

Alkali-Metal Ion Catalysis and Inhibition in S_NAr Reaction of 1-Halo-2,4-dinitrobenzenes with Alkali-Metal Ethoxides in Anhydrous Ethanol

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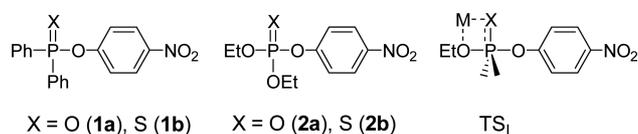
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A kinetic study is reported for S_NAr reaction of 1-fluoro-2,4-dinitrobenzene (**5a**) and 1-chloro-2,4-dinitrobenzene (**5b**) with alkali-metal ethoxides (EtOM, M = Li, Na, K and 18-crown-6-ether complexed K) in anhydrous ethanol. The second-order rate constant increases in the order $k_{\text{EtOLi}} < k_{\text{EtONa}} < k_{\text{EtOK}} < k_{\text{EtOK/18C6}}$ for the reaction of **5a** and $k_{\text{EtOLi}} < k_{\text{EtONa}} < k_{\text{EtOK}} < k_{\text{EtOK/18C6}}$ for that of **5b**. This indicates that M⁺ ion behaves as a catalyst or an inhibitor depending on the size of M⁺ ion and the nature of the leaving group (F⁻ vs. Cl⁻). Substrate **5a** is more reactive than **5b**, although the F⁻ in **5a** is *ca.* 10 pK_a units more basic than the Cl⁻ in **5b**, indicating that the reaction proceeds through a Meisenheimer complex in which expulsion of the leaving group occurs after the rate-determining step (RDS). M⁺ ion would catalyze the reaction by increasing either the nucleofugality of the leaving group through a four-membered cyclic transition state or the electrophilicity of the reaction center through a π -complex. However, the enhanced nucleofugality would be ineffective for the current reaction, since expulsion of the leaving group occurs after the RDS. Thus, it has been concluded that M⁺ ion catalyzes the reaction by increasing the electrophilicity of the reaction center through a π -complex between M⁺ ion and the π -electrons in the benzene ring.

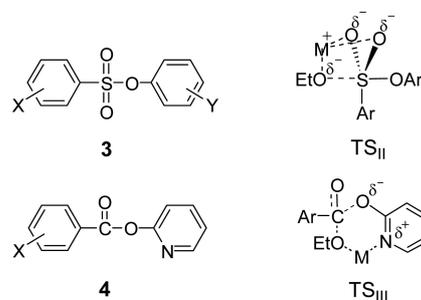
Key Words : Alkali-metal ion, Lewis acid catalyst, Inhibitor, Nucleofugality, Electrophilicity

Introduction

Alkali-metal ions are ubiquitous in nature and play an important role in biological processes (*e.g.*, Na⁺/K⁺ pump to maintain high K⁺ and low Na⁺ concentration in mammalian cells).¹ Alkali-metal ions have also been reported to catalyze (or inhibit) acyl-group transfer reactions, an important class of reactions in biological processes as well as organic syntheses.²⁻⁸ The first study of alkali-metal ion effects on acyl-group transfer reactions was carried out by Buncl and his coworkers for nucleophilic substitution reactions of 4-nitrophenyl diphenylphosphinate (**1a**) with alkali-metal ethoxides (EtOM, M = Li, Na and K) in anhydrous ethanol.^{2a} They have found that M⁺ ion catalyzes the reaction and the catalytic effect increases as the size of M⁺ ion decreases (*e.g.*, K⁺ < Na⁺ < Li⁺).² However, the catalytic effect was reported to disappear in the presence of complexing agents such as 18-crown-6-ether (18C6) for K⁺ ion, 15-crown-5-ether (15C5) for Na⁺ ion and [2,1,1]-cryptand for Li⁺ ion. In contrast, we have reported that the corresponding reaction of 4-nitrophenyl diphenylphosphinothioate (**1b**) is inhibited by Li⁺ ion but is catalyzed by K⁺ and 18C6-crowned-K⁺ ions.⁵ A similar result has been reported for the corresponding reactions of highly toxic insecticides paraoxon (**2a**) and parathion (**2b**) with EtOM,⁶ indicating that the effect of M⁺ ion is dependent on the nature of the electrophilic center (*e.g.*, P=O and P=S). Thus, M⁺ ion has been suggested to catalyze the reactions by increasing the electrophilicity of the reaction center through a transition-state (TS) structure similar to TS_I.



