

Metal Ion Catalysis in Nucleophilic Substitution Reaction of 4-Nitrophenyl Picolinate with Alkali Metal Ethoxides in Anhydrous Ethanol

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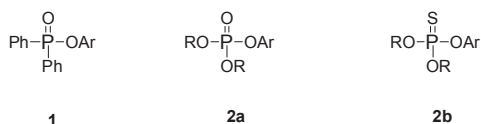
Pseudo-first-order rate constants (k_{obsd}) were measured spectrophotometrically for nucleophilic substitution reactions of 4-nitrophenyl picolinate (**6**) with alkali metal ethoxides (EtOM, $M^+ = K^+$, Na^+ and Li^+) in anhydrous ethanol at 25.0 ± 0.1 °C. The plot of k_{obsd} vs. [EtOM] exhibits upward curvature regardless of the nature of M^+ ions. However, the plot for the reaction of **6** with EtOK is linear with significantly decreased k_{obsd} values when 18-crown-6-ether (18C6, a complexing agent for K^+ ion) is added in the reaction medium. Dissection of k_{obsd} into k_{EtO^-} and k_{EtOM} (i.e., the second-order rate constant for the reaction with dissociated EtO^- and ion-paired EtOM, respectively) has revealed that ion-paired EtOM is 3 ~ 17 times more reactive than dissociated EtO^- . The reaction has been proposed to proceed through a 5-membered cyclic transition state, in which M^+ ion increases the electrophilicity of the reaction site. Interestingly, Na^+ ion exhibits the largest catalytic effect. The presence of a nitrogen atom in the pyridine moiety of **6** has been suggested to be responsible for the high Na^+ ion selectivity.

Key Words: Metal ion catalysis, Ion pair, Ethanolysis, Electrophilicity, Nucleofugality

Introduction

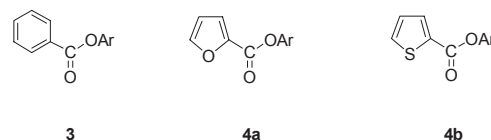
The effect of metal ions on nucleophilic substitution reactions of esters has intensively been investigated due to their importance in chemical and biological processes.¹⁻¹³ Metal ions have often been reported to behave as a Lewis acid catalyst. Since Lewis acidity increases with increasing the charge of metal ions, most studies have been focused on multivalent metal ions (e.g., Mg^{2+} , Ca^{2+} , Ni^{2+} , Co^{3+} , La^{3+}).1-5

However, the effect of alkali metal ions has much less been investigated.⁶⁻¹³ Buncl et al. have initiated a systematic study for nucleophilic substitution reactions of 4-nitrophenyl diphenylphosphinate (**1**) with alkali metal ethoxides (EtOM, $M^+ = Li^+$, Na^+ , K^+) in anhydrous ethanol and found that M^+ ions catalyze the reaction in the order $Li^+ > Na^+ > K^+$.⁶ We have also found that M^+ ions act as a catalyst in alkaline ethanolysis of 4-nitrophenyl diethyl phosphate (**2a**, paraoxon) and the catalytic effect decreases as the size of M^+ ions increases (i.e., $Li^+ > Na^+ > K^+$).⁹ In contrast, Li^+ ion inhibited the corresponding reaction of 4-nitrophenyl diethyl phosphorothioate (**2b**, parathion) while K^+ and Na^+ ions catalyzed the reaction.⁹ These results indicate that the effect of M^+ ions is dependent on the nature of the electrophilic centers (e.g., $P=O$ vs. $P=S$).



The effect of alkali metal ions has been investigated in alkaline ethanolysis of carboxylic esters such as 4-nitrophenyl benzoate (**3**),^{10a} 2-furoate (**4a**)^{10b} and 2-thiophenecarboxylate (**4b**).^{10c}

It has been reported that M^+ ions behave as a catalyst in the order $K^+ > Na^+ > Li^+$ for the reaction of **3**, although the catalytic effect is not significant.^{10a} A little larger catalytic effect has been found for the reactions of **4a** and **4b** with the same catalytic order (i.e., $K^+ > Na^+ > Li^+$).^{10b,c}

