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Alkyl and dialkylammonium tetrafluoroborate catalyzed *cis–trans* isomerization of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane

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Abstract—Alkyl and dialkylammonium tetrafluoroborate promoted *cis–trans* isomerization of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane (**1**) in DMSO-d_6 were studied. The isomerization equilibrium constant K are within the range of 3.74–3.30 from 22 to 47 °C. Thermodynamic parameters of ΔH° and ΔS° for the isomerization were −0.95 kcal/mol and −0.59 cal/mol-K respectively. The isomerization rate is first order in [*cis*-**1**] and second order in [$R_nNH_{4-n}BF_4$]. Both components of $R_nNH_{4-n}^+$ and BF_4^- are essential for the catalytic *cis–trans* isomerization. The catalytic strength follows the decreasing order of $^+H_3N(CH_2)_6NH_3^+ > n\text{-}C_8H_{17}NH_3^+ > n\text{-}C_{16}H_{33}NH_3^+ > Me_3CNH_3^+ > PhCH_2NH_3^+ > Et_2NH_2^+ \gg Ph_2CHNH_3^+$, Et_3NH^+. Inversion region was observed in the plot of $\ln(k_f/T)$ versus $(1/T)$ with the ceiling located at around 38 °C. The positive activation enthalpy of 9 kcal/mol was estimated at 22–32 °C. The activation enthalpy turns to be slightly negative at $T > 38$ °C.

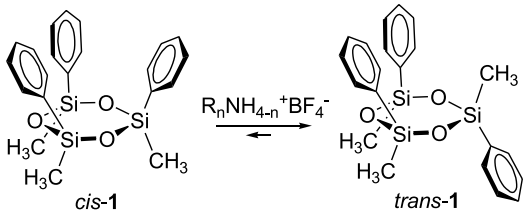
1. Introduction

Because of their special physical properties and chemical stability, polysiloxanes have been widely used in electrical, textile, plastic, paper, automobile, with minor amounts going into food and medical products.[1] Among the synthetic approaches for polysiloxanes, cationic and anionic ring opening polymerization of cyclic siloxanes attract many research teams to study.[2] In particular, the ring-opening process has been considered as a key step to control the kinetics and mechanisms of the polymerization.[3] Many research results suggested that chelation of metal cations by the siloxane moieties would importantly affect the polymerization process.[4] Explorations of the interactions between siloxane monomers and metal cations or R_4N^+ ions have been reported.[5] However, systematic studies on the interactions between cyclic siloxanes and $R_nNH_{4-n}^+$ are rare. As our continuous interest in hydrogen bonding interactions as well as cation binding,[6] we have recently investigated the possibility of using hydrogen bond donor as a catalyst to activate cyclic siloxanes for reaction. Herein we report novel conditions of alkyl or dialkylammonium tetrafluoroborate promoted *cis–trans* isomerization of *cis*-1,3,5-trimethyl-1,3,5-triphenyl-cyclotrisiloxane (*cis*-**1**) (Scheme 1).

cis–trans Isomerization of *cis*-**1** by $ZnCl_2$ or $FeCl_3$ as the catalyst in CH_3NO_2 at elevated temperature has been first reported by Spielvogel and Frye.[7] Later on, the use of pyridinium chloride or $PhNH_3Cl$ in DMF as a catalyst for the isomerization has also been reported.[8] However, pyridinium acetate was found to be inactive under similar conditions, implying that the counter anion indeed plays an important role on the above isomerization process. A ring opening reaction mechanism was proposed by the authors in that case.

1.1. R_nNH_{4-n} BF_4 promoted *cis–trans* isomerization of *cis*-1

The synthesis of *cis*-**1** has been reported in previous literature.[9] The structure of *cis*-**1** was further confirmed by X-ray crystallographic analysis before use.[10,11] ^1H NMR of *cis*-**1** in DMSO-d_6 (Fig. 1) shows a singlet of methyl protons at δ 0.55 ppm, which is corresponding to the resonance of the methyl protons. *cis*-**1** (14.9 mM) is stable in DMSO-d_6



Scheme 1.

Keywords: *cis–trans* Isomerization; Isomerization; Polymerization.
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for several days without causing any change on the spectrum. On addition of $NH_3(CH_2)_6NH_3(BF_4)_2$ or n-$C_8H_{17}NH_3BF_4$ (5 mM), two additional methyl singlets of the *trans*-isomer at δ 0.46 and 0.41 ppm, with the integration ratio of 2:1, gradually appeared. These results suggested that the ammonium salt acts as a catalyst to promote the *cis–trans* isomerization.

