The Effect of Alkali Metal Ions on Nucleophilic Substitution Reactions of *p*- and *m*-Nitrophenyl 2-Thiophenenates with Alkali Metal Ethoxides in Absolute Ethanol

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Received May 21, 1996

Rate constants have been measured spectrophotometrically for the reactions of *p*- and *m*-nitrophenyl 2-thiophenecarboxylate (**5a** and **5b**, respectively) with alkali metal ethoxides (EtO⁻M⁺) in absolute ethanol at 25.0 ± 0.1 ℃. The reactivity of EtO⁻M⁺ exhibits dependence on the size of alkali metal ions, *i.e.* the reactivity of EtO⁻M⁺ toward **5a** decreases in the order EtO⁻K⁺≥EtO⁻Na⁺>EtO⁻Li⁺>EtO⁻, while the one toward **5b** does in the order EtO⁻Na⁺≥EtO⁻K⁺ >EtO⁻Li⁺>EtO⁻. This result indicates that ion paired EtO⁻M⁺ is more reactive than dissociated EtO⁻, and alkali metal ions form complexes with the substrate more strongly at the transition state than at the ground state. The catalytic effect shown by alkali metal ions appears to be less significant in the reaction of **5** than in the corresponding reaction of **4**, indicating that complexation of alkali metal ions with **5** is not as strong as the one with **4**.

Introduction

Studies of metal ion effects on nucleophilic substitution reactions have been intensively performed due to their important roles in chemistry and biochemistry.[1~6] One of the important roles has been suggested to be electrophilic (Lewis acid) catalyst in acyl- or phosphoryl-transfer reactions.[1~3] Therefore, most studies have been focused on polyvalent metal ions,[1~3] and effects of alkali metal ions on the reactions of carboxylic or phosphoric acid derivatives have not attracted a great deal of attention until recently.[4~6]

Buncel and his coworkers have reported that alkali metal ions show catalytic effect in the reaction of a phosphinate ester (**1**) with alkali metal ethoxides (EtO⁻M⁺) in absolute ethanol.[4a,b] The catalytic effect shown by alkali metal ions was reported to decrease with increasing the ionic radius of the cation (*e.g.* Li⁺>Na⁺>K⁺>K⁺ with excess 18-crown-6 ether).[4a,b] Interestingly, a contrasting result was reported for the corresponding reaction of a sulfonate ester (**2**) with EtO⁻M⁺, *i.e.* Li⁺ ion exhibits inhibitory effect, while K⁺ and Na⁺ ions show catalytic effect.[4c,d] We have recently reported that alkali metal ions influence little effect to the reaction of a carboxylate ester (**3**) with EtO⁻M⁺ in absolute ethanol[5b] but significant effect to the corresponding reaction of **4**, *i.e.* alkali metal ions exhibit catalytic effect in the order K⁺> Na⁺>Li⁺>K⁺-18C6.[5d] These results clearly implies that the effect of alkali metal ions on acyl-transfer reactions appears to be dependent on the size of alkali metal ions as well as the nature of the substrates (*e.g.* phosphinate, sulfonate and carboxylate esters).

|		
1	**2**	**3**
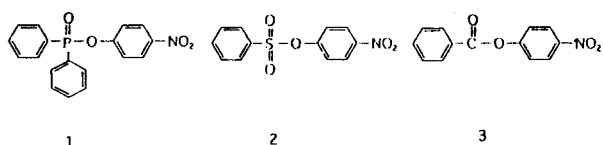
Although many theories have been suggested to account for the catalytic or inhibitory effects shown by alkali metal ions, their exact roles are not fully understood. We have

expanded our study to the reaction of **5** with EtO⁻M⁺ in absolute ethanol in order to investigate the role of alkali metal ions in acyl-transfer reactions as shown in Scheme 1. The replacement of an oxygen atom by a sulfur atom in the heterocyclic moiety of the substrate would not cause a significant change in structure of the substrate. However, one can expect a remarkable change in its complexing ability with alkali metal ions due to significant difference in polarizability between O and S. Comparison of the data obtained from the reactions of **4** and **5** would be considered to give us a useful information on understanding of alkali metal ion effects.

