DOI 10.5012/bkcs.2011.32.7.2423

Alkali Metal Ion Catalysis and Inhibition in Nucleophilic Substitution Reactions of 3,4-Dinitrophenyl Diphenylphosphinothioate with Alkali Metal Ethoxides in Anhydrous Ethanol: Effect of Changing Electrophilic Center from P=O to P=S

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Received May 31, 2011, Accepted June 9, 2011

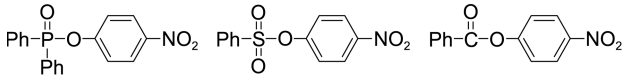
Pseudo-first-order rate constants (k_{obsd}) have been measured spectrophotometrically for nucleophilic substitution reactions of 3,4-dinitrophenyl diphenylphosphinothioate **9** with alkali metal ethoxides (EtOM, M = Li, Na, K) in anhydrous ethanol at 25.0 ± 0.1 °C. The plot of k_{obsd} *vs*. [EtOM] is linear for the reaction of **9** with EtOK. However, the plot curves downwardly for those with EtOLi and EtONa while it curves upwardly for the one with EtOK in the presence of 18-crown-6-ether (18C6). 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 the reactivity increases in the order $k_{EtOLi} < k_{EtONa} < k_{EtO^-} \approx k_{EtOK} < k_{EtOK/18C6}$, indicating that the reaction is inhibited by Li^+ and Na^+ ions but is catalyzed by 18C6-crowned K^+ ion. The reactivity order found for the reactions of **9** contrasts to that reported previously for the corresponding reactions of **1**, i.e., $k_{EtOLi} > k_{EtONa} > k_{EtOK} > k_{EtO^-} \approx k_{EtOK/18C6}$, indicating that the effect of changing the electrophilic center from P=O to P=S on the role of M^+ ions is significant. A four-membered cyclic transition-state has been proposed to account for the M^+ ion effects found in this study, e.g., the polarizable sulfur atom of the P=S bond in **9** interacts strongly with the soft 18C6-crowned K^+ ion while it interacts weakly with the hard Li^+ and Na^+ ions.

Key Words : Alkali metal ion, Catalysis, Inhibition, Ion pair, HSAB principle

Introduction

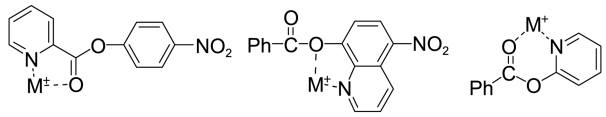
Metal ion effects on acyl-group transfer reactions have intensively been investigated due to their importance in biological processes as well as in synthetic interests.[1-12] It is known that metal ions behave as a Lewis acid catalyst in acyl-group transfer reactions. Since Lewis acidity increases with increasing positive charges, most studies have been focused on multivalent metal ions (e.g., Mg^{2+}, Mn^{2+}, Zn^{2+}, La^{3+}, Eu^{3+}, Co^{3+}).[1-5] The effect of alkali metal ions on acyl-group transfer reactions has much less been investigated although they are ubiquitous in nature including biological systems (e.g., a Na^+ pump which functions to keep high K^+ and low Na^+ concentration in mammalian cells).[6-12]

The first systematic study on alkali metal ions has been performed by Buncel et al. for nucleophilic substitution reactions of 4-nitrophenyl diphenylphosphinate **1** with alkali metal ethoxides EtOM ($M^+ = Li^+$, Na^+ and K^+) in anhydrous ethanol.[6] They found that alkali metal ions catalyze the reactions and the catalytic effect increases as the charge density of M^+ ions increases (i.e., $Li^+ > Na^+ > K^+$).[6] A contrasting M^+ ion effect has been reported for the corresponding reactions of 4-nitrophenyl benzenesulfonate **2**, i.e., the catalytic effect decreases with increasing the charge density of M^+ ions,[7] indicating that M^+ ion effect is dependent on the nature of the electrophilic centers (e.g., P=O *vs*. SO_2).



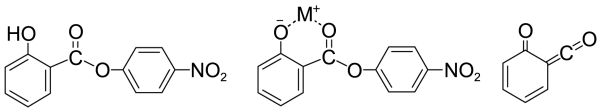
1 **2** **3**

Reactions of carboxylic esters (e.g., **3**) with EtOM have also been investigated.[10] The effect of M^+ ions has been reported to be insignificant except for the reactions of substrates which can form a 5- or 6-membered cyclic complex with M^+ ions (e.g., **4**M^+, **5**M^+ or **6**M^+).[10] In alkaline ethanolyses of 4-nitrophenyl picolinate **4**,[10a] 8-(5-nitroquinoly) benzoate **5**[10b] and 2-pyridyl benzoate **6**,[10c] we have shown that M^+ ions exhibit large catalytic effect by increasing the electrophilicity of the carbonyl carbon or by enhancing the nucleofugality of the leaving group through formation of a 5- or 6-membered cyclic complex.

