

Communications

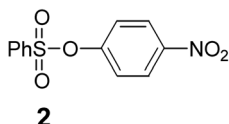
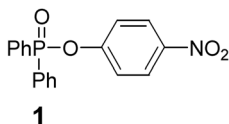
Effect of Alkali Metal Ions on Rate of Alkaline Ethanolysis of Diphenyl Sulfite

Ik-Hwan Um,^{*} Seung-Eun Lee,^a and Jee-Eun Park

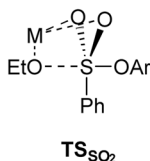
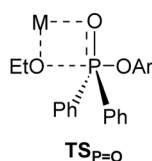
Division of Nano Sciences and Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea. ^{*}E-mail: ihum@ewha.ac.kr
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The reactivity of alkali metal ethoxides (EtO^-M^+ , $\text{M}^+ = \text{K}^+, \text{Na}^+, \text{and Li}^+$) toward phosphorus-centered electrophiles has been intensively investigated.¹⁻⁵ The first study was performed by Buncel *et al.* for nucleophilic substitution reactions of 4-nitrophenyl diphenylphosphinate (**1**) with EtO^-M^+ in anhydrous ethanol.¹ They found that the plot of k_{obsd} vs $[\text{EtO}^-\text{M}^+]$ exhibits an upward curvature, while the reaction in the presence of a complexing agent (*e.g.*, 18-crown-6-ether or [2,2,2] cryptand for the reaction with EtO^-K^+) results in a linear plot.¹ The reactivity has been reported to decrease in the order $\text{EtO}^-\text{Li}^+ > \text{EtO}^-\text{Na}^+ > \text{EtO}^-\text{K}^+ > \text{EtO}^-$.¹ A similar result has been reported for alkaline ethanolysis of 4-nitrophenyl phenylphosphonate,² 4-nitrophenyl diphenyl phosphate,³ 4-nitrophenyl methylphenylphosphinate,⁴ and 4-nitrophenyl dimethylphosphinate.⁵

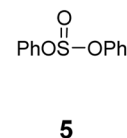
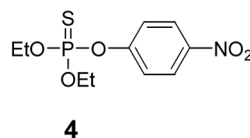
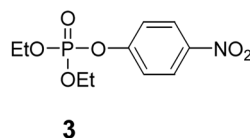


A contrasting reactivity order has been reported for reactions of a sulfur centered electrophile.⁶ Buncel *et al.* have shown that the reactivity of EtO^-M^+ decreases in the order $\text{EtO}^-\text{K}^+ > \text{EtO}^-\text{Na}^+ > \text{EtO}^- > \text{EtO}^-\text{Li}^+$ for the reactions of 4-nitrophenyl benzenesulfonate (**2**).⁶ The contrasting reactivity order found for the reactions of **1** and **2** has been attributed to the difference in numbers of ligand oxygens which can complex M^+ ions as illustrated in the transition-state structures $\text{TS}_{\text{P=O}}$ and TS_{SO_2} .⁶ This is because M^+ ions can interact with only one ligand oxygen atom in $\text{TS}_{\text{P=O}}$, while interactions with two ligand oxygen atoms are possible in TS_{SO_2} .⁶

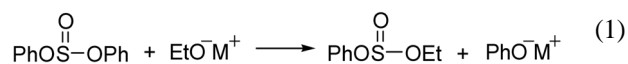


Our recent communication has shown that alkali metal ions behave as a catalyst in alkaline ethanolysis of paraoxon (**3**) and the catalytic effect decreases as the size of the metal

ions increases (*i.e.*, $\text{EtO}^-\text{Li}^+ > \text{EtO}^-\text{Na}^+ > \text{EtO}^-\text{K}^+$), while the reactivity of EtO^-M^+ decreases in the order $\text{EtO}^-\text{K}^+ > \text{EtO}^-\text{Na}^+ > \text{EtO}^-\text{Li}^+$ in the reactions of parathion (**4**).⁷ Such an opposite metal ion effect has also been found for reactions of the methyl analogues of **3** and **4** (*i.e.*, methyl paraoxon and methyl parathion, respectively) with EtO^-M^+ , indicating that the reactivity of alkali metal ethoxides is also dependent on the nature of the electrophilic center (*e.g.*, P=O to P=S).⁸