Experimental

Material. The aryl 2-thiophenecarboxylates (**5a** and **5b**) were easily prepared by the literature procedures[7] using 2-thiophenecarboxyl chloride and *p*- or *m*-nitrophenol in the presence of triethylamine in dried ether. Their purity was checked by means of melting points and spectral data such as IR and ¹H NMR characteristics. Absolute ethanol was prepared by the method described in the literature[7] under a nitrogen atmosphere. Solutions of alkali metal ethoxides were prepared by dissolving the corresponding alkali metal in absolute ethanol under a nitrogen atmosphere. The con-
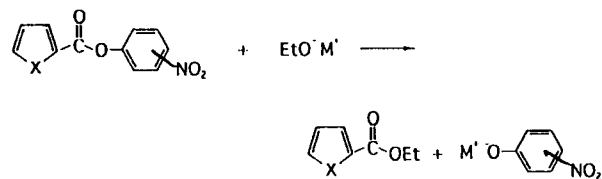
X = O, 4a : p-nitrophenyl 2-furoate

4b : m-nitrophenyl 2-furoate

X = S, 5a : p-nitrophenyl 2-thiophenecarboxylate

5b : m-nitrophenyl 2-thiophenecarboxylate

centration of the stock solutions of EtO^-M^+ was titrated against potassium hydrogen phthalate.

Kinetics. The kinetic studies were performed with a Hitachi U-2000 Model UV-VIS spectrophotometer equipped with a Neslab RTE-110 Model constant temperature circulating bath to keep the temperature in the UV cell at 25.0 ± 0.1 ℃. The reactions were followed by monitoring the appearance of the leaving *p*- or *m*-nitrophenoxide at 400 nm. All the reactions were carried out under *pseudo*-first-order conditions in which the concentration of alkali metal ethoxides was usually 20 times greater than that of the substrates. Other detailed kinetic methods are similar to the one described previously.[8]

Results

All the reactions studied here obeyed *pseudo*-first-order kinetics up to over 90% of the total reaction. *Pseudo*-first-order rate constants (k_{obs}) were obtained from the equation, $\ln (A_\infty - A_t) = -k_{obs} \cdot t + c$. The error in any particular measured rate constant is estimated to be less than 3%.

As shown in Figure 1, the reactivity of EtO^-K^+ decreases upon addition of 18-crown-6 ether (18-C-6) up to near 3 equivalents of EtO^-K^+, and levels off beyond that point. This implies that 4 equivalents of 18-C-6 is sufficient to complex K^+ ion completely as a coronate. Therefore, 4 equivalents of 18-C-6 were used to eliminate K^+ ion effect on reaction rates and to get second-order rate constant for free ethoxide ion. In Table 1 and 2 are summarized *pseudo*-first order rate constants for the reactions of EtO^-M^+ with **5a** and **5b**, respectively, in absolute ethanol at 25.0 ± 0.1 ℃. The data are demonstrated graphically in Figures 2 and 3. The results of ion pairing treatment are summarized in Table 3 and demonstrated graphically in Figures 4 and 5.
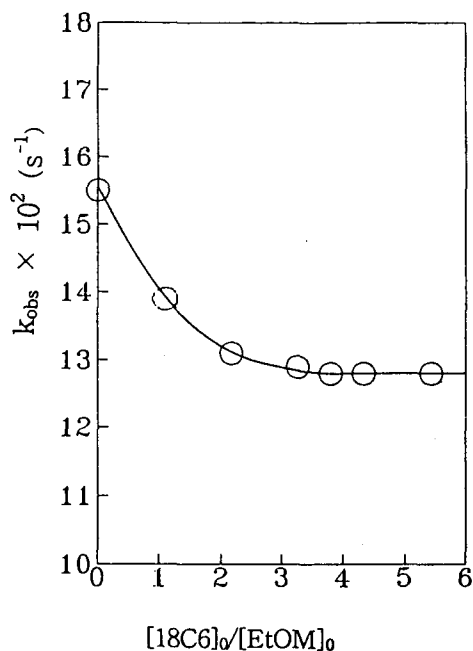

Figure 1. Effect of added 18C6 on the reaction of *p*-nitrophenyl 2-thiophenecarboxylate (**5a**) with EtOK in EtOH at 25.0 ℃. $([EtOK]_0 = 15.3 \times 10^{-3}$ M).

