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The Effect of Alkali Metal Ions on Nucleophilic Substitution Reactions of Aryl 2-Furoates with Alkali Metal Ethoxides in Ethanol

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Rate constants have been measured spectrophotometrically for the nucleophilic substitution reactions of *p*- and *m*-nitrophenyl 2-furoates (**4** and **5**, respectively) with alkali metal ethoxides ($\text{EtO}^- \text{M}^+$) in absolute ethanol at 25°C. The reactivity of $\text{EtO}^- \text{M}^+$ toward **4** is in the order $\text{EtO}^- \text{K}^+ > \text{EtO}^- \text{Na}^+ > \text{EtO}^- \text{Li}^+ > \text{EtO}^- \text{K}^+ + 18\text{-crown-6 ether}$. This is further confirmed by an ion pairing treatment method. The present result indicates that (1) ion paired $\text{EtO}^- \text{M}^+$ is more reactive than dissociated EtO^- ; (2) the alkali metal ions (K^+ , Na^+ , Li^+) behave as a catalyst; (3) the catalytic effect increases with increasing the size of the metal ion. A similar result has been obtained for the reaction of **5**, however, the catalytic effects shown by the metal ions are more significant in the reaction of **5** than in that of **4**.

Introduction

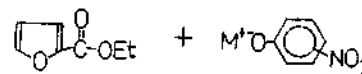
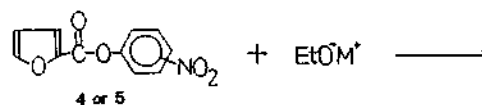
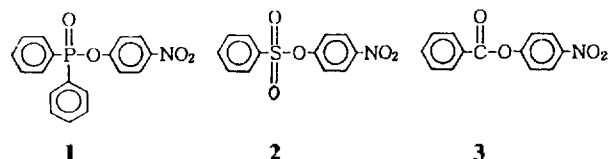
The effect of metal ions on acyl-transfer reactions has been intensively studied due to their important roles in biological processes.¹⁻³ However, most investigations have been focused on divalent metal ions such as Mg^{2+} , Zn^{2+} , Cu^{2+} , ... etc.,^{4,5} and studies of alkali metal ions have been initiated only recently.⁶⁻⁹

Buncel and his coworkers found significant effect of alkali metal ions on the reactions of alkali metal ethoxides ($\text{EtO}^- \text{M}^+$) with *p*-nitrophenyl diphenyl phosphinate (**1**) and with *p*-nitrophenyl benzenesulfonate (**2**) in absolute ethanol.^{6,7} In the reaction of the phosphinate ester (**1**) alkali metal ions behave as a catalyst, and the catalytic effect increases with increasing the charge density of the metal ion (e.g., $\text{Li}^+ > \text{Na}^+ > \text{K}^+$).⁶ On the contrary, Li^+ ion exhibits inhibitory effect while K^+ ion shows largest catalytic effect in the reaction of the sulfonate ester (**2**).⁷ Recently, we have found that the alkali metal ions exhibit inhibitory effect on the reaction of the phosphinate ester (**1**) with alkali metal phenoxides ($\text{ArO}^- \text{M}^+$),⁸ but no effect on the reaction of a carboxylic ester (**3**) with $\text{EtO}^- \text{M}^+$ in absolute ethanol.⁹ In this way, the effect of alkali metal ions appears to be significantly dependent on the type of substrates and nucleophiles as well as on the size of alkali metal ions.

Several explanations have been suggested to rationalize the catalytic or inhibitory effect of the alkali metal ions.⁶⁻⁸ However, their roles in the acyl-transfer reactions are not fully understood.^{10,11} In order to investigate the role of alkali metal ions in acyl-transfer reactions, we have chosen the following reaction system.

Experimental

Materials. The aryl 2-furoates (**4** and **5**) were prepared by a known procedure¹² using *p*- or *m*-nitrophenol and 2-furoyl chloride 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 literature¹² under a nitrogen atmosphere. Solutions of alkali metal ethoxides were prepared by dissolving the corresponding alkali metal in the absolute ethanol under a nitrogen



- 4** : *p*-nitrophenyl 2-furoate
5 : *m*-nitrophenyl 2-furoate
 M⁺: K⁺, Na⁺, Li⁺, K⁺ + 18C6

Scheme 1.