We have extended our study to the reactions of diphenyl sulfite (**5**) with EtO^-M^+ in anhydrous ethanol as shown in eq. (1) to investigate the effect of changing the electrophilic center from SO_2 (**2**) to SO (**5**). Sulfite **5** has only one possible ligand oxygen. Thus, one can expect that the effect of M^+ ions for the reactions of **5** is contrast to that reported for the reactions of sulfonate **2**, if the number of ligand oxygens is an important factor to determine metal ion effects as suggested by Buncel *et al.*



The kinetic study was performed spectrophotometrically by monitoring the appearance of the leaving 4-nitrophenoxide ion. All the reactions in current study obeyed pseudo-first-order kinetics. It is estimated from replicate runs that the uncertainty in the k_{obsd} values is less than $\pm 3\%$.

Figure 1 shows that the reactivity of alkali metal ethoxide is strongly dependent on the size of alkali metal ions (*i.e.*, $\text{EtO}^-\text{K}^+ > \text{EtO}^-\text{Na}^+ > \text{EtO}^-\text{Li}^+$). Besides, the plot of k_{obsd} vs. $[\text{EtO}^-\text{M}^+]$ exhibits an upward curvature for the reactions with EtO^-K^+ and EtO^-Na^+ but a downward curvature for those with EtO^-Li^+ . Interestingly, the reactivity pattern found in the current reactions is exactly the same as that reported for the reactions of **2**. Thus, the proposal⁶ that the number of ligand oxygens is an important factor to determine metal ion effect appears to be invalid.

To get more quantitative information about the M^+ ion effect, k_{obsd} values have been dissected into the respective k_{EtO^-} and $k_{\text{EtO}^-\text{M}^+}$ (*i.e.*, the second-order rate constants for the

^aPresent address: Advanced PKG Development Central R & D Institute, Samsung Electro-Mechanics, Gyunggi 443-743, Korea

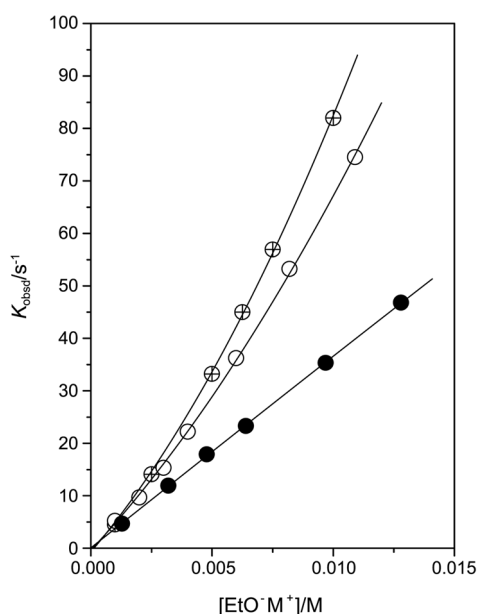


Figure 1. Kinetic data for the reactions of diphenyl sulfite (**5**) with EtO^-K^+ (\oplus), EtO^-Na^+ (\circ), and EtO^-Li^+ (\bullet) in anhydrous EtOH at 25.0 ± 0.1 °C.

reaction with the dissociated EtO^- and the ion-paired EtO^-M^+ , respectively). EtO^-M^+ has been reported to exist as dimers or other aggregates in the high concentration (> 0.1 M).⁹ However, in concentration below 0.1 M as in the current study, EtO^-M^+ has been suggested to exist mainly as dissociated and ion-paired species.⁹ An ion-pair association constant K_{assn} can be expressed as eq. (2), and $[\text{EtO}^-]_{\text{eq}} = [\text{M}^+]_{\text{eq}}$ at the equilibrium. Since both dissociated EtO^- and ion-paired EtO^-M^+ can react with substrates **5**, one can derive a rate equation as eqs. (3) and (4). Eq. (5) can be obtained from eqs. (2) and (4).