To elucidate the role of the salt in this reaction, contrast experiments were run for comparison. When *cis*-**1** (0.1 M) was treated with n-$C_8H_{17}NH_3Cl$ (0.1 M) at 25 °C for three days, no reaction was observed. On the other hand, polymerization of *cis*-**1** (0.1 M), instead of *cis–trans* isomerization, slowly proceeded in the presence of $LiBF_4$ (0.1 M). When *cis*-**1** (0.1 M) was treated with a mixture of n-$C_8H_{17}NH_3Cl$ and $LiBF_4$, *cis–trans* isomerization occurred along with some degree of polymerization. On the contrary, LiCl (0.08 M) would lead to *cis–trans* isomerization but in much slower rate. Even in the presence of relatively high concentration of LiCl, only 5% of *trans*-**1** was observed after one day.

All these results indicate that the *cis–trans* isomerization requires the coexistence of both n-$C_8H_{17}NH_3^+$ and BF_4^- as the catalysts. Either n-$C_8H_{17}NH_3^+$ or BF_4^- alone does not effectively promote the *cis–trans* isomerization. The same reaction occurred in CD_3CN, along with some degree of polymerization. On the other hand, when BF_4^- had been replaced by ClO_4^- ion, a complicated reaction mixture was obtained. All this indicated that BF_4^- should have a specific role for this isomerization.

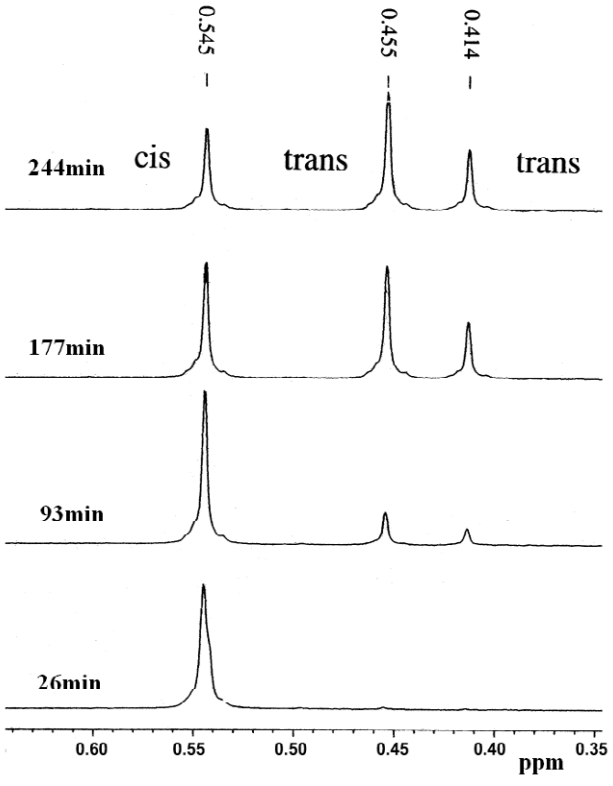


Figure 1. ^{1}H NMR spectra of $NH_3(CH_2)_6NH_3(BF_4)_2$ (4.46 mM) catalyzed *cis–trans* isomerization of *cis*-**1** (14.9 mM) at 25.0±0.1 °C in DMSO-d_6 at: (a) 26 min; (b) 93 min; (c) 177 min; (d) 244 min.

1.2. Kinetics and thermodynamics

Kinetic studies revealed that the isomerization of *cis*-**1** to *trans*-**1** is first order in [*cis*-**1**].[8] The equilibrium constants for the *cis–trans* isomerization of **1**, defined as $K=k_f^{cat}/k_b^{cat}=[trans]_{eq}/[cis]_{eq}$, were evaluated at various temperatures in

$$cis\text{-}\mathbf{1} \underset{k_b^{cat}}{\overset{k_f^{cat}}{\rightleftharpoons}} trans\text{-}\mathbf{1}$$

DMSO-d_6 and are listed in Table 1. The equilibrium constants K are within the range of 3.74–3.30 from 22–47 °C. Thermodynamic parameters of ΔH° and ΔS° were determined from a linear plot of ln K versus $1/T$ and were found to be −0.95 kcal/mol and −0.59 cal/mol-K respectively. Although the sign of ΔH° is consistent with the prediction based on the ring strain energy (E_s) measurements, in which *cis*-cyclotrisiloxane isomer has slightly higher ring strain than the *trans* one,[12] the ΔH° of −0.95 kcal/mol is relatively small in comparison to the reported ΔE_s of −2.1 kcal/mol. The negative entropy of −0.59 cal/mol-K may be attributed to the siloxane-DMSO interactions that restricted the degree of freedom of the solvent molecules. Noteworthy to mention are the facts that the literature values of [*trans*]/[*cis*] were found to be nearly equal to 3 either in methylcyclohexane[13] or in nitromethane,[7] indicating that the solvent effects on the equilibrium are small.