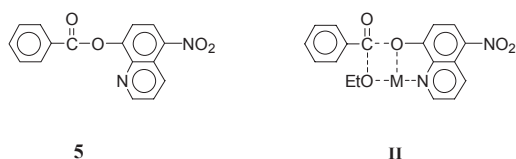


We have proposed that the reactions of **4a** and **4b** proceed through transition states I_a and I_b , respectively, in which M^+ ion increases the electrophilicity of the $C=O$ bond as a Lewis acid catalyst.^{10b,c} Thus, the enhanced electrophilicity through I_a and I_b has been concluded to be responsible for the larger M^+ ion effect observed in the reactions of **4a** and **4b** than in the corresponding reactions of **3**, since such 5-membered cyclic transition states are not possible for the latter reaction.^{10b,c}

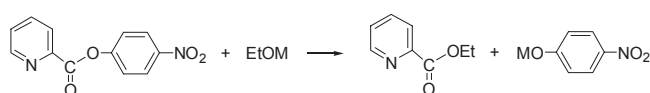


The effect of M^+ ions has also been studied for alkaline ethanolysis of 5-nitro-8-quinolyl benzoate (**5**).^{10e} The reaction has been suggested to proceed through transition state II, in which M^+ ion increases the nucleofugality of the leaving group.^{10e} Interestingly, the order of catalytic effect has been found to be unusual, i.e., $Na^+ > K^+ > Li^+$. Such high Na^+ ion selectivity has been ascribed to the presence of a nitrogen atom in cyclic transition state II.^{10e}

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Our study has been extended to the reaction of 4-nitrophenyl picolinate (**6**) with EtOM in anhydrous ethanol to get further information on M^+ ion effects (Scheme 1). We wish to report that M^+ ions catalyze the reaction in the order $Na^+ > K^+ > Li^+$. The origin of metal ion catalysis and the high Na^+ ion selectivity is also proposed together with a plausible transition-state structure.



$M^+ = Li^+, Na^+ \text{ and } K^+$

Scheme 1

Results and Discussion

The kinetic study was performed spectrophotometrically under pseudo-first-order conditions with a large excess of EtOM. All reactions in the current study obeyed pseudo-first-order kinetics. Pseudo-first-order rate constants (k_{obsd}) were obtained from the slope of the linear plots of $\ln(A_\infty - A_t)$ vs. t . It is estimated from replicate runs that the uncertainty in the k_{obsd} values is less than $\pm 3\%$. The k_{obsd} values and kinetic conditions for the reactions of **6** with EtOM are summarized in Table 1 and graphically illustrated in Figure 1.

Effect of alkali metal ion on reactivity. As shown in Figure 1, the reactivity of EtOM is highly dependent on the nature of M^+ ions, e.g., the k_{obsd} value at a given $[\text{EtOM}]$ decreases in the order $\text{EtONa} > \text{EtOK} > \text{EtOLi}$. Besides, plots of k_{obsd} vs. $[\text{EtOM}]$ exhibit upward curvature when the crown ether is absent in the medium. In contrast, the plot for the reaction with EtOK in the presence of 18-crown-6-ether (18C6, a complexing agent for K^+ ion) is linear with significantly decreased k_{obsd} values. Thus, one can suggest that M^+ ions behave as a catalyst in the reaction of **6** and the catalytic effect increases in the order $Li^+ < K^+ < Na^+$.

To show that the catalytic effect of M^+ ions disappears when crown ethers are added in the medium, the reaction of **6** with EtONa was performed in the presence of 15-crown-5-ether (15C5), a complexing agent for Na^+ ion. As shown in Figure 2, the k_{obsd} value at $[\text{EtONa}] = 5.10 \text{ mM}$ decreases rapidly upon addition of 15C5 up to $[\text{15C5}]/[\text{EtONa}] = 2$ and then remains nearly constant thereafter. This indicates clearly that 15C5 complexes Na^+ ion almost completely when $[\text{15C5}]/[\text{EtONa}] = 2$ and the crowned Na^+ ion does not behave as a catalyst.

Dissection of k_{obsd} into k_{EtO^-} and k_{EtOM} . To quantify the catalytic effect shown by M^+ ions, k_{obsd} values have been dissected into k_{EtO^-} and k_{EtOM} , i.e., the second-order rate constants for the reactions with dissociated EtO^- and ion-paired EtOM, respec-

Table 1. Kinetic data for reactions of **6** with EtOM in anhydrous EtOH at $25.0 \pm 0.1^\circ\text{C}$.