$$K_{\text{assn}} = [\text{EtO}^-\text{M}^+]_{\text{eq}}/[\text{EtO}^-]_{\text{eq}}[\text{M}^+]_{\text{eq}} \quad (2)$$

$$\text{Rate} = k_{\text{EtO}^-}[\text{EtO}^-]_{\text{eq}}[\mathbf{5}] + k_{\text{EtO}^-\text{M}^+}[\text{EtO}^-\text{M}^+]_{\text{eq}}[\mathbf{5}] \quad (3)$$

$$k_{\text{obsd}} = k_{\text{EtO}^-}[\text{EtO}^-]_{\text{eq}} + k_{\text{EtO}^-\text{M}^+}[\text{EtO}^-\text{M}^+]_{\text{eq}} \quad (4)$$

$$k_{\text{obsd}}/[\text{EtO}^-]_{\text{eq}} = k_{\text{EtO}^-} + K_{\text{assn}} k_{\text{EtO}^-\text{M}^+} [\text{EtO}^-]_{\text{eq}} \quad (5)$$

One might expect that the plot of $k_{\text{obsd}}/[\text{EtO}^-]_{\text{eq}}$ vs $[\text{EtO}^-]_{\text{eq}}$ would be linear and pass through a common intercept regardless of the size of M^+ ions, if the current reactions proceed as mentioned above. In fact, as shown in Figure 2, all plots are linear and pass through a common intercept. Accordingly, one can determine k_{EtO^-} and $K_{\text{assn}}k_{\text{EtO}^-\text{M}^+}$ values from the intercept and the slope of the linear plots, respectively.

The k_{EtO^-} value determined from the intercept is $3700 \pm 100 \text{ M}^{-1}\text{s}^{-1}$. Since the K_{assn} values of EtO^-Li^+ , EtO^-Na^+ , and EtO^-K^+ have been reported to be 212, 102 and 90 M^{-1} , respectively,¹⁰ the corresponding $k_{\text{EtO}^-\text{M}^+}$ value can be calculated from the slope of the linear plots shown in Figure 2. The $k_{\text{EtO}^-\text{M}^+}$ values determined in this way are 16200, 11900, and $3580 \text{ M}^{-1}\text{s}^{-1}$ for the reactions EtO^-K^+ , EtO^-Na^+ and EtO^-Li^+ , in turn. The current result shows that ion-paired EtO^-K^+ and EtO^-Na^+ are more reactive than the dissociated EtO^- by 4.4 and 3.2 times, respectively, while the ion-paired

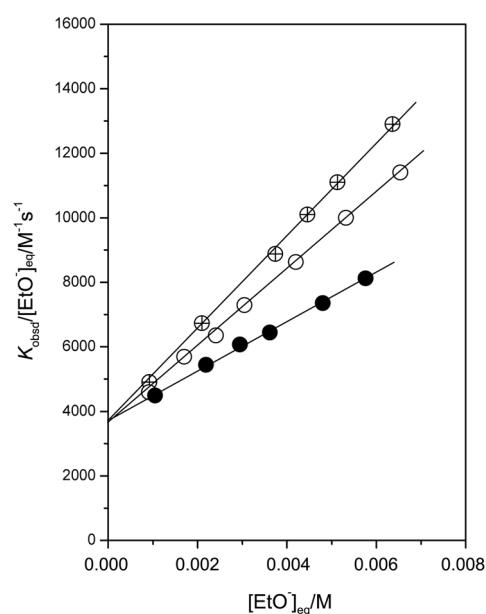


Figure 2. Plots illustrating dissection of k_{obsd} into k_{EtO^-} and $k_{\text{EtO}^-\text{M}^+}$ for the reactions of diphenyl sulfite (**5**) with EtO^-K^+ (\oplus), EtO^-Na^+ (\circ), and EtO^-Li^+ (\bullet) in anhydrous EtOH at 25.0 ± 0.1 °C.

EtO^-Li^+ is slightly less reactive than the free EtO^- .

The reactivity order of EtO^-M^+ found for the reactions of **5** in this study is clearly the same as that reported for reactions of **2** although substrates **2** and **5** have different numbers of ligand oxygens. Thus, one can conclude that the number of ligand oxygens cannot be an important factor to determine the metal ion effect. The reactivity order of EtO^-M^+ found for the reactions of **2** and **5** (*i.e.*, $\text{EtO}^-\text{K}^+ > \text{EtO}^-\text{Na}^+ > \text{EtO}^-\text{Li}^+$) appears to be typical for reactions of the sulfur centered electrophiles.

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