Table 1. Kinetic data for the reaction of **4** with alkali metal ethoxides in the presence and absence of excess complexing agents in EtOH at 25°C

| EtO ⁻ M ⁺ | [EtO ⁻ M ⁺] ₀ × 10 ³ (M) | k _{obs} × 10 ² (s ⁻¹) |
|--|---|---|
| EtO ⁻ Li ⁺ | 1.56 | 4.18 |
| | 2.32 | 6.34 |
| | 3.07 | 8.59 |
| | 3.81 | 10.8 |
| | 4.54 | 13.1 |
| | 5.25 | 15.2 |
| EtO ⁻ Na ⁺ | 1.64 | 5.11 |
| | 2.43 | 8.11 |
| | 3.22 | 11.9 |
| | 3.99 | 15.0 |
| | 4.76 | 18.6 |
| | EtO ⁻ K ⁺ | 1.45 |
| 2.16 | | 7.84 |
| 2.85 | | 11.2 |
| 3.54 | | 14.6 |
| 4.21 | | 18.2 |
| EtO ⁻ K ⁺ + 18C6 ([18C6]/[EtO ⁻ K ⁺] ₀ = 4) | | 0.777 |
| | 1.50 | 3.96 |
| | 2.17 | 5.90 |
| | 2.79 | 7.62 |
| | 3.37 | 9.07 |
| | 6.08 | 16.3 |

atmosphere. The concentrations of the stock solutions of EtO⁻M⁺ were titrated against potassium hydrogen phthalate.

Kinetics. The kinetic study was 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°C. Reaction rates were measured by following absorbance changes due to the release of *p*- or *m*-nitrophenoxide ion. All reactions were carried out under pseudo-first-order conditions with the concentration of EtO⁻M⁺ in excess. Other detailed kinetic methods are similar to the one described previously.¹³

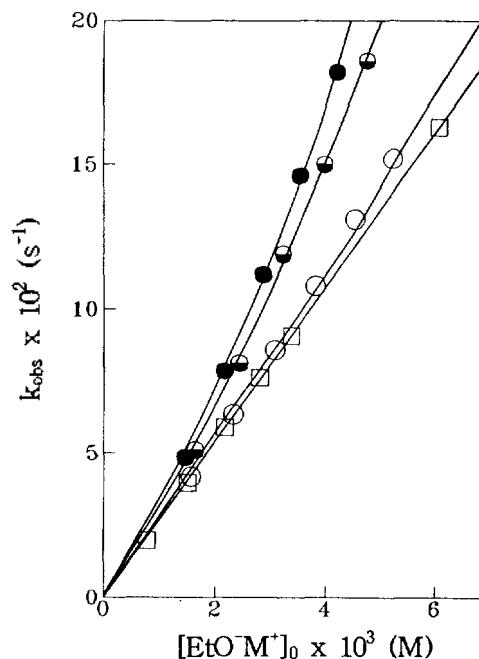
Results

Reactions of alkali metal ethoxides with **4** and **5** were studied spectrophotometrically in absolute ethanol at 25°C under pseudo-first-order conditions. Pseudo-first-order rate constants (k_{obs}) were obtained from the Guggenheim equation, ln(A_∞ - A_t) = -k_{obs}t + c, which were linear over 90% of total reaction. It is estimated that the error in any particular measured rate constant is less than 3%.

In Tables 1 and 2 are summarized pseudo-first-order rate constants for the reactions of EtO⁻M⁺ with **4** and **5**, respectively, in absolute ethanol at 25°C. The data are shown graphically in Figures 1 and 2. The results of ion pairing treatment are demonstrated in Table 3 and Figures 3 and 4.