Discussion

The Effect of Alkali Metal Ions on Reaction Rate.

As shown in Figure 2, the reactivity of ethoxide toward **5a** is dependent on its counter cation ions, *i.e.* EtO^-K^+ and EtO^-Na^+ exhibit upward curvatures while EtO^-Li^+ and EtO^-K^+ with excess 18-C-6 show linear lines in the plots of k_{obs} *vs* concentration of EtO^-M^+. The reactivity of EtO^-K^+ and EtO^-Na^+ is similar each other but larger than that of EtO^-Li^+ and EtO^-K^+ with excess 18-C-6. Similar results can be seen in Figure 3 for the corresponding reactions of **5b**. However, the effect of alkali metal ions on reaction rates appears to be greater for the reaction of **5b** than that of **5a**, based on the degree of the upward curvatures in Figures 2 and 3.

The upward curvatures obtained in Figures 2 and 3 clearly suggest that alkali metal ions behave as a catalyst in the present system. The finding of catalytic effect shown by alkali metal ions in the present system is interesting, since such effect has been reported to be negligible in aryl acetates or benzoates system.[5c] A more in-depth analysis is required to explain the present results. Possible reasons how alkali metal ions catalyze the present acyl-transfer reaction are discussed below.

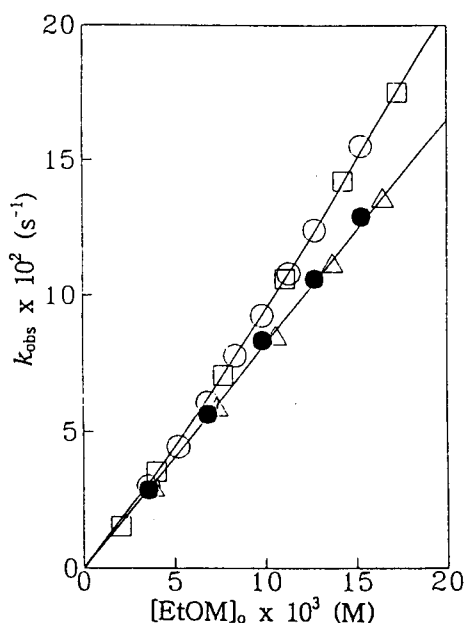### Dissection of Nucleophilicity of Free and Ion Paired Ethoxides.

Alkali methal ethoxides have been sugge-

Table 1. Kientic data for the reaction of **5a** with alkali metal ethoxides in the absence and presence of excess complexing agent (18C6) in EtOH at 25.0 ± 0.1 ℃
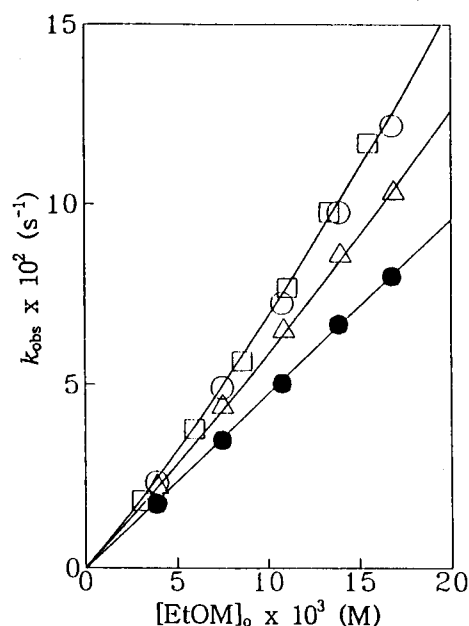
EtO^-M^+	$[EtO^-M^+]_0 \times 10^3$ (M)	$k_{obs} \times 10^2$ (s^{-1})
EtO^-Li^+	3.81	2.98
	7.34	5.93
	10.6	8.52
	13.7	11.2
	16.5	13.6
EtO^-Na^+	2.04	1.52
	3.99	3.53
	7.69	7.06
	11.1	10.6
	14.3	14.2
	17.3	17.5
EtO^-K^+	3.54	3.00
	5.20	4.45
	6.81	6.07
	8.36	7.78
	9.85	9.25
	11.3	10.8
	12.7	12.4
	15.3	15.5
$EtO^-K^+ + 18C6$	3.54	2.86
$([18C6]/[EtO^-K^+]_0 = 4)$	6.81	5.64
	9.85	8.33
	12.7	10.6
	15.3	12.9