The mathematical expression for the first order kinetics described above is shown as the following equation.

$$\ln\left(\frac{[cis\text{-}\mathbf{1}]_t}{[cis\text{-}\mathbf{1}]_0}-\frac{1}{K+1}\right)=-k_f^{cat}\left(1+\frac{1}{K}\right)t+\ln\left(\frac{K}{K+1}\right)$$

In the kinetic expression, $[cis\text{-}\mathbf{1}]_o$ is the initial concentration of [*cis*-**1**], k_f^{cat} is the rate constant for the forward reaction, t is the reaction time elapsed, $[cis\text{-}\mathbf{1}]_t$ is the concentration of [*cis*-**1**] at time t.[14] Linear regression of $\ln\{[cis\text{-}\mathbf{1}]_t/[cis\text{-}\mathbf{1}]_0-1/(K+1)\}$ versus t gave a slope of $-k_f^{cat}(1+1/K)$. Since the equilibrium constant K had been measured in the previous equilibrium experiments, the values of k_f^{cat} could then be calculated. In most of the kinetic runs, the data were collected up to 80% conversion and the linearity of the plots are usually good with the correlation coefficient larger than 0.99. Since the value of k_f^{cat} obtained above should be a function of concentration of the catalyst, we tentatively proposed an empirical formula of $k_f^{cat}=k_f[R_nNH_{4-n}BF_4]_o^P$, in which $[R_nNH_{4-n}BF_4]_o$ is the concentration of the alkylammonium tetrafluoroborate used in the reaction, and the original first order kinetic equation could be re-expressed as follows.

Table 1. Equilibrium constants $K=[trans]_{eq}/[cis]_{eq}$ and the Gibbs free energy change for the *cis–trans* isomerization of *cis*-**1** at various temperatures

Temperature (°C)	K	ΔG° (kcal/mol)
22.0±0.2	3.74	−0.774
26.0±0.2	3.65	−0.770
37.0±0.2	3.44	−0.761
47.0±0.2	3.30	−0.759

Table 2. Determination of the reaction order P from a plot of $\ln[k_f^{cat}]$ versus $\ln[R_nNH_{4-n}BF_4]$

$R_nNH_{4-n}^+$	Reaction order
n-$C_8H_{17}NH_3^+$ [a]	2.53
$PhCH_2NH_3^+$ [a]	2.07
$^+H_3N(CH_2)_6NH_3^+$ [a]	2.05
n-$C_8H_{17}NH_3^+$ [b]	2.14

[a] At $T=25.0\pm0.1$ °C.
[b] At $T=47.0\pm0.1$ °C.

$$-\frac{d[cis\text{-}\mathbf{1}]}{dt} = k_f^{cat}[cis\text{-}\mathbf{1}] = k_f[R_nNH_{4-n}BF_4]_o^p[cis\text{-}\mathbf{1}].$$

Table 2 summarized the reaction orders p obtained from the slope of the plots of $\ln(k_f^{cat})$ versus $\ln[R_nNH_{4-n}BF_4]_o$. For the ammonium salts we studied, the p values at 25 °C were found to be or slightly larger than 2 with an average of 2.2 ± 0.2. Fractional order in pyridinum chloride catalyzed *cis–trans* isomerization has been previously reported in literature.[8]