Table 2. Kinetic data for the reaction of **5** with alkali metal ethoxides in the presence and absence of excess complexing agents in EtOH at 25°C

| EtO ⁻ M ⁺ | [EtO ⁻ M ⁺] ₀ × 10 ³ (M) | k _{obs} × 10 ² (s ⁻¹) |
|----------------------------------|--|---|
| EtO ⁻ Li ⁺ | 2.37 | 4.93 |
| | 3.14 | 6.58 |
| | 3.90 | 8.31 |
| | 4.64 | 9.97 |
| | 6.10 | 13.3 |
| | EtO ⁻ Na ⁺ | 1.88 |
| 2.49 | | 6.35 |
| 3.08 | | 8.07 |
| 3.67 | | 9.82 |
| 4.25 | | 12.2 |
| EtO ⁻ K ⁺ | | 1.59 |
| | 2.37 | 6.47 |
| | 3.13 | 9.02 |
| | 3.88 | 11.8 |
| | 4.62 | 15.1 |
| | EtO ⁻ K ⁺ + 18C6 ([18C6]/[EtO ⁻ K ⁺] ₀ = 4) | 2.16 |
| 2.79 | | 3.95 |
| 3.37 | | 4.75 |
| 3.91 | | 5.69 |
| 6.73 | | 10.2 |

**Figure 1.** Kinetic data for the reactions of **4** with EtO⁻Li⁺ (○), EtO⁻Na⁺ (●), EtO⁻K⁺ (●), and EtO⁻K⁺ in the presence of excess 18C6 (□) in EtOH at 25°C.

Discussion

As shown in Figure 1, the plot of k_{obs} versus concentration of EtO⁻M⁺ exhibits upward curvatures for the reaction of

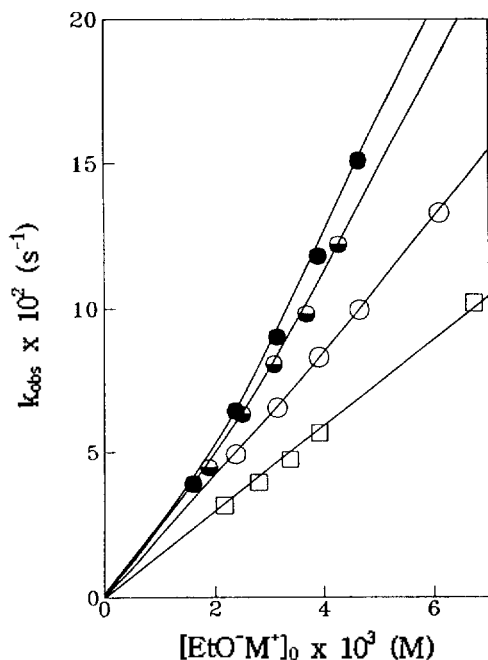


Figure 2. Kinetic data for the reactions of 5 with EtO^-Li^+ (○), EtO^-Na^+ (◐), EtO^-K^+ (●), and EtO^-K^+ in the presence of excess 18C6 (◻) in EtOH at 25°C.

p-nitrophenyl 2-furoate (4). However, a linearity is observed when 18-crown-6 ether, a complexing agent is present in excess, indicating that the alkali metal ions behave as catalysts in the present reaction system. The finding of catalytic effect of alkali metal ions is significant, since they were previously reported to show no catalytic effect in the reaction of carboxylic esters with EtO^-M^+ in absolute ethanol.⁹ Similar results were obtained for the reaction of *m*-nitrophenyl 2-furoate (5) as shown in Figure 2. However, the catalytic effect appears to be more significant in the reaction of 5 than 4, based on the degree of upward curvatures.

The catalytic effect observed in the present reaction system increases with increasing the size of alkali metal ion, *i.e.* $\text{Li}^+ < \text{Na}^+ < \text{K}^+$. The order of metal ion effect in the present system is opposite to the one observed in the phosphinate system (1)⁶ but similar to the one in the sulfonate system (2).⁷

Dissection of Nucleophilicity of Free and Ion Paired Ethoxides. Alkali metal ethoxides are known to exist as dissociated free ethoxide (EtO^-) and ion paired alkali metal ethoxides (EtO^-M^+) in absolute ethanol, when the concentration is relatively low ($< 0.1 \text{ M}$).¹⁴ Other associated

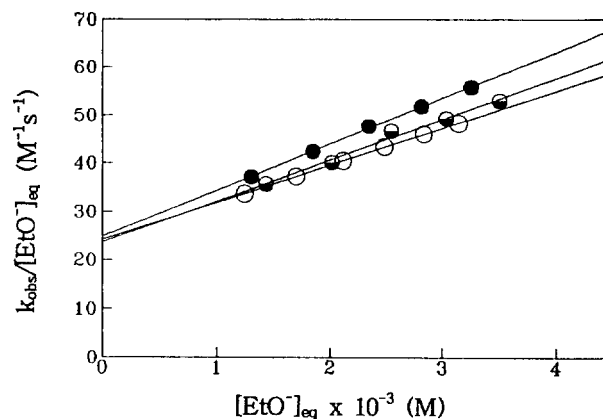


Figure 3. Plots illustrating dissection of observed rates into rate constants due to dissociated and ion paired ethoxide for the reactions of 4 with EtO^-Li^+ (○), EtO^-Na^+ (◐), and EtO^-K^+ (●), in EtOH at 25°C.