Table 2. Kinetic data for the reaction of **5b** with alkali metal ethoxides in the absence and presence of excess complexing agent (18C6) in EtOH at 25.0±0.1 ℃
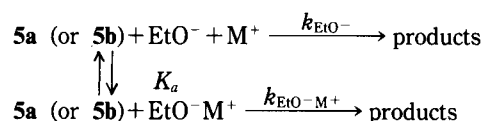
EtO⁻M⁺	[EtO⁻M⁺]×10³ (M)	$k_{obs}\times10^2$ (s⁻¹)
EtO⁻Li⁺	3.90	2.99
	7.51	4.48
	10.9	6.58
	14.0	8.68
	16.9	10.4
EtO⁻Na⁺	3.08	1.83
	5.94	3.78
	8.59	5.65
	11.1	7.83
	13.4	9.78
	15.5	11.7
EtO⁻K⁺	3.88	2.32
	7.48	4.92
	10.8	7.26
	13.9	9.77
	16.8	12.2
EtO⁻K⁺+18C6	3.88	1.75
([18C6]/[EtO⁻K⁺]₀=4)	7.48	3.48
	10.8	5.03
	13.9	6.67
	16.8	8.02

Figure 3. Kinetic data for the reaction of *m*-nitrophenyl 2-thiophenecarboxylate (**5b**) with EtOLi (△), EtONa (□), EtOK (○), and EtOK in the presence of excess 18C6 (●) in EtOH at 25.0 ℃.

Figure 2. Kinetic data for the reaction of *p*-nitrophenyl 2-thiophenecarboxylate (**5a**) with EtOLi (△), EtONa (□), EtOK (○), and EtOK in the presence of excess 18C6 (●) in EtOH at 25.0 ℃.

sted to exist as dissociated free ethoxide (EtO⁻) and ion paired alkali metal ethoxides (EtO⁻M⁺) in absolute ethanol, when the concentration is relatively low (<0.1 M).[9] Dimers

and other aggregates were also reported to exist in higher concentration.[9] Since the concentration of EtO⁻M⁺ used in the present study is far below 0.1 M, one might consider that the major species in the reaction mixture would be free ethoxide (EtO⁻) and ion paired one (EtO⁻M⁺). Therefore, the present substrates (**5a** and **5b**) would be considered to react competitively with EtO⁻ and EtO⁻M⁺, as shown in Scheme 2.

$$\textbf{5a } (or \textbf{ 5b}) + EtO^- + M^+ \xrightarrow{\quad k_{EtO^-}\quad} products$$

$$\uparrow\downarrow\ K_a$$

$$\textbf{5a } (or \textbf{ 5b}) + EtO^-M^+ \xrightarrow{\quad k_{EtO^-M^+}\quad} products$$

The rate equation and observed *pseudo*-first-order rate constant (k_{obs}) can be expressed as in equations (1) and (2), in which [5], [EtO⁻] and [EtO⁻M⁺] represent the concentration of **5a** (or **5b**), free ethoxide and ion paired alkali metal ethoxide at the equilibrium, respectively. Similarly, k_{EtO^-} and $k_{EtO^-M^+}$ stand for the second-order rate constant for the reaction of **5a** (or **5b**) with free ethoxide and ion paired ethoxide, respectively.