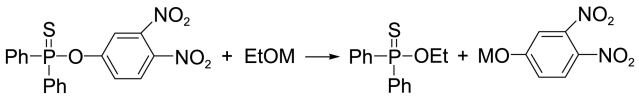


4M^+ **5**M^+ **6**M^+

We have recently shown that M^+ ions strongly inhibit reactions of 4-nitrophenyl 2-hydroxybenzoate **7** with EtOM through formation of a stable complex **7**M^+.[11] However, in the presence of complexing agents (e.g. 18-crown-6-ether for K^+ and 15-crown-5-ether for Na^+ ion), pseudo-first-order rate constant increases significantly but is independent of EtO^- concentrations, indicating that the reaction proceeds unimolecularly.[11] Accordingly, in the presence of complexing agents, the reaction of **7** has been concluded to proceed



through an E1cb mechanism with ketene **8** as a reactive intermediate.[11] In contrast, in the absence of complexing agents, we have shown that M^+ ion inhibits the reaction by forming complex **7**M^+ which prevents the ketene process.[11]



M = Li, Na, K, K/18C6.

Scheme 1

We have extended our study to nucleophilic substitution reactions of 3,4-dinitrophenyl diphenylphosphinothioate **9** with EtOM ($M^+ = Li^+$, Na^+, K^+, K^+/18C6) in anhydrous ethanol to get further information on the role of M^+ ions (Scheme 1). We have introduced a polarizable electrophilic center (i.e., P=S) to investigate the effect of changing the electrophilic center from P=O to P=S on the role of M^+ ions by comparing the kinetic results obtained in this study with those reported previously for the corresponding reactions of 4-nitrophenyl diphenylphosphinate **1**.

Results and Discussion

The kinetic study was performed spectrophotometrically under pseudo-first-order conditions in which the concentration of EtOM was in large excess over that of **9**. All reactions in the current study obeyed pseudo-first-order kinetics. Pseudo-first-order rate constants (k_{obsd}) were calculated from the slope of linear plots of ln $(A_\infty - A_t)$ *vs*. time. It is estimated from replicate runs that the uncertainty in the k_{obsd} values is less than ± 3%. The kinetic results are summarized in Table S1 in the Supporting Information. The second-order rate constants for the reactions of **9** with the dissociated EtO^- and ion-paired EtOM (i.e., k_{EtO^-} and k_{EtOM}, respectively) were calculated from the ion-pairing treatment of the kinetic data and are summarized in Table 1.

Effect of M^+ ions on Reactivity. As shown in Figure 1(a), the reactivity of EtOM toward **9** is dependent on the nature of M^+ ions, e.g., the k_{obsd} value at a given concentration increases in the order EtOLi < EtONa < EtOK < EtOK/18C6. It is also noted that the plot of k_{obsd} *vs*. [EtOM] is linear for the reaction with EtOK. However, the reactions with EtOLi and EtONa result in downward curvature while the one with EtOK in the presence of 18C6 exhibits upward curvature. Interestingly, the current results are opposite to those reported previously for the corresponding reactions of **1**,[6] i.e., the plot of k_{obsd} *vs*. [EtOM] shown in Figure 1(b) exhibits upward curvature for the reactions with EtOM (M = Li, Na, and K) but the one for the reaction with EtOK in the presence of 18C6 is linear with significantly decreased k_{obsd} values. Furthermore, the upward curvature is most significant for the reactions with EtOLi. Thus, the current study shows that the effect of changing the electrophilic center from P=O to P=S on the role of M^+ ions is indeed significant.