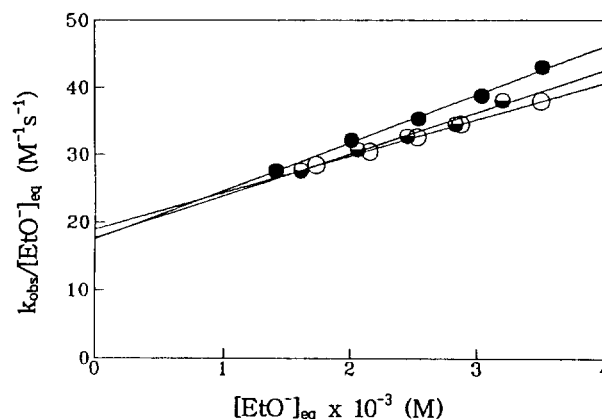


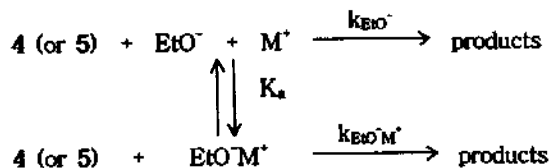
Figure 4. Plots illustrating dissection of observed rates into rate constants due to dissociated and ion paired ethoxide for the reactions of 5 with EtO^-Li^+ (○), EtO^-Na^+ (◐), and EtO^-K^+ (●), in EtOH at 25°C.

species such as dimers and aggregates were also reported to exist in higher concentration.¹⁴ Since the concentrations of EtO^-M^+ in the present system are much lower than 0.1 M, the main species in the solution would be free ethoxide EtO^- and ion paired ethoxide EtO^-M^+ . Therefore, the substrates (4, 5) would react competitively with free ethoxide EtO^- and with ion paired ethoxide EtO^-M^+ in the present system, as shown in Scheme 2.

Consequently, the rate law and the observed pseudo-first-

Table 3. Second-order rate constants (at 25°C) for various ethoxide species from ion pairing treatment of kinetic data for the reactions of 4 and 5 with EtO^-M^+ in EtOH

| EtO^-M^+ | <i>p</i> -nitrophenyl 2-furoate (4) | | <i>m</i> -nitrophenyl 2-furoate (5) | |
|--|---|---|---|---|
| | k_{EtO^-} ($\text{M}^{-1}\text{s}^{-1}$) | $k_{\text{EtO}^-\text{M}^+}$ ($\text{M}^{-1}\text{s}^{-1}$) | k_{EtO^-} ($\text{M}^{-1}\text{s}^{-1}$) | $k_{\text{EtO}^-\text{M}^+}$ ($\text{M}^{-1}\text{s}^{-1}$) |
| EtO^-Li^+ | 24.2 ± 0.1 | 36.2 ± 0.2 | 19.0 ± 0.3 | 25.6 ± 0.5 |
| EtO^-Na^+ | 23.7 ± 1.5 | 83.1 ± 5.7 | 17.7 ± 1.1 | 60.8 ± 4.4 |
| EtO^-K^+ | 24.9 ± 0.4 | 106 ± 2 | 17.5 ± 0.7 | 79.3 ± 2.9 |
| $\text{EtO}^-\text{K}^+ + 18\text{C6}$ | 27.0 ± 0.2 | | 15.6 ± 0.4 | |



Scheme 2.

order rate constant (k_{obs}) can be expressed as in equations (1) and (2), in which [4 (or 5)], [EtO⁻], [EtO⁻M⁺] represent the concentration of substrate 4 (or 5), free ethoxide, and ion paired alkali metal ethoxides, respectively. Similarly, k_{EtO^-} and $k_{\text{EtO}^-\text{M}^+}$ stand for the second-order rate constant for the reaction of 4 (or 5) with free ethoxide and ion paired ethoxide, respectively.