$$Rate = k_{EtO^-}\cdot[EtO^-]\,[5] + k_{EtO^-M^+}\cdot[EtO^-M^+]\,[5] \tag{1}$$

$$k_{obs} = k_{EtO^-}\cdot[EtO^-] + k_{EtO^-M^+}\cdot[EtO^-M^+] \tag{2}$$

Since K_a, association constant of alkali metal ethoxides shown in Scheme 2, can be expressed as in equation (3), equation (2) can be reduced as in equation (4).

$$K_a = \frac{[EtO^-M^+]}{[EtO^-]\,[M^+]} = \frac{[EtO^-M^+]}{[EtO^-]^2} \tag{3}$$

$$\frac{k_{obs}}{[EtO^-]} = k_{EtO^-} + K_a\,k_{EtO^-M^+}\,[EtO^-] \tag{4}$$

The plot of $k_{obs}/[EtO^-]$ *vs* [EtO⁻] should give a linear

line with slope K_a $k_{EtO^--M^+}$ and intercept k_{EtO^-}. In fact, as evident from Figures 4 and 5, the plots are linear for all the alkali metal ethoxides. Since the K_a values in absolute ethanol at 25 ℃ are available in literature,[9] k_{EtO^-} and $k_{EtO^--M^+}$ values for a given EtO^-M^+ system can be calculated from the intercept and slope of each plot. The calculated values of k_{EtO^-} and $k_{EtO^--M^+}$ are summarized in Table 3 together with the data for the corresponding reactions of **4a** and **4b**
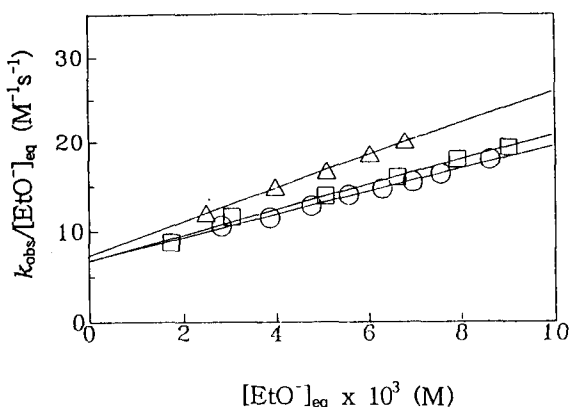

Figure 4. Plots illustrating dissection of observed rates *via* Eq. 4 into rate constants due to dissociated and ion-paired ethoxide for the reaction of *p*-nitrophenyl 2-thiophenecarboxylate (**5a**) with EtOLi (△), EtONa (□), and EtOK (○) in EtOH at 25.0 ℃.
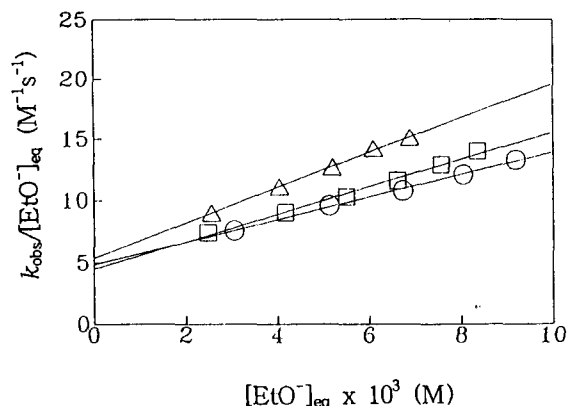

Figure 5. Plots illustrating dissection of observed rates *via* Eq. 4 into rate constants due to dissociated and ion-paired ethoxide for the reaction of *m*-nitrophenyl 2-thiophenecarboxylate (**5b**) with EtOLi (△), EtONa (□), and EtOK (○) in EtOH at 25.0 ℃.

for a comparison purpose. The k_{EtO^-} values obtained in this way are practically same as the one obtained from the slope of the plots of k_{obs} *vs* $[EtO^-M^+]$ with excess 18-C-6.