Although the reaction order obtained above is not exactly equal to 2, particularly in the case of $C_8H_{17}NH_3BF_4$ where the p value was found to be 2.53 in the regression, their second order plots of k_f^{cat} versus $[R_nNH_{4-n}BF_4]^2$ are very linear with the correlation coefficient larger than 0.99. Therefore, we tentatively assigned the reaction order p as 2. To compare the catalytic strength of different alkylammonium tetrafluoroborates, their k_f values (Table 3) were evaluated at 25 ± 0.1 °C with $[R_nNH_{4-n}BF_4]_o$ around 6 mM. Their reactivity follows the decreasing order of $^+H_3N(CH_2)_6NH_3^+ > n$-$C_8H_{17}NH_3^+ > n$-$C_{16}H_{33}NH_3^+ > Me_3CNH_3^+ > PhCH_2NH_3^+ > Et_2NH_2^+ \gg Ph_2CHNH_3^+$, Et_3NH^+. Less hindered primary alkylammonium cations such as n-$C_8H_{17}NH_3^+$, n-$C_{16}H_{33}NH_3^+$ and $^+H_3N(CH_2)_6NH_3^+$ show highest reactivity for the *cis–trans* isomerization. For ammonium cations bearing larger substituent such as $Me_3CNH_3^+$ and $PhCH_2NH_3^+$, or secondary alkylammonium cations such as $Et_2NH_2^+$, their k_f values drop significantly by almost one order of magnitude. In addition, very sterically hindered $Ph_2CHNH_3^+$ and Et_3NH^+ or tetraalkylammonium tetrafluoroborates such as Et_4NBF_4 basically show no catalytic reactivity in our study.

The *cis–trans* isomerization also proceeds in CD_3CN but in much slower rate. The isomerization kinetics was found to be second order in $[C_8H_{17}NH_3BF_4]$ with the k_f value of 1.6 min^{-1} M^{-2} under the condition of $[R_nNH_{4-n}BF_4]_o=6$ mM, which is 2 order of magnitude slower than that in DMSO-d_6.

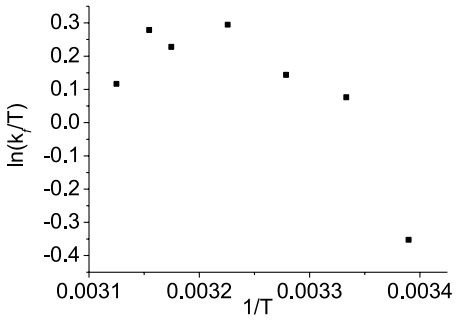


Figure 2. A plot of $\ln(k_f/T)$ versus $1/T$.

To further understand the reaction mechanism of the *cis–trans* isomerization, temperature variation experiments were carried out, in which n-$C_8H_{17}NH_3BF_4$ was used as the catalyst. The order p in $[n$-$C_8H_{17}NH_3BF_4]$ in the kinetic expression changed slightly from 2.53 to 2.14 when the temperature was varied from 25 °C to 47 °C. Although variation of the reaction order with temperature could be attributed to the intrinsic behavior of this reaction, experimental errors arising from independent kinetic runs as well as linear regression may also lead to similar extents of uncertainty. Since the variation of the reaction order is relatively small, we keep therefore our assumption that the order of p is equal to 2 for the following evaluation. The k_f for n-$C_8H_{17}NH_3BF_4$ were measured at seven different temperatures and the data are shown in Figure 2. Inversion region was observed in the plot of $\ln(k_f/T)$ versus $(1/T)$ with the ceiling at around 38 °C. The positive activation enthalpy of 9 kcal/mol was estimated at the temperature region of 22–32 °C.[8] The activation enthalpy turns to slightly negative at the temperature region higher than 38 °C. This observation suggested a complex reaction mechanism for the catalytic isomerization. Nevertheless, the existence of the inversion region could possibly be rationalized by an associative mechanism with a pre-complexation step followed by a rate determining *cis–trans* isomerization step. When the temperature increases, the rate determining *cis–trans* isomerization step is accelerated while the pre-complexation step is retarded. When the temperature is high enough, the entropically less favored pre-complex formation may become unfavorable that the pre-equilibrium kinetics is no longer valid. This will lead to a non-linear plot of $\ln(k_f/T)$ versus $(1/T)$ in the temperature variation experiments.

Although the explanation for the slightly negative activation enthalpy at the high temperature region may not be immediately obvious, the associative mechanistic argument of pre-complex formation is consistent with at least two

Table 3. Catalytic rate constants k_f for various alkylammonium tetrafluoroborates