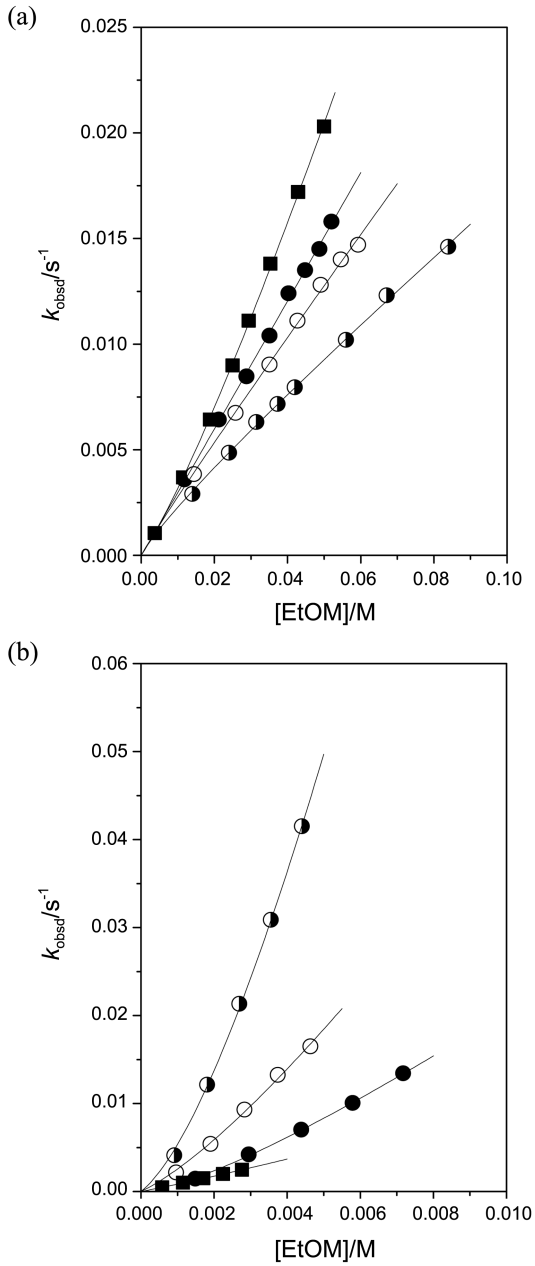
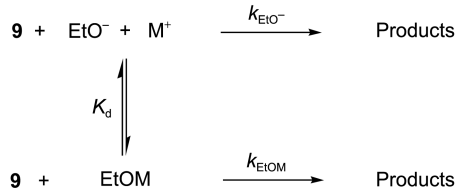


Figure 1. Plots of k_{obsd} *vs*. [EtOM] for the reactions of 3,4-dinitrophenyl diphenylphospinothioate **9** (a) and 4-nitrophenyl diphenylphosphinate **1** (b) with EtOLi (◑), EtONa (○), EtOK (●), and with EtOK in the presence of 18C6 (■) in anhydrous EtOH at 25.0 ± 0.1 °C. [18C6]/[EtOK] = 5.0. The kinetic data for the reactions of **1** with EtOM were taken from ref. 6.

The downward curvature found for the reactions of **9** with EtOLi and EtONa indicates that Li^+ and Na^+ ions behave as an inhibitor while the upward curvature observed for the reaction with EtOK in the presence of 18C6 implies that the 18C6-crowned K^+ ion catalyzes the reaction. To quantify the catalytic (or inhibitory) effect, k_{obsd} will be dissected into



Scheme 2

k_{EtO^-} and k_{EtOM}, the second-order rate constant for the reaction with dissociated EtO^- and ion-paired EtOM, respectively in the following section.

Dissection of k_{obsd} into k_{EtO^-} and k_{EtOM}. It has been reported that EtOM exists as dimers or other aggregates in a high concentration region (e.g., [EtOM] > 0.1 M) but as dissociated EtO^- and ion-paired EtOM when [EtOM] < 0.1 M.[13] Since the concentration of EtOM in the current reactions is lower than 0.1 M, one might expect that substrate **9** would react with the dissociated EtO^- and ion-paired EtOM as shown in Scheme 2.

Eq. (1) can be derived on the basis of the mechanism proposed in Scheme 2. Under pseudo-first-order kinetic conditions (e.g., [EtOM] >> [**9**]), k_{obsd} can be expressed as eq (2). Since the dissociation constant $K_d = [EtO^-]_{eq}[M^+]_{eq}/[EtOM]_{eq}$, and $[EtO^-]_{eq} = [M^+]_{eq}$ at equilibrium, eq. (2) can be converted to eq. (3).

$$\text{Rate} = k_{EtO^-}[EtO^-]_{eq}[\mathbf{9}] + k_{EtOM}[EtOM]_{eq}[\mathbf{9}] \quad (1)$$