$$\text{rate} = k_{\text{EtO}^-}[\text{EtO}^-][\text{4 or 5}] + k_{\text{EtO}^-\text{M}^+}[\text{EtO}^-\text{M}^+][\text{4 or 5}] \quad (1)$$

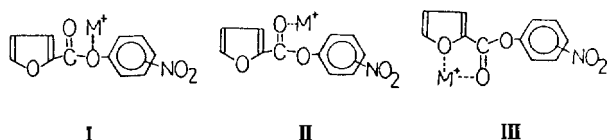
$$k_{\text{obs}} = k_{\text{EtO}^-}[\text{EtO}^-] + k_{\text{EtO}^-\text{M}^+}[\text{EtO}^-\text{M}^+] \quad (2)$$

Since K_a values for the association constants of alkali metal ethoxides in absolute ethanol at 25°C are available in the literature,¹⁴ equation (2) can be simplified into equation (3).

$$\frac{k_{\text{obs}}}{[\text{EtO}^-]} = k_{\text{EtO}^-} + K_a k_{\text{EtO}^-\text{M}^+}[\text{EtO}^-] \quad (3)$$

Therefore, the plot of $k_{\text{obs}}/[\text{EtO}^-]$ versus $[\text{EtO}^-]$ should give a linear line with slope $K_a k_{\text{EtO}^-\text{M}^+}$ and intercept k_{EtO^-} . In fact, the plots are linear for all the alkali metal ethoxides and yield $k_{\text{EtO}^-\text{M}^+}$ and k_{EtO^-} values as shown in Figures 3 and 4. The calculated values of k_{EtO^-} and $k_{\text{EtO}^-\text{M}^+}$ are summarized in Table 3. The k_{EtO^-} values obtained in this way are practically same as the one obtained from the slope of plots of k_{obs} versus $[\text{EtO}^-\text{K}^+]_0$ in the presence of excess 18C6. Besides, all the calculated values of second-order rate constants are consistent with the kinetic results, i.e. the second-order rate constant increases in the order $k_{\text{EtO}^-} < k_{\text{EtO}^-\text{Li}^+} < k_{\text{EtO}^-\text{Na}^+} < k_{\text{EtO}^-\text{K}^+}$ as shown in Table 3. Thus, the present results clearly indicate that the ion paired alkali metal ethoxides are more reactive than free ethoxide ion in the present system.

Role of Alkali Metal Ions. The catalytic effect of alkali metal ions was once attributed to formation of complex between an alkali metal ion and the oxygen atom in the leaving phenoxide, since the complexation as in the structure I would increase nucleofugality of the leaving group.^{6,9} However, this effect would be only effective when the leaving group departure is involved in the rate-determining step. It has generally been suggested that acyl-transfer reactions of the present type proceed *via* a stepwise mechanism, i.e. rate-determining formation of a tetrahedral intermediate followed by a fast leaving group departure.¹³ Therefore, the contribution of complex I is considered to be negligible in the present system.

The complexation of alkali metal ions (M⁺) with carbonyl

oxygen as in the structure II would increase electrophilicity of the carbonyl carbon in the substrate. Such a complexation would be stronger for the reaction of the substrate containing P=O or S=O bond than C=O bond. It is because the charge polarization of P=O or S=O double bond is considered to be much greater than that of C=O bond due to poor orbital overlapping between a 2p orbital of O and a large 3p orbital of P or S. Therefore, alkali metal ions would form weaker complexes with the oxygen atom in C=O bond than the one in P=O or S=O bond, which would account for the absence of alkali metal ion effect in the previous carboxylic system.

