

# Communications

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

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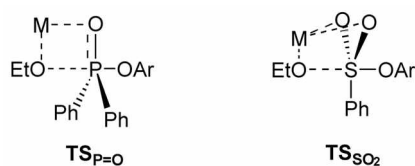
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The reactivity of alkali metal ethoxides ( $\text{EtO}^- \text{M}^+$ ,  $\text{M}^+ = \text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Li}^+$ ) toward phosphorus-centered electrophiles has been intensively investigated.<sup>1-5</sup> The first study was performed by Buncl *et al.* for nucleophilic substitution reactions of 4-nitrophenyl diphenylphosphinate (**1**) with  $\text{EtO}^- \text{M}^+$  in anhydrous ethanol.<sup>1</sup> They found that the plot of  $k_{\text{obsd}}$  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  $\text{EtO}^- \text{K}^+$ ) results in a linear plot.<sup>1</sup> The reactivity has been reported to decrease in the order  $\text{EtO}^- \text{Li}^+ > \text{EtO}^- \text{Na}^+ > \text{EtO}^- \text{K}^+ > \text{EtO}^-$ .<sup>1</sup> A similar result has been reported for alkaline ethanolysis of 4-nitrophenyl phenylphosphonate,<sup>2</sup> 4-nitrophenyl diphenyl phosphate,<sup>3</sup> 4-nitrophenyl methylphenylphosphinate,<sup>4</sup> and 4-nitrophenyl dimethylphosphinate.<sup>5</sup>

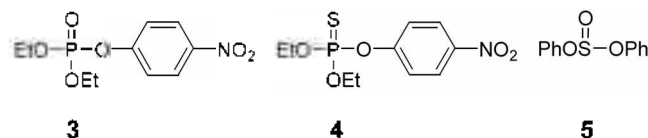


A contrasting reactivity order has been reported for reactions of a sulfur centered electrophile.<sup>6</sup> Buncl *et al.* have shown that the reactivity of  $\text{EtO}^- \text{M}^+$  decreases in the order  $\text{EtO}^- \text{K}^+ > \text{EtO}^- \text{Na}^+ > \text{EtO}^- > \text{EtO}^- \text{Li}^+$  for the reactions of 4-nitrophenyl benzenesulfonate (**2**).<sup>6</sup> 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  $\text{M}^+$  ions as illustrated in the transition-state structures  $\text{TS}_{\text{P=O}}$  and  $\text{TS}_{\text{SO}_2}$ .<sup>6</sup> This is because  $\text{M}^+$  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  $\text{TS}_{\text{SO}_2}$ .<sup>6</sup>

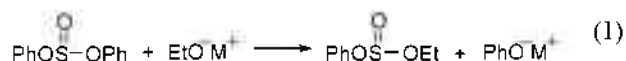


Our recent communication has shown that alkali metal ions behave as a catalyst in alkaline ethanolysis of paraoxon (**3**) and the catalytic effect decreases as the size of the metal

ions increases (*i.e.*,  $\text{EtO}^- \text{Li}^+ > \text{EtO}^- \text{Na}^+ > \text{EtO}^- \text{K}^+$ ), while the reactivity of  $\text{EtO}^- \text{M}^+$  decreases in the order  $\text{EtO}^- \text{K}^+ > \text{EtO}^- \text{Na}^+ > \text{EtO}^- \text{Li}^+$  in the reactions of parathion (**4**).<sup>7</sup> 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  $\text{EtO}^- \text{M}^+$ , indicating that the reactivity of alkali metal ethoxides is also dependent on the nature of the electrophilic center (*e.g.*,  $\text{P}=\text{O}$  to  $\text{P}=\text{S}$ ).<sup>8</sup>



We have extended our study to the reactions of diphenyl sulfite (**5**) with  $\text{EtO}^- \text{M}^+$  in anhydrous ethanol as shown in eq. (1) to investigate the effect of changing the electrophilic center from  $\text{SO}_2$  (**2**) to  $\text{SO}$  (**5**). Sulfite **5** has only one possible ligand oxygen. Thus, one can expect that the effect of  $\text{M}^+$  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 Buncl *et al.*

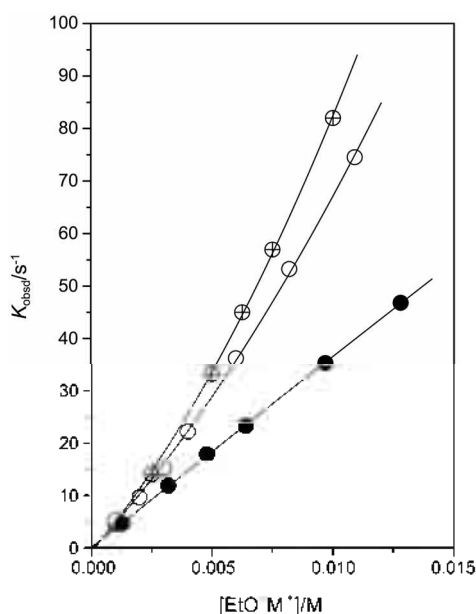


The kinetic study was performed spectrophotometrically by monitoring the appearance of the leaving 4-nitrophenoxide ion. All the reactions in current study obeyed pseudo-first-order kinetics. It is estimated from replicate runs that the uncertainty in the  $k_{\text{obsd}}$  values is less than  $\pm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