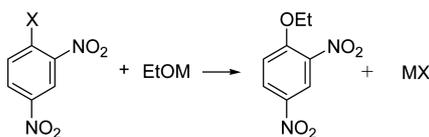
The role of M⁺ ions has also been investigated for reactions of SO₂ and C=O centered electrophiles. M⁺ ion has been reported to catalyze the reaction of Y-substituted-phenyl X-substituted-benzenesulfonates (**3**) with EtOM by increasing the electrophilicity of the reaction center through TS_{II}.⁷ In contrast, we have reported that M⁺ ion catalyzes the corresponding reaction of 2-pyridyl X-substituted-benzoates (**4**) by enhancing nucleofugality of the leaving group through TS_{III}.⁸



The effect of M⁺ ion on S_NAr reactions of activated aromatic or heteroaromatic compounds has not been investigated experimentally, although S_NAr reactions have a similarity to acyl-group transfer reactions. The apparent similarity is the nucleophilic addition step in S_NAr reaction and the addi-

tion step to carbonyl group in ester. In both cases addition to the sp² carbon leads to rehybridization to sp³ to produce a tetrahedral intermediate. Elimination of the leaving group in subsequent step(s) restores the sp² carbon. A fundamental difference is that addition to a typical electron-deficient aromatic substrate in an S_NAr reaction entails loss of aromaticity in the formation of the Meisenheimer complex. Thus, one might expect that M⁺ ion would also catalyze S_NAr reactions by increasing either the electrophilicity of the reaction center or the nucleofugality of the leaving group depending on the reaction mechanism.

We have previously carried out S_NAr reactions of 1-X-2,4-dinitrobenzenes with a series of cyclic secondary amines in MeCN and reported that the reaction proceeds through a Meisenheimer complex with one or two intermediates depending on the nature of X (*i.e.*, a zwitterionic tetrahedral intermediate T[±] and its deprotonated form T⁻ when X = F but without the deprotonation process to form T⁻ from T[±] when X = Cl, Br and I).⁹ Our study has now been extended to the S_NAr reaction of 1-X-2,4-dinitrobenzene (X = F and Cl) with EtOM (M = Li, Na, K and 18C6-complexed K) in anhydrous ethanol (Scheme 1). We wish to report that M⁺ ion behaves as a catalyst or as an inhibitor depending on the size of M⁺ ion and the nature of the leaving groups (*i.e.*, F⁻ and Cl⁻).



X = F (**5a**), Cl (**5b**).

M = Li, Na, K, 18C6-complexed-K.

Scheme 1

Results and Discussion

All the reactions in this study proceeded with quantitative formation of 1-ethoxy-2,4-dinitrobenzene as determined spectrophotometrically. First-order kinetics were observed under pseudo-first-order conditions in which EtOM concentration was in large excess of the substrate concentration. Pseudo-first-order rate constants (k_{obsd}) were calculated from the slope of the plots of $\ln(A_{\infty} - A_t)$ vs. t , which were linear over 90% reaction (*e.g.*, $R^2 > 0.9995$). It is estimated from replicate runs that the uncertainty in the k_{obsd} values is less than $\pm 3\%$. The second-order rate constants for the reactions with the dissociated EtO⁻ and ion-paired EtOM (*i.e.*, k_{EtO^-} and k_{EtOM} , respectively) were calculated from ion-pairing treatment of the kinetic data and are summarized in Table 1.

Effects of Alkali-Metal Ion on Reactivity. As shown in Figure 1, the reactivity of EtOM toward substrate **5a** is highly dependent on the nature of the M⁺ ion, *e.g.*, the k_{obsd} value at a given concentration of EtOM increases in the order EtOLi < EtONa < EtOK < EtOK/18C6. Besides, the reactivity difference increases with increasing the concentration of EtOM.