$R_nNH_{4-n}^+$	$[R_nNH_{4-n}BF_4]$ (10^{-3} M)	k_f^{cat} (min^{-1})	k_f [k_{rel}] (min^{-1} M^{-2})
n-$C_8H_{17}NH_3^+$ (**2**)	5.37	1.04×10^{-2}	360 [1]
$^+H_3N(CH_2)_6NH_3^+$ (**3**)	5.78	1.53×10^{-2}	459 [1.3]
n-$C_{16}H_{33}NH_3^+$ (**4**)	5.99	5.07×10^{-3}	141 [0.39]
$Me_3CNH_3^+$ (**5**)	6.37	1.23×10^{-3}	30 [0.103]
$PhCH_2NH_3^+$ (**6**)	6.18	1.12×10^{-3}	29 [0.078]
$Et_2NH_2^+$ (**7**)	5.86	6.00×10^{-4}	18 [0.046]
Et_3NH^+ (**8**)	5.83	Very slow	—
$Ph_2CHNH_3^+$ (**9**)	7.73	Very slow	—
$PheNH_3^+$ (**10**)	5.89	Very slow	—

features: (1) Sterically hindered alkylammonium salts that do not favor the pre-complex formation usually show low catalytic activity for the reaction; (2) Heat releasing but entropically unfavored pre-complex formation may be a key reason for the slightly negative activation enthalpy at higher temperature region.[15]

Since hydrogen bonding between organic acids and cyclotrisiloxane has long been proposed in literature,[16] it is reasonable to suggest that hydrogen bond complexation may involve in this *cis–trans* isomerization. However, the chemical instability of *cis*-**1** in the ammonium salt solution hampered the direct study of the hydrogen bond intermediate. To elucidate the possibility of hydrogen bond complex formation, we selected a system of hexamethylcyclotrisiloxane (D_3)/$PhCH_2NH_3BF_4$ in CD_3CN as the model to investigate. D_3 is chemically stable and would not lead to other products in the presence of RNH_3BF_4. In addition, $PhCH_2NH_3BF_4$ is the least reactive primary alkylammonium salt in the list we have studied. Furthermore, the reactivity of the isomerization in CD_3CN is lower according to previous results.

In CD_3CN, up-field shift of the N–H signal of $PhCH_2NH_3BF_4$ (0.09 M), from 6.5 ppm approaching to 5.9 ppm, was observed when the added amount of D_3 gradually increased. The data is summarized in Table 4. These results suggested that hydrogen bond complexation of $RNH_3^+\cdots D_3$ occurs in this case. The unusual direction of upfield-shift of the N–H signal may be due to the change of the coordination shell throughout complexation. Hydrogen bond accepting properties of nitriles have recently been studied by combining crystallographic data as well as theoretical calculation.[17] Before complexation, the RNH_3^+ should be coordinated with either CD_3CN or BF_4^-. Since both of them will have hydrogen bonding with RNH_3^+, the N–H signal is relatively down-field shift. On complexation, the coordination shell of RNH_3^+ will be partially occupied by a D_3 molecule, leading to an up-field shift of the N–H signal. Similar results were obtained for *n*-$C_{16}H_{33}NH_3BF_4$. Since DMSO and acetonitrile are hydrogen bond acceptors with similar polarity,[18] we expected that formation of $RNH_3^+\cdots$*cis*-**1** as a reactive intermediate in DMSO is possible.

The role of BF_4^- is also an interesting target to study. Perfluorinated complex anions such as BF_4^-, or PF_6^- have been regarded as non-nucleophilic and inert of innocent anions.[19] If BF_4^- involves in the catalytic process, one may expect that changing the concentration of BF_4^- would lead to significant effect on the reaction rate. Therefore, we have attempted using Et_4NBF_4 as independent BF_4^- source to control the BF_4^- concentration. However, addition of Et_4NBF_4 to the solution of RNH_3BF_4 does not significantly alter the reaction rate of isomerization. We tentatively attributed this result to the ion pair association of Et_4NBF_4.[20] In particular, in the absence of hydrogen bond interactions, solvation of the bulky Et_4N^+ with DMSO is expected to be poor. Furthermore, we have observed the reactivity-suppression effects of Et_4NCl on RNH_3BF_4. In an independent experiment, we discovered that the catalytic strength of *n*-$C_{16}H_{33}NH_3BF_4$ (5.9 mM) was reduced by 60% in the presence of Et_4NCl (14 mM). This result is consistent with the above assumption of ion-pair formation. Addition of Et_4N^+ salt to a solution of RNH_3BF_4 would lead to Et_4NBF_4 ion-pair formation, reducing the effective concentration of free BF_4^- ions, and hence suppressing the catalytic reactivity of the RNH_3BF_4 solution.