Unlike ordinary carboxylic ester system, chelation of a 5-membered ring would be possible as in the structure III for the present system. However, such a chelation would be possible for both the ground state (GS) and the transition state (TS), and result in stabilization of GS and TS. Therefore, the effect of metal ions on rate would be dependent on the magnitude of the GS and the TS contribution. The fact that alkali metal ions behave as a catalyst implies that the TS contribution is greater than the GS one in the present system. It is quite reasonable if one admits that the charge polarization of a C=O bond in the GS would be much smaller than the one in the TS. This argument is further supported from the experimental result that metal ion effect is more significant for the reaction of 5 than 4. This is because the charge polarization of the C=O bond in 5 would be more significant than the one in 4, based on the magnitude of their Brønsted β values.¹⁵

Buncel *et al.* explained the order of metal ion effect on the reaction of 1 with EtO⁻M⁺ in terms of charge density,⁶ since the metal ion effect increases in the order K⁺ < Na⁺ < Li⁺. A similar explanation was given by Suh.¹⁰ However, their explanation can not be applied to the present system, since the order of metal ion effect on the reactions of 4 and 5 with EtO⁻M⁺ is opposite to the one observed in the corresponding reaction of 1, i.e. the catalytic effect decreases in the order K⁺ > Na⁺ > Li⁺ in the present system. Unlike substrate 1, the present substrates (4 and 5) contain two oxygen atoms which could donate electron pair to the alkali metal ion. Besides, the negative charge can be dispersed on the two oxygen atoms in the TS. Since the effect of alkali metal ions in the present system increases with increasing the size of the metal ion, the charge density would be no longer important for a charge dispersed system. Therefore, the important factor governing the catalytic behavior of the alkali metal ion is the size of the metal ion which can influence the strength of chelation III in the reaction of charge dispersed substrates as in the present system.

Conclusions

The present study has allowed us to conclude the following. (1) Alkali metal ions behave as a catalyst for the reaction of 4 (or 5) with alkali metal ethoxides in absolute ethanol. The catalytic effect increases with increasing the size of the metal ion, i.e. K⁺ > Na⁺ > Li⁺. (2) The catalytic effect of the metal ion is more significant for the reaction of 5 than that of 4. (3) The chelation of EtO⁻M⁺ with TS as in structure III is considered to be responsible for the catalytic effect. (4) The size is considered to be more important than the

charge density of the metal ion for the formation of chelation III in the present system.

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A Molecular Orbital Study of the Electronic Structure and the Ring Inversion Process in Cp_2TiS_3 Complex

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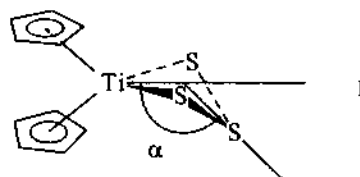
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Ab initio and extended Hückel calculations have been applied to discuss the electronic structure, ring inversion barrier, and geometry of the Cp_2TiS_3 compound. The deformation of four membered ring in the planar geometry is originated from a second-order Jahn-Teller distortion due to the small energy gap between HOMO and LUMO on the basis of extended Hückel calculations. The puckered C_2 geometry is stabilized by the interaction of the x^2-y^2 metal orbital with the hybrid orbital in sulfur. *Ab initio* calculations have been carried out to explore the ring inversion process for the model Cl_2TiS_3 compound. We have optimized C_1 and C_{2v} structures of the model compound at the RHF level. The energy barriers for the ring inversion are sensitive to the used basis set. With 4-31G* for the Cl and S ligands, the barriers are computed to be 8.41 kcal/mol at MP2 and 8.02 kcal/mol at MP4 level.

Introduction

The factors that determine the ring size and chain lengths in elemental sulfur are poorly understood instead of intensive studies.¹ The versatility of sulfur atoms as a ligand has been recently established in transition metal complexes. The trend of sulfur to form metal complexes is probably due to its intrinsic nucleophilic property and electron donor ability. A number of metallacyclosulfanes, MS_x , where $x=2$ to 5, have been prepared.² The ring inversion barriers in these complexes have been measured by variable temperature NMR studies. The activation energy for the TiS_5 ring inversion in Cp_2TiS_5 complex has been measured to be 16.5 kcal/mol by Abel *et al.*³ and the electronic structure and potential energy surface for the process of the six-membered

ring have been studied by various methods including *ab initio* calculations.⁴ $Cp_2^*TiS_3$ (Cp^* =pentamethylcyclopentadienyl) complex has been reported to be its ground state geometry in a puckered four membered ring, and the angle α in **1** is 131° .⁵ This complex has similar structure to the puckered



cyclobutane. The interesting feature is the energy barrier for the ring flipping from one side to the other. It has been measured to be 9.6 kcal/mol by NMR technique.⁵ This bar-