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

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

The concentrations of $[EtO^-]_{eq}$ and $[EtOM]_{eq}$ can be calculated from the reported K_d values (i.e., $K_d = 4.72 \times 10^{-3}$, 9.80×10^{-3}, and 11.1×10^{-3} M for EtOLi, EtONa, and EtOK, in turn)[14] and the initial concentration [EtOM] using eqs. (4) and (5). It has been reported that EtO^- and 18C6-crowned K^+ ion form a weak ion pair,[15] and the K_d value reported for EtOK/18C6 is 60.2×10^{-3} M.[9a] Thus, one might expect that the plot of $k_{obsd}/[EtO^-]_{eq}$ *vs.* $[EtO^-]_{eq}$ would be linear with a positive intercept. In fact, the plots shown in Figure 2 are linear with a positive intercept, although the reaction with EtOK in the presence of 18C6 exhibits slightly smaller intercept than the reactions with other EtOM. Thus, one can suggest that the proposed mechanism as well as the derived equations are correct.

$$[EtOM] = [EtO^-]_{eq} + [EtOM]_{eq} \quad (4)$$

$$[EtO^-]_{eq} = [-K_d + (K_d^2 + 4K_d[EtOM])^{1/2}]/2 \quad (5)$$

The k_{EtO^-} and k_{EtOM}/K_d values have been determined from the intercept and the slope of the linear plots, respectively. The k_{EtOM} values can be calculated from the k_{EtOM}/K_d values determined above and the reported K_d value for EtOM. The k_{EtO^-} and k_{EtOM} values calculated in this way are summarized in Table 1.

Effect of Modification of Electrophilic Center from P=O to P=S. As shown in Table 1, the second-order rate constant for the reactions of **9** increases in the order $k_{EtOLi} < k_{EtONa} < k_{EtO^-} \approx k_{EtOK} < k_{EtOK}$/18C6, indicating that the dissociated EtO^- is more reactive than the ion-paired EtOLi and EtONa but less reactive than EtOK in the presence of 18C6. This is consistent with the argument in the preceding section that Li^+ and Na^+ ions behave as an inhibitor while the 18C6-crowned K^+ ion catalyzes the reaction on the basis of the curved plots of k_{obsd} *vs.* [EtOM]. However, the reactivity order found in this study contrasts to that reported previously for the corresponding reactions of **1**,[6] i.e., $k_{EtOLi} > k_{EtONa} > k_{EtOK} > k_{EtO^-} \approx k_{EtOK}$/18C6, indicating that changing the electrophilic center from P=O to P=S is significant.

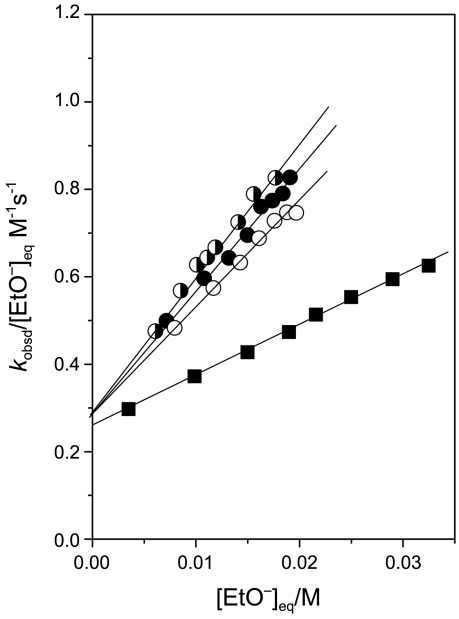


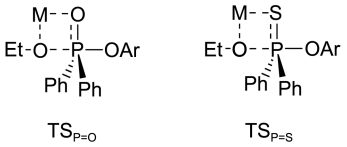
Figure 2. Plots illustrating dissection of k_{obsd} into k_{EtO^-} and k_{EtOM} for the reactions of 3,4-dinitrophenyl diphenylphospinothioate **9** with EtOLi (◑), EtONa (○), EtOK (●), and with EtOK in the presence of 18C6 (■) in anhydrous EtOH at 25.0 ± 0.1 °C. [18C6]/[EtOK] = 5.0.