[EtOK]/ mM	$k_{\text{obsd}}/\text{s}^{-1}$	[EtONa]/ mM	$k_{\text{obsd}}/\text{s}^{-1}$	[EtOLi]/ mM	$k_{\text{obsd}}/\text{s}^{-1}$
1.29	0.970	1.14	1.16	1.23	0.735
2.57	2.46	2.28	3.19	2.46	1.73
3.86	4.31	3.42	5.85	3.69	2.74
5.14	6.27	4.56	8.94	4.93	3.91
6.43	8.50	5.70	12.6	6.16	5.05
7.71	10.9	6.84	16.5	7.39	6.31
9.00	13.3	7.98	20.3	8.62	7.55
10.3	15.8	9.12	24.5	9.85	8.91
11.6	18.8	10.3	29.3	11.1	10.3
-	-	11.4	33.5	-	-

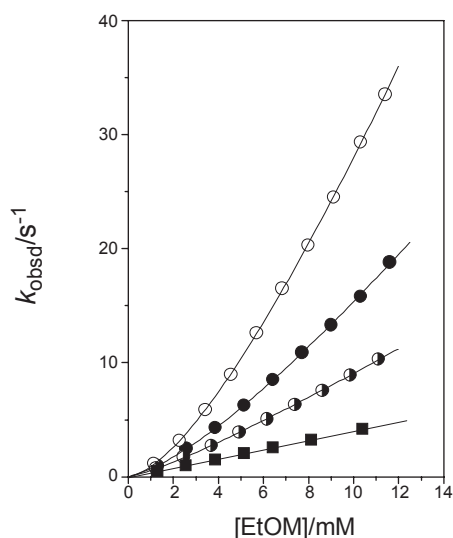


Figure 1. Plots of k_{obsd} vs. $[\text{EtOM}]$ for reactions of **6** with EtOK (●), EtONa (○), EtOLi (◐), and with EtOK in the presence of 18C6 (■) in anhydrous EtOH at $25.0 \pm 0.1^\circ\text{C}$. $[\text{18C6}]/[\text{EtOK}] = 2$.

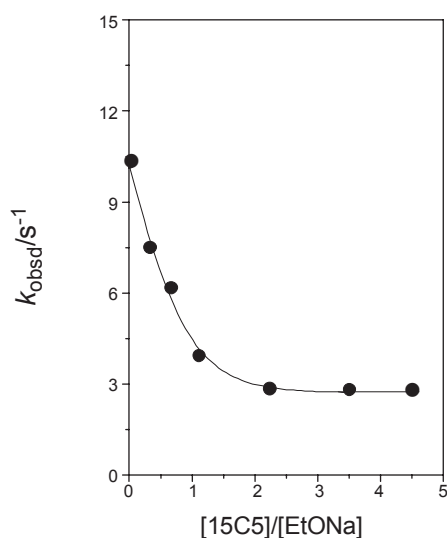


Figure 2. Plot showing effect of added 15C5 on k_{obsd} for the reaction of **6** with EtONa in anhydrous EtOH at $25.0 \pm 0.1^\circ\text{C}$. $[\text{EtONa}] = 5.10 \text{ mM}$.

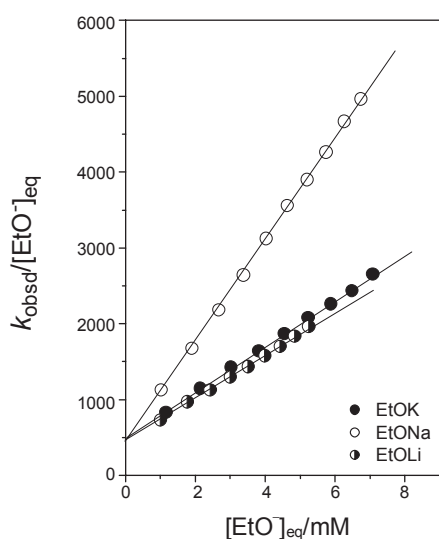
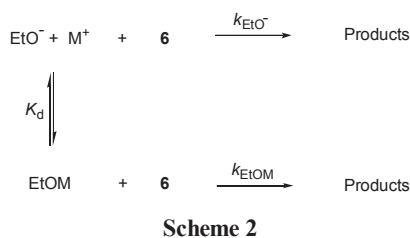


Figure 3. Plots illustrating dissection of k_{obsd} into k_{EtO^-} and k_{EtOM} for reactions of **6** with EtOM in anhydrous EtOH at 25.0 ± 0.1 °C.

tively. Alkali metal ethoxides have been reported to exist as dimers or other aggregates in a high concentration region (e.g., $[\text{EtOM}] > 0.1$ M).¹⁴ However, it has been suggested that EtOM exists as dissociated and ion-paired species in concentration below 0.1 M.¹⁴ Since the current reactions were performed in a low concentration region (e.g., $[\text{EtOM}] < 0.012$ M), one might expect that both dissociated EtO^- and ion-paired EtOM react with substrate **6** as shown in Scheme 2.