The calculated second-order rate constants appear to be consistent with the kinetic results, *i.e.* the second-order rate constant for the reaction of **5a** increases in the order k_{EtO^-} $\leq k_{EtO^--Li^+} < k_{EtO^--Na^+} \leq k_{EtO^--K^+}$. Similar results are obtained for the corresponding reaction of **5b**. Therefore, the present results clearly imply that ion paired alkali metal ethoxides are more reactive than free ethoxide ion toward **5a** and **5b** in absolute ethanol.

As shown in Table 3, k_{EtO^-} values for the reactions of **5** appear to be about 3-4 times smaller than those of **4**. Similarly, $k_{EtO^--M^+}$ values for the reactions of **5** are 4-8 times smaller than those of **4**. The replacement of the oxygen atom in the heterocyclic acyl moiety of the substrate by a sulfur atom (**4→5**) would cause a decrease in the electrophilicity of the carbonyl carbon of the acyl moiety, since S is less electronegative than O. In fact, thiophene-2-carboxylic acid has been reported to be less acidic than its oxygen analogue, furan-2-carboxylic acid.[10] Therefore, one might attribute the difference in reactivity between **4** and **5** to the difference in the acidity of furan-2-carboxylic acid and thiophene-2-carboxylic acid.
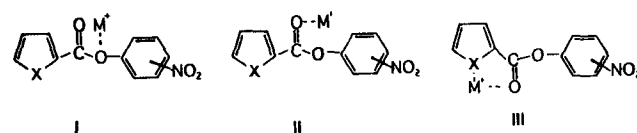
Role of Alkali Metal Ions. Complexation between alkali metal ion and the oxygen atom of the leaving phenoxide as in the structure I has once been suggested to be responsible for the catalytic effect shown by alkali metal ions,[4] since such a complexation would increase nucleofugality of the leaving group. However, this effect is considered to be effective only when the leaving group departure is involved in the rate-determining step, (*e.g.* in the case of a concerted or step-wise mechanism in which the leaving group departure occurs in the rate-determining step). Since the present type acyl-transfer reaction has been reported to proceed *via* a rate-determining formation of a tetrahedral intermediate followed by a fast leaving group departure,[8,11] complex I would contribute little to the catalytic effect shown by alkali metal ions in the present system.

The complexation of alkali metal ions with the carbonyl oxygen as in the structure II would accelerate the reaction

Table 3. Second-order rate constants for various ethoxide species from ion pairing treatment of kinetic data for the reactions of **5a** and **5b** with EtO^-M^+ in $EtOH^a$ at 25.0±0.1 ℃

EtO^-M^+	*p*-nitrophenyl 2-thiophenecarboxylate (**5a**)		*m*-nitrophenyl 2-thiophenecarboxylate (**5b**)	
	k_{EtO^-} $(M^{-1}s^{-1})$	$k_{EtO^--M^+}$ $(M^{-1}s^{-1})$	k_{EtO^-} $(M^{-1}s^{-1})$	$k_{EtO^--M^+}$ $(M^{-1}s^{-1})$
EtO^-Li^+	7.34±0.20 (24.2±0.1)	8.83±0.19(36.2±0.2)	5.39±0.15 (19.0±0.3)	6.70±0.14 (25.6±0.5)
EtO^-Na^+	6.76±0.36 (23.7±1.5)	13.8±0.6 (83.1±5.7)	4.50±0.31 (17.7±1.1)	10.8±0.5 (60.8±4.4)
EtO^-K^+	6.75±0.21 (24.9±0.4)	14.2±0.4 (106±2)	4.87±0.19 (17.5±0.7)	10.0±0.3 (79.3±2.9)
$EtO^-K^+ + 18C6$	8.51±0.07 (27.0±0.2)		4.87±0.05 (15.6±0.4)	

a The data in parentheses are obtained from ref. 5d for the corresponding reactions of **4a** and **4b**, respectively.