Table 1. Summary of second-order rate constants (k_{EtO^-} and k_{EtOM}) calculated from ion-pairing treatment of the kinetic data for the reactions of 3,4-dinitrophenyl diphenylphosphinothioate **9** with EtOM in anhydrous ethanol at 25.0 ± 0.1 °C

EtOM	$k_{EtO^-}/M^{-1}s^{-1}$	$k_{EtOM}/M^{-1}s^{-1}$	k_{EtOM}/k_{EtO^-}
EtOLi	0.307	0.142	0.46
EtONa	0.298	0.232	0.78
EtOK	0.298	0.302	1.0
EtOK/18C6	0.258	0.693	2.7

It has been suggested that M^+ ions catalyze the reactions of **1** with EtOM through a cyclic transition-state as modeled by $TS_{P=O}$, in which M^+ ion increases electrophilicity of the electrophilic center as a Lewis acid catalyst.[6] It is well known that M^+ ions and negatively charged oxygen atoms have been classified as a hard acid and a hard base, respectively. Thus, one might expect that the interaction between M^+ ion and the negatively charged oxygen atom of the P=O bond would increase with increasing the hardness of M^+ ions (i.e., $Li^+ > Na^+ > K^+ >$ 18C6-crowned K^+) on the

basis of the hard-soft acids and bases (HSAB) principle.[16] This idea accounts for the order of the catalytic effect of M^+ ions reported for the reactions of **1**.



One can suggest a similar transition-state structure (e.g., $TS_{P=S}$) for the reactions of **9**, although the interaction between the negatively charged sulfur atom of the P=S bond and the hard Li^+ and Na^+ ions would not be strong on the basis of the HSAB principle, since a negatively charged sulfur atom has been classified as a soft base.[16] However, one might suggest that the 18C6-crowned K^+ ion, in which the positive charge is highly dispersed on the six oxygen atoms in 18C6, is a soft acid. Thus, the 18C6-crowned K^+ ion would exert a strong interaction with the polarizable sulfur atom in the P=S bond. This argument accounts for the contrasting M^+ effects found for the reactions of **1** and **9**, i.e., M^+ ion catalyzes the reactions of **1** in the order $Li^+ > Na^+ > K^+ > K^+/18C6$, while the reactions of **9** are inhibited by Li^+ and Na^+ but catalyzed by 18C6-crowned K^+ ion.

Conclusions

The current study has allowed us to conclude the following: (1) The plot of k_{obsd} *vs*. [EtOM] is linear for the reaction of **9** with EtOK. However, the reactions with EtOLi and EtONa exhibit downward curvature in the plot while the one with EtOK in the presence of 18C6 results in upward curvature. (2) Dissection of k_{obsd} into k_{EtO^-} and k_{EtOM} has shown that the reactivity increases in the order $k_{EtOLi} < k_{EtONa} < k_{EtO^-} \approx k_{EtOK} < k_{EtOK/18C6}$, indicating that the reaction of **9** is inhibited by Li^+ and Na^+ ions but is catalyzed by 18C6-crowned K^+ ion. (3) The current reactivity order contrasts to that reported previously for the corresponding reactions of **1**, i.e., $k_{EtOLi} > k_{EtONa} > k_{EtOK} > k_{EtO^-} \approx k_{EtOK/18C6}$, indicating that the effect of changing the electrophilic center from P=O to P=S on the role of M^+ ions is indeed significant. (4) Four-membered cyclic transition-states $TS_{P=O}$ and $TS_{P=S}$ have been proposed for the reactions of **1** and **9**, respectively to account for the contrasting M^+ ion effects. (5) The HSAB principle is operative in the current study, e.g., the polarizable sulfur atom of the P=S bond in **9** interacts strongly with the soft 18C6-crowned K^+ ion while it interacts weakly with the hard Li^+ and Na^+ ions.

Experimental Section

Materials. Compound **9** was readily prepared as described previously from the reaction of diphenylphosphinodithioic acid with 3,4-dinitrophenol in the presence of 4-(dimethylamino)-pyridine and *N*,*N*-dicyclohexylcarbodiimide in methylene chloride.[17] The crude compound **9** was purified by column chromatography. The stock 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. 18-Crown-6-ether was recrystallized from acetonitrile and dried under vacuum. The anhydrous ethanol used was further dried over magnesium and distilled under N_2 just before using.

Kinetics. Kinetic study was performed using a UV-vis spectrophotometer equipped with a constant-temperature circulating bath. The reactions were followed by monitoring the appearance of the leaving 3,4-dinitrophenoxide at 400 nm. Generally, reactions were followed up to 9-10 half-lives and k_{obsd} values were calculated using the equation, $\ln (A_\infty - A_t)$ *vs*. t.

Product Analysis. 3,4-Dinitrophenoxide 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.

Acknowledgments. This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0075488). Ji-Sun Kang is also grateful for the BK 21 Scholarship.

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