One can derive a rate equation as eq (1) based on the mechanism proposed in Scheme 2. Since the reactions were performed under pseudo-first-order conditions, k_{obsd} can be expressed as eq (2). It is noted that the dissociation constant $K_d = [\text{EtO}^-][\text{M}^+]/[\text{EtOM}]$, and $[\text{EtO}^-] = [\text{M}^+]$ at the equilibrium. Thus, eq (2) becomes eq (3). The concentration of EtO^- and EtOM at equilibrium can be calculated from the reported K_d and the initial $[\text{EtOM}]$.

$$\text{Rate} = k_{\text{EtO}^-} [\text{EtO}^-][\mathbf{6}] + k_{\text{EtOM}} [\text{EtOM}][\mathbf{6}] \quad (1)$$

$$k_{\text{obsd}} = k_{\text{EtO}^-} [\text{EtO}^-] + k_{\text{EtOM}} [\text{EtOM}] \quad (2)$$

$$k_{\text{obsd}}/[\text{EtO}^-] = k_{\text{EtO}^-} + k_{\text{EtOM}} [\text{EtO}^-]/K_d \quad (3)$$

One might expect that the plots of $k_{\text{obsd}}/[\text{EtO}^-]$ vs. $[\text{EtO}^-]$ are

Table 2. Summary of second-order rate constants from ion-pairing treatment of kinetic data for reactions of **6** with EtOM in anhydrous EtOH at 25.0 ± 0.1 °C.

EtOM	$k_{\text{EtO}^-}/\text{M}^{-1}\text{s}^{-1}$	$k_{\text{EtOM}}/\text{M}^{-1}\text{s}^{-1}$	$k_{\text{EtOM}}/k_{\text{EtO}^-}$
EtOK	486	3370	6.93
EtONa	385	6640	17.2
EtOLi	436	1350	3.10

linear and pass through a common intercept regardless of the nature of M^+ ions. This is because the intercept represents k_{EtO^-} , which is independent of M^+ ions as shown in eq (3). In fact, the plots shown in Figure 3 exhibit excellent linear correlation with nearly the same intercept, indicating that the mechanism proposed in Scheme 2 and eqs (1) - (3) are correct. Accordingly, k_{EtOM}/K_d and k_{EtO^-} can be determined from the slope and intercept of the linear plots, respectively. Since the K_d values have been reported to be 4.72×10^{-3} , 9.80×10^{-3} , and 11.1×10^{-3} M for EtOLi, EtONa, and EtOK, respectively,¹⁵ the k_{EtOM} values can be calculated from the k_{EtOM}/K_d values. The k_{EtO^-} and k_{EtOM} values determined in this way are summarized in Table 2.

Table 2 shows that the k_{EtO^-} value ranges from $385 \text{ M}^{-1}\text{s}^{-1}$ to $486 \text{ M}^{-1}\text{s}^{-1}$. The accurate k_{EtO^-} value can be obtained directly from the slope of the linear plot of k_{obsd} vs. $[\text{EtOK}]$ for the reaction of **6** with EtOK performed in the presence of 18C6 (see Figure 1). This is because EtOK would exist as dissociated free EtO^- and K^+ ion complexed by 18C6 when $[\text{18C6}]/[\text{EtOK}] = 2$, and the crowned K^+ ion does not catalyze the reaction. The k_{EtO^-} value determined in this way is $408 \text{ M}^{-1}\text{s}^{-1}$, which is practically the same as the mean of the k_{EtO^-} values in Table 2 (i.e., $436 \text{ M}^{-1}\text{s}^{-1}$).

One can see that the k_{EtOM} values are 3 ~ 17 times larger than the k_{EtO^-} values, indicating that the ion-paired EtOM is more reactive than the dissociated EtO^- . Besides, the k_{EtOM} value increases in the order $k_{\text{EtOLi}} < k_{\text{EtOK}} < k_{\text{EtONa}}$. This is consistent with the preceding argument that M^+ ions behave as a catalyst in the current reactions and the catalytic effect increases in the order $\text{Li}^+ < \text{K}^+ < \text{Na}^+$.