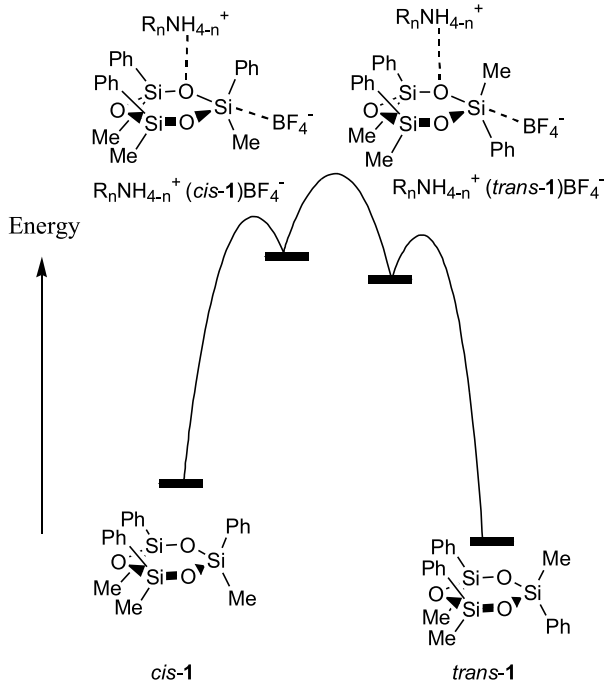
Since ion pair association in organic solvents is complicated,[21] detailed study of the reaction order would be relatively difficult. Although it is known that BF_4^- would dissociate into BF_3+F^- at high temperature,[19,22] it is unlikely to undergo this process in our case because the reactions were carried out only at room temperature or slightly above room temperature. Furthermore, the present of F^- would lead to polymerization[23] that has not been observed during *cis–trans* isomerization. On the other hand, BF_4^- has been proposed to act as a nucleophile to coordinate directly and react with group IV compound.[24] Although mechanistically we do not have evidence for the complexation of *cis*-**1** with BF_4^-, our results again indicated that BF_4^- is not truly innocent.

Although the details of the mechanism are not completely understood, pre-complexation involving $R_nNH_{4-n}^+$, BF_4^- and *cis*-**1** before isomerization to the *trans* isomer is plausible. We therefore proposed a mechanistic schematic diagram shown in Scheme 2. We believed that a push–pull mechanism involving hydrogen bond interaction between

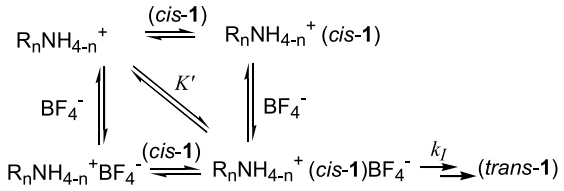
Table 4. N–H Chemical shifts of $PhCH_2NH_3BF_4$ in the presence of various amounts of D_3

$[D_3]/[PhCH_2NH_3BF_4]$	δ (N–H) (ppm)
0	6.51
0.21	6.39
1.85	6.18
3.15	6.05
4.64	5.98
6.33	5.93

At $T=25.0\pm0.1$ °C with $[PhCH_2NH_3BF_4]=0.09$ M.



Scheme 2.



Scheme 3.

$R_nNH_{4-n}^+$ and the oxygen atom of the Si–O–Si units, and probably coordination of BF_4^- with the silicon atoms are operating for the *cis–trans* isomerization.

On the basis of this assumption, a putative mechanism is proposed as shown in Scheme 3. We have already discussed the possibility of $R_nNH_{4-n}^+$(*cis*-**1**) complex formation. Since there is a positive charge on $R_nNH_{4-n}^+$(*cis*-**1**), further formation of a reactive ion pair intermediate of $R_nNH_{4-n}^+$(*cis*-**1**)BF_4^- is not impossible. On the other hand, the possibility of the formation of $R_nNH_{4-n}^+$(*cis*-**1**) BF_4^- through the ion pair of $R_nNH_{4-n}^+BF_4^-$ could not be eliminated. Once the $R_nNH_{4-n}^+$(*cis*-**1**)BF_4^- is formed, pseudorotational isomerization of $R_nNH_{4-n}^+$(*cis*-**1**)BF_4 at the pentacoordinated silicon atom may occur to give $R_nNH_{4-n}^+$(*trans*-**1**)BF_4^-, followed by dissociation of the ion-pair complex would give *trans*-**1** as the product. This type of pseudorotational mechanism is known as the Berry pseudorotation and turnstile twists that have been studied and reviewed in literature.[25]

A rate equation could then be derived on the basis of the reaction scheme, in which $