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  $k_{\text{obsd}}$  vs.  $[\text{EtO}^- \text{M}^+]$  exhibits an upward curvature for the reactions with  $\text{EtO}^- \text{K}^+$  and  $\text{EtO}^- \text{Na}^+$  but a downward curvature for those with  $\text{EtO}^- \text{Li}^+$ . Interestingly, the reactivity pattern found in the current reactions is exactly the same as that reported for the reactions of **2**. Thus, the proposal<sup>6</sup> 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  $\text{M}^+$  ion effect,  $k_{\text{obsd}}$  values have been dissected into the respective  $k_{\text{EtO}^-}$  and  $k_{\text{EtO}^- \text{M}^+}$  (*i.e.*, the second-order rate constants for the

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

reaction with the dissociated  $\text{EtO}^-$  and the ion-paired  $\text{EtO}^- \text{M}^+$ , respectively).  $\text{EtO}^- \text{M}^+$  has been reported to exist as dimers or other aggregates in the high concentration ( $> 0.1$  M).<sup>9</sup> However, in concentration below 0.1 M as in the current study,  $\text{EtO}^- \text{M}^+$  has been suggested to exist mainly as dissociated and ion-paired species.<sup>9</sup> An ion-pair association constant  $K_{\text{assn}}$  can be expressed as eq. (2), and  $[\text{EtO}^-]_{\text{eq}} = [\text{M}^+]_{\text{eq}}$  at the equilibrium. Since both dissociated  $\text{EtO}^-$  and ion-paired  $\text{EtO}^- \text{M}^+$  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).

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

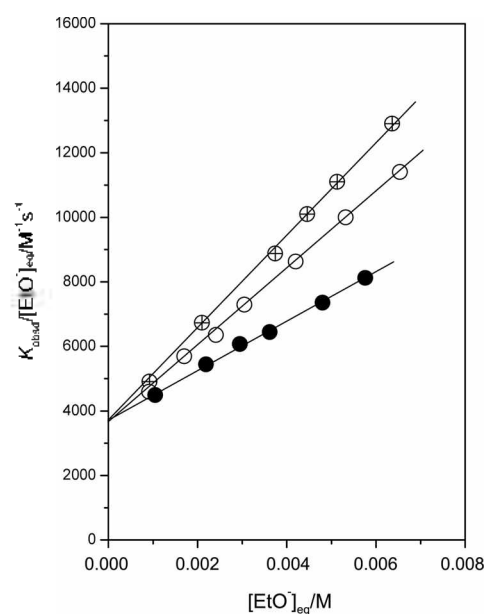
$$\text{Rate} = k_{\text{EtO}^-}[\text{EtO}^-]_{\text{eq}}[\mathbf{5}] + k_{\text{EtO}^- \text{M}^+}[\text{EtO}^- \text{M}^+]_{\text{eq}}[\mathbf{5}] \quad (3)$$

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

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

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  $\text{M}^+$  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  $k_{\text{EtO}^-}$  and  $K_{\text{assn}}k_{\text{EtO}^- \text{M}^+}$  values from the intercept and the slope of the linear plots, respectively.

The  $k_{\text{EtO}^-}$  value determined from the intercept is  $3700 \pm 100 \text{ M}^{-1}\text{s}^{-1}$ . Since the  $K_{\text{assn}}$  values of  $\text{EtO}^- \text{Li}^+$ ,  $\text{EtO}^- \text{Na}^+$ , and  $\text{EtO}^- \text{K}^+$  have been reported to be 212, 102 and  $90 \text{ M}^{-1}$ , respectively,<sup>10</sup> 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  $\text{EtO}^- \text{K}^+$ ,  $\text{EtO}^- \text{Na}^+$  and  $\text{EtO}^- \text{Li}^+$ , in turn. The current result shows that ion-paired  $\text{EtO}^- \text{K}^+$  and  $\text{EtO}^- \text{Na}^+$  are more reactive than the dissociated  $\text{EtO}^-$  by 4.4 and 3.2 times, respectively, while the ion-paired



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

$\text{EtO}^- \text{Li}^+$  is slightly less reactive than the free  $\text{EtO}^-$ .

The reactivity order of  $\text{EtO}^- \text{M}^+$  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  $\text{EtO}^- \text{M}^+$  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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