Origin of M^+ ion catalysis. Reactivity of **6** can be increased by increasing nucleofugality of the leaving group or electrophilicity of the C=O bond. Thus, one might suggest transition state III or IV for the current reactions. The M^+ ion in III increases nucleofugality of the leaving group as a Lewis acid catalyst, while that in IV enhances electrophilicity of the C=O bond.



It is well known that the leaving 4-nitrophenoxide is much less basic and a better leaving group than EtO^- . Besides, alkaline hydrolyses of carboxylic esters have generally been reported to proceed through a stepwise mechanism.^{16,17} Thus, one might expect that the reaction of **6** proceeds also through a stepwise mechanism, in which expulsion of the leaving group occurs after

the rate-determining step (RDS). In this case, catalysis through transition state III is not likely.

Alternatively, one can suggest that M^+ ions increase the electrophilicity of the reaction site through transition state IV, which is similar to those suggested for the reactions of **4a** and **4b** with EtOM (i.e., I_a and I_b) except presence of a different heteroatom in the 5-membered ring moiety (i.e., N, O, and S). Stability of cyclic transition states I_a , I_b and IV would be strongly influenced by the nature of their heteroatoms. Thus, one might expect that the magnitude of M^+ ion catalysis (e.g., k_{EtOM}/k_{EtO^-} ratio) for the reaction of **6** would be different from that for the corresponding reaction of **4a** and **4b**. In fact, as shown in Table 2, the k_{EtOM}/k_{EtO^-} ratio is 3 ~ 17, which is much larger than those reported for the corresponding reactions of **4a** and **4b** (i.e., the reported k_{EtOM}/k_{EtO^-} ratios are 1.5 ~ 4.3^{10b} and 1.2 ~ 2.1^{10c} for the reactions of **4a** and **4b**, respectively).

It is also noted that the order of catalytic effect found in this study (i.e., $Na^+ > K^+ > Li^+$) is quite different from that reported previously for the corresponding reactions of **1** and **2a** (i.e., $K^+ < Na^+ < Li^+$) and for those of **2b**, **3**, **4a** and **4b** (i.e., $K^+ > Na^+ > Li^+$). The high Na^+ ion selectivity found in this study is unusual. However, similar Na^+ ion selectivity has recently been reported for the corresponding reaction of 5-nitro-8-quinolyl benzoate (**5**), in which complex II has been suggested to be responsible for the M^+ ion catalysis.^{10c} A common feature of transition states II and IV is presence of an N atom in the 5-membered ring moiety. Thus, presence of an N atom in the 5-membered cyclic transition state IV is considered to be responsible for the high Na^+ ion selectivity found in this study.

Conclusions

The current study has allowed us to conclude the following: (1) Ion-paired EtOM is 3 ~ 17 fold more reactive than dissociated EtO^- toward substrate **6**. (2) M^+ ions catalyze the current reaction and the catalytic effect is in the order $Na^+ > K^+ > Li^+$. (3) The catalytic effect found in this study is much larger than that reported for the corresponding reactions of similar carboxylic esters (e.g., **4a**, **4b**). (4) The reaction proceeds through transition state IV, which can increase the electrophilicity of the reaction site. (5) The N atom in the 5-membered cyclic transition state IV is responsible for the high Na^+ ion selectivity found in this study.

Experimental Section

Materials. Compound **6** was prepared from the reaction of picolinic acid and 4-nitrophenol in the presence of dicyclohexylcarbodiimide and 4-dimethylaminopyridine in methylene chloride. The crude compound **6** was purified by column chromatography. The solutions of EtOM were prepared by dissolving the respective alkali metal in anhydrous ethanol under N_2 and stored in the refrigerator. The concentrations of EtOM were determined by titration with mono potassium phthalate. Crown ethers (18C6 and 15C5) were recrystallized from acetonitrile and dried under vacuum. The anhydrous ethanol was further dried over magnesium and distilled under N_2 just before use.

Kinetics. Kinetic study was performed using a stopped-flow

spectrophotometer equipped with a constant-temperature circulating bath. The reactions were followed by monitoring the appearance of the leaving 4-nitrophenoxide at 400 nm. Reactions were followed generally for 9 - 10 half-lives and k_{obsd} were calculated using the equation, $\ln(A_\infty - A_t)$ vs. t .

Product analysis. 4-Nitrophenoxide was liberated quantitatively and identified as one of the reaction products by comparison of the UV-vis spectra after completion of the reactions with those of the authentic samples under the reaction conditions.

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