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rate by increasing electrophilicity of the carbonyl carbon. The substrate containing $P=O$ or $S=O$ bonds would be considered to form stronger complexation with alkali metal ions than the one containing $C=O$ bond, since the charge polarization of $P=O$ and $S=O$ bonds is more significant than that of $C=O$ bond due to poor orbital overlapping between a 2p orbital of O and a 3p orbital of P or S. This is consistent with the previous reports that the effect of alkali metal ions is significant for the reactions of 1 and 2, but nearly absent for the corresponding reaction of 3.[5b]

Unlike 3, the present substrates (5a and 5b) would form a 5-membered ring chelation as in the structure III. Such a chelation would be possible both in the ground state (GS) and transition state (TS), and stabilize the GS and TS. The fact that alkali metal ions accelerate the reaction rates indicates that chelation III is more significant for the TS than for the GS in the present system. This is quite reasonable, since the charge polarization of the $C=O$ bond in the TS would be more significant than the one in the GS. This argument is also consistent with the fact that alkali metal ion effect is larger for the reaction of 5b than 5a, since the negative charge density developing in the carbonyl oxygen at the TS of the rate-determining step would be greater in 5b than in 5a, based on the magnitude of the Brönsted β values.[11a]

The catalytic effect shown by alkali metal ions for the reaction of 1 has been reported to increase with increasing the charge density of the metal ion (*e.g.* $Li^+>Na^+>K^+>K^+$-18C6).[4a,b] Buncel *et al.* explained the order of metal ion effect in terms of charge density, since the interaction between metal ion and oxygen of the $P=O$ bond in 1 would become greater as the positive charge density of the metal ion increases.[4a,b] A similar explanation was given by Suh.[3c] However, the order of alkali metal ion effect in the present system is quite different from the one obtained from the corresponding reaction of 1, *i.e.* $K^+\geq Na^+>Li^+>K^+$-18C6 for the reaction of 5a and $Na^+\geq K^+>Li^+>K^+$-18C6 for that of 5b. Therefore, it is clear that the argument concerning charge density of metal ion cannot be applied to the present system.

Unlike substrates 1, 2 and 3, substrates 4 and 5 can form chelation III, since the two oxygen atoms in 4 or one oxygen and one sulfur atom in 5 can donate electron pairs to the alkali metal ions. In order to form a strong chelation, the size of alkali metal ion is considered to play an important role, rather than the charge density of the alkali metal ions. The decreasing catalytic effect with increasing charge density of the metal ions in the reactions of 4 and 5 accounts for this argument nicely.

The fact that metal ion effect is smaller for the reaction of 5 than that of 4 implies that chelation III in 5 would not be as strong as the one in 4. One might attribute this to the hard and soft acids and bases principle,[12] since the interaction of the hard alkali metal ion with the soft sulfur atom in 5 would not be as strong as the one with the hard oxygen atom in 4. However, one cannot exclude a possibility of a conformational change as shown below (IV $\rightleftharpoons$ V) upon the replacement of oxygen atom by sulfur atom (4→5), since the conformer IV cannot form a chelation III. More systematic studies are underway for a complete interpretation of the effect of alkali metal ion on the present acyl-transfer

reaction.

IV   V
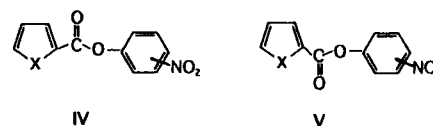
Conclusions

The present study has allowed us to conclude the following. (1) Ion paired alkali metal ethoxides are more reactive than dissociated ethoxide, and alkali metal ions behave as a catalyst in the reactions of 5 with EtO^-M^+ in absolute ethanol. (2) Their catalytic effects are larger in the reactions of 5b than in those of 5a. (3) The effect of metal ion is much smaller in the reactions of 5 than in those of 4, indicating that chelation III in 5 is not as strong as the one in 4.

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Synthesis and Characterization of Bis(N,N-dimethyl-2-aminomethylthiophenium)Tetrahalocuprate(II)

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Received May 31, 1996

Bis(N,N-dimethyl-2-aminomethylthiophenium)tetrahalocuprate(II) salt, (dmamtH)$_2$CuCl$_4$ and (dmamtH)$_2$CuBr$_4$ were prepared and characterized by spectroscopic (IR, UV-Vis, EPR, XPS), electrochemical method, and magnetic susceptibility measurement. The experimental results reveal that the compounds have pseudotetrahedral symmetry around copper(II) site due to the steric hinderance of the bulky 2-(dimethylaminomethyl)thiophene in the complex. The N-H···Cl type hydrogen bonding is expected in (dmamtH)$_2$CuCl$_4$ from the XPS and IR data. Magnetic susceptibility data show that both of the compounds follow Curie-Weiss law in the range of 77-300 K with negative Weiss constant exhibiting antiferromagnetic interaction between copper(II) ions in solid state.

