by a two-stage rather than a concerted mechanism, the change in solvent in the present study and the advent of metal ion catalysis could combine to effect a change in the reaction mechanism.

uncovering the source of the metal ion effect in this nucleophilic displacement process.

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