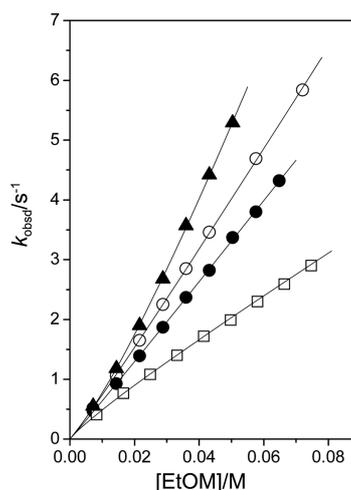


Figure 1. Plots of k_{obsd} vs. [EtOM] for the reactions of 1-fluoro-2,4-dinitrobenzene (**5a**) with EtOLi (□), EtONa (●), EtOK (○) and EtOK/18C6 (▲) in anhydrous EtOH at 25.0 ± 0.1 °C. [18C6]/[EtOK] = 2.0.

Interestingly, EtOK is more reactive in the presence of 18C6 than in the absence of the complexing agent. It is also noted that the plots of k_{obsd} vs. [EtOM] are nonlinear, *e.g.*, the plots for the reactions with EtOK and EtOK/18C6 curve upward while the one for the reaction with EtOLi curves downward. Such upward curvature is typical for reactions in which alkali-metal ion behaves as a catalyst.²⁻⁸ In contrast, the downward curvature observed for the reaction with EtOLi indicates that Li⁺ ion acts as an inhibitor.⁶ Thus, one can suggest that the reaction of **5a** is catalyzed by Na⁺, K⁺ and 18C6-crowned K⁺ ions but is inhibited by Li⁺ ion on the basis of the curved plots.

Similarly curved plots are demonstrated in Figure 2 for the corresponding reactions of 1-chloro-2,4-dinitrobenzene (**5b**), *e.g.*, upward curvature for the reactions with EtOK and EtOK/18C6, and downward curvature for the reaction with EtOLi. Interestingly, the plot for the reaction with EtONa

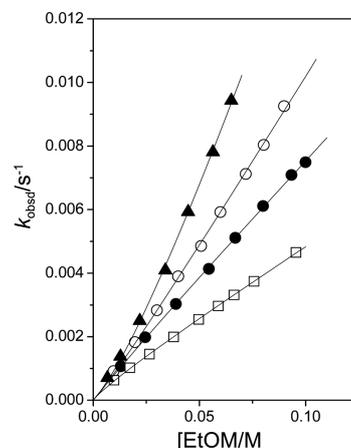


Figure 2. Plots of k_{obsd} vs. [EtOM] for the reactions of 1-chloro-2,4-dinitrobenzene (**5b**) with EtOLi (□), EtONa (●), EtOK (○) and EtOK/18C6 (▲) in anhydrous EtOH at 25.0 ± 0.1 °C. [18C6]/[EtOK] = 2.0.

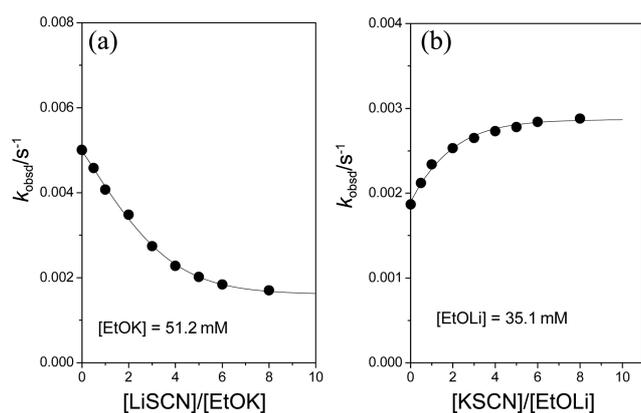
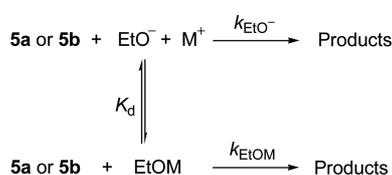


Figure 3. Effect of added LiSCN and KSCN on reactivity for the reaction of 1-chloro-2,4-dinitrobenzene (**5b**) with EtOK (a) and EtOLi (b) in EtOH at 25.0 ± 0.1 °C.

curves slightly downward. This is in contrast to the result for the corresponding reaction of **5a** shown in Figure 1. It is also noted that the reactivity of EtOM increases in the order EtOLi < EtONa < EtOK < EtOK/18C6. Thus, one can suggest that K^+ and 18C6-crowned K^+ ions catalyze the reaction while Na^+ and Li^+ ions inhibit the reaction on the basis of the curved plots shown in Figure 2.

To examine the above idea that the reaction of **5b** is catalyzed by K^+ ion but is inhibited by Li^+ ion, the reaction of **5b** has been carried out in the presence of KSCN and LiSCN. Our preliminary experiment revealed that both KSCN and LiSCN do not react with **5b** in anhydrous ethanol. However, as shown in Figure 3(a), the k_{obsd} value for the reaction with a fixed concentration of EtOK decreases rapidly upon addition of LiSCN up to *ca.* $[LiSCN]/[EtOK] = 4$ and then modestly thereafter. In contrast, the k_{obsd} value for the reaction with a fixed EtOLi concentration increases upon addition of KSCN up to *ca.* $[KSCN]/[EtOLi] = 3$ and then the increase is insignificant upon further addition of KSCN. These results clearly support the preceding suggestion that the current reaction is catalyzed by K^+ ion but is inhibited by Li^+ ion.

Dissection of k_{obsd} into k_{EtO^-} and k_{EtOM} . The k_{obsd} values have been dissected into the second-order rate constants for the reactions with the dissociated EtO^- and ion-paired EtOM (*i.e.*, k_{EtO^-} and k_{EtOM} , respectively) to quantify the catalytic or inhibitory effect exerted by M^+ ion. EtOM has been reported to exist as dissociated EtO^- and ion-paired EtOM when $[EtOM] < 0.1$ M.¹⁰ It is noted that the concentration of EtOM used in this study was lower than 0.1 M. Thus, substrates **5a** and **5b** would react with the dissociated EtO^- and



Scheme 2. Reactions of **5a** or **5b** with the dissociated EtO^- and ion-paired EtOM.

ion-paired EtOM as shown in Scheme 2.

Eq. (1) can be derived on the basis of the reactions proposed in Scheme 2. Under pseudo-first-order kinetic conditions (*e.g.*, $[EtOM] \gg [5a \text{ or } 5b]$), k_{obsd} can be expressed as Eq. (2). Note that the dissociation constant $K_d = [EtO^-]_{eq} [M^+]_{eq} / [EtOM]_{eq}$ and $[EtO^-]_{eq} = [M^+]_{eq}$ at equilibrium. Thus, Eq. (2) can be converted to Eq. (3). The concentrations of $[EtO^-]_{eq}$ and $[EtOM]_{eq}$ can be calculated from the reported K_d value for EtOM and the initial concentration $[EtOM]$ using Eqs. (4) and (5).

$$\text{Rate} = k_{EtO^-} [EtO^-]_{eq} [5a \text{ or } 5b] + k_{EtOM} [EtOM]_{eq} [5a \text{ or } 5b] \quad (1)$$

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

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

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

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

Thus, one might expect that the plot of $k_{obsd} / [EtO^-]_{eq}$ vs. $[EtO^-]_{eq}$ would be linear if the reaction proceeds as proposed in Scheme 2. Besides, the intercept of the plots should be independent of the size of M^+ ion, since it represents the second-order rate constant for the reaction with the dissociated EtO^- (*i.e.*, k_{EtO^-}). In fact, the plots shown in Figure 4 are linear for the reactions of **5a** and **5b** with a common intercept, indicating that the derived equations based on Scheme 2 are correct. Accordingly, the k_{EtO^-} and k_{EtOM} / K_d values have been calculated from the intercept and the slope of the linear plots, respectively. The k_{EtOM} value can be calculated from the above k_{EtOM} / K_d values and the reported K_d value for EtOM (*e.g.*, $K_d = 60.2 \times 10^{-3}$, 11.1×10^{-3} , 9.80×10^{-3} and 4.72×10^{-3} M for EtOK/18C6, EtOK, EtONa and EtOLi, in turn).¹¹ In Table 1 are summarized the calculated k_{EtO^-} and k_{EtOM} values for the reactions of **5a** and **5b**.

As shown in Table 1, the second-order rate constant for the reaction of **5a** with the ion-paired EtOM (*i.e.*, k_{EtOM}) increases in the order EtOLi < EtONa < EtOK < EtOK/18C6. It is also noted that the ion-paired EtONa, EtOK and EtOK/18C6 are

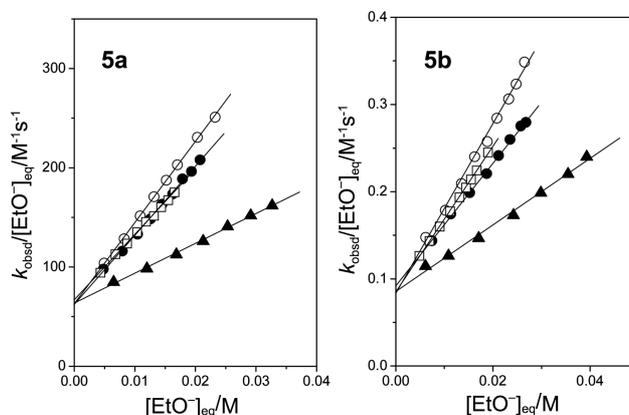


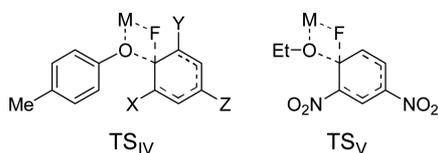
Figure 4. Plots of $k_{obsd} / [EtO^-]_{eq}$ vs $[EtO^-]_{eq}$ for the reactions of 1-fluoro-2,4-dinitrobenzene (**5a**) and 1-chloro-2,4-dinitrobenzene (**5b**) with EtOLi (\square), EtONa (\bullet), EtOK (\circ) and EtOK/18C6 (\blacktriangle) in anhydrous EtOH at 25.0 ± 0.1 °C. $[18C6]/[EtOK] = 2.0$.

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 1-Fluoro-2,4-dinitrobenzene (**5a**) and 1-Chloro-2,4-dinitrobenzene (**5b**) with EtOM in Anhydrous EtOH at 25.0 ± 0.1 °C

EtOM	5a		5b	
	$k_{\text{EtOM}}/\text{M}^{-1}\text{s}^{-1}$	$k_{\text{EtO}^-}/\text{M}^{-1}\text{s}^{-1}$	$k_{\text{EtOM}}/\text{M}^{-1}\text{s}^{-1}$	$k_{\text{EtO}^-}/\text{M}^{-1}\text{s}^{-1}$
EtOLi	30.6 ± 0.4	67.2 ± 1.1	0.0394 ± 0.0003	0.0847 ± 0.0010
EtONa	68.5 ± 1.2	61.5 ± 1.7	0.0693 ± 0.0011	0.0916 ± 0.0023
EtOK	91.0 ± 0.9	62.4 ± 1.3	0.109 ± 0.003	0.0800 ± 0.0050
EtOK/18C6	182 ± 4	63.2 ± 1.5	0.228 ± 0.008	0.0857 ± 0.0037

more reactive than the dissociated EtO⁻, while the ion-paired EtOLi is less reactive than the dissociated EtO⁻. This is consistent with the preceding suggestion that the reaction of **5a** is catalyzed by Na⁺, K⁺ and 18C6-crowned K⁺ ions but is inhibited by Li⁺ ion. A similar result is shown for the corresponding reaction of **5b**, although **5b** is significantly less reactive than **5a**. The reactivity order will be discussed in the following section.

Origin of M⁺ Ion Catalysis. M⁺ ion could catalyze the current S_NAr reaction by increasing the nucleofugality of the leaving group (*i.e.*, F⁻ or Cl⁻ ion) or by enhancing the electrophilicity of the reaction center. Recently, Jones *et al.* have carried out computational investigations on the S_NAr reaction of activated fluorobenzenes with alkali-metal phenoxides.¹² The results their DFT calculations have shown that the presence of alkali-metal ion does not increase the rate of reaction but plays an important role through TS_{IV}, in which M⁺ ion facilitates expulsion of the leaving group.¹²

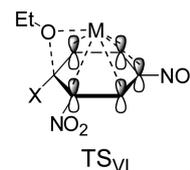


One might suggest a similar TS structure for the current reaction (*i.e.*, TS_v, in which M⁺ ion would increase the nucleofugality of the leaving group). It is apparent that enhanced nucleofugality would be effective only for reactions in which expulsion of the leaving group occurs in the RDS, but would be ineffective when expulsion of the leaving group occurs after the RDS. The current reaction is expected to proceed through a Meisenheimer complex, in which expulsion of the leaving group (*i.e.*, F⁻ or Cl⁻) occurs after the RDS. This is because EtO⁻ is significantly more basic and a poorer nucleofuge than F⁻ or Cl⁻. Furthermore, Table 1 shows that **5a** is over 700 times more reactive than **5b**, although F⁻ in **5a** is *ca.* 10 pK_a units more basic than Cl⁻ in **5b**. Apparently, this is possible only for reactions in which expulsion of the leaving group occurs after the RDS but is not possible if expulsion of the leaving group is involved in the RDS. Thus, one can conclude the current reaction proceeds through a stepwise mechanism in which expulsion of the leaving group occurs after the RDS. Accordingly, the increased nucleofugality through TS_v cannot be responsible for the M⁺ ion catalysis found in this study.

The above argument can be further supported by the order

of catalytic effect found in this study. It is apparent that the interaction between M⁺ ion and the F atom in **5a** (or the Cl atom in **5b**) would be stronger as the size of M⁺ ions decreases (or as the charge density increases). Thus, one might expect that the catalytic effect exerted by M⁺ ion would be in the order Li⁺ > Na⁺ > K⁺ > 18C6-crowned K⁺, if M⁺ ion catalyzes the current reaction by increasing the nucleofugality of the leaving group through TS_v. However, Table 1 shows that the reaction is inhibited by Li⁺ ion but is catalyzed by Na⁺, K⁺ and 18C6-complexed-K⁺ ions. This is not possible if the current reaction proceeds through TS_v.

A possibility that might explain the effect of the M⁺ ions is that the reaction of **5a** and **5b** proceeds through a TS structure similar to TS_{VI}, in which M⁺ ion increases the electrophilicity of the reaction center through the π-complex.¹³ Since the π-electrons in the benzene ring is highly polarizable, the π-complex would be more stabilized as the size of M⁺ ion increases. Because the polarizability of M⁺ ion increases with increasing its size. This idea can be further supported by the experimental result that the catalytic effect increases with increasing the size of the alkali-metal ions.



Conclusions

The kinetic study on the S_NAr reactions of **5a** and **5b** with EtOM has led us to conclude the following: (1) Plots of k_{obsd} vs. [EtOM] curve upward or downward depending on the nature of M⁺ ions, indicating that M⁺ ion behaves as a catalyst or an inhibitor. (2) Dissection of k_{obsd} into k_{EtO^-} and k_{EtOM} has revealed that the reactivity increases in the order $k_{\text{EtOLi}} < k_{\text{EtO}^-} < k_{\text{EtONa}} < k_{\text{EtOK}} < k_{\text{EtOK}/18\text{C}6}$ for the reaction of **5a** and $k_{\text{EtOLi}} < k_{\text{EtONa}} < k_{\text{EtO}^-} < k_{\text{EtOK}} < k_{\text{EtOK}/18\text{C}6}$ for the reaction of **5b**. (3) Substrate **5a** is over 700 times more reactive than **5b**, although the F⁻ in **5a** is *ca.* 10 pK_a units more basic than the Cl⁻ in **5b**. This indicates that expulsion of the leaving group occurs after the RDS. (4) The rate of the leaving-group expulsion could be accelerated by M⁺ ion through TS_v. However, the enhanced nucleofugality would be ineffective for the current reaction, since expulsion of the leaving group occurs after the RDS. (5) M⁺ ion catalyzes the

reaction by increasing the electrophilicity of the reaction center through a π -complex as illustrated in TS_{VI}.

Experimental Section

Materials. 1-X-2,4-dinitrobenzenes **5a** (X=F) and **5b** (X=Cl) are commercially available. The solutions of EtOM were prepared by dissolving the respective alkali metal in anhydrous ethanol under N₂ and stored in the refrigerator. The concentrations of EtOM were determined by titration with standard HCl solution. 18-Crown-6-ether was recrystallized from acetonitrile and dried over P₂O₅ in vacuo. The anhydrous ethanol used was further dried over magnesium and distilled under N₂. Other chemicals were of the highest quality available.

Kinetics. Kinetic study was performed using a stopped-flow spectrophotometer for the reaction of **5a** and a UV-vis spectrophotometer for that of **5b** equipped with a constant-temperature circulating bath. The reactions were followed by monitoring the appearance of 1-ethoxy-2,4-dinitrobenzene at 295 nm. Pseudo-first-order conditions with the EtOM concentration at least 20 times greater than substrate concentration were used. Generally, reactions were followed for 9-10 half-lives and k_{obsd} were calculated from the slope of the linear plots of $\ln(A_{\infty} - A_t)$ vs. t .

Product Analysis. 1-Ethoxy-2,4-dinitrobenzene was formed quantitatively and identified as one of the products by comparison of the UV-vis spectra under the same kinetic conditions.

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