Introduction

The 4-coordinated tetrahalocuprate(II) ions have been found to possess a variety of geometries from square planar to near-tetrahedral symmetry.[1~4] This stereochemistry of tetrahalocuprate(II) ions is strongly influenced by the nature of the countercation. When the cation is relatively large, the square planar CuX$_4^{2-}$ units are distorted to pseudotetrahedral symmetry due to the steric hinderance of the cation. The final structure is determined by a balance between the ligand field stabilization energy of the square planar geometry (so called the Jahn-Teller effect) and the destabilization effect of the ligand-ligand repulsions. It is interesting that spectroscopic and magnetic properties of tetrahalocuprate(II) ion with pseudotetrahedral structure are similar to those of type(I) Cu(II) ion involved in the blue copper protein. Therefore the pseudotetrahedral tetrahalocuprate(II) complexes have been suggested as simple model compounds of the copper protein,[5] and physical and chemical studies about the coordination environment have been undertaken.[6]

Recently we reported that (dmamt)CuCl$_2$ compound has pseudotetrahedral symmetry around copper(II) site due to the steric hinderance of the bulky 2-(dimethylaminomethyl) thiophene.[7] Moreover, the investigation of (dmamtH)$_2$CoCl$_4$ indicates that a N-H···Cl type hydrogen bonding exists in (dmamtH)$_2$CoCl$_4$ by the single crystal X-ray analysis.[8]

In this study, we prepared a series of tetrahedrally distorted copper complexes with the tetrachlorocuprate(II) and tetrabromocuprate(II) of protonated 2-(dimethylaminomethyl) thiophene (dmamtH$^+$). We examined whether the hydrogen

bonding is present in (dmamtH)$_2$CuCl$_4$ as in (dmamtH)$_2$CoCl$_4$ and the influence of hydrogen bonding on the geometry around Cu(II) site. The prepared complexes were characterized by spectroscopic (IR, UV-Vis., EPR, XPS), electrochemical method, and magnetic susceptibility measurement.

Experimental

All chemicals were of the best available reagent or spectroscopic grades. The (dmamtH)$_2$CuCl$_4$ was prepared by reaction of stoichiometric quantities of 2-(dimethylaminomethyl) thiophene·HCl salt and anhydrous copper(II) chloride. 2-(Dimethylaminomethyl)thiophene·HCl salt was prepared by adding an excess of concentrated hydrochloric acid into 2-(dimethylaminomethyl)thiophene (6 mmol) in 20 mL mixture solvent of ethanol/triethylorthoformate (5 : 1). Copper(II) chloride (3 mmol) was dissolved in 10 mL of the same solvent. The solutions were mixed and heated with stirring for several hours and allowed to cool slowly in ice bath. The precipitates were isolated by filtration and rinsed with ethanol. The (dmamtH)$_2$CuBr$_4$ was also prepared from the similar method using anhydrous copper(II) bromide.

Anal. Calcd. for (dmamtH)$_2$CuCl$_4$, green, C$_{14}$H$_{24}$N$_2$S$_2$CuCl$_4$: C, 34.32; H, 4.93; N, 5.72. Found: C, 33.42; H, 4.81; N, 5.43. Anal. Calcd. for (dmamtH)$_2$CuBr$_4$, black, C$_{14}$H$_{24}$N$_2$S$_2$CuBr$_4$: C, 25.18; H, 3.60; N, 4.20. Found: C, 24.93; H, 3.73; N, 4.40. The C, H, N analytical data were obtained for the prepared complexes by using a Carlo Erba Instruments E. A. 1108 Elemental Analyzer in the Korea Basic Science Center (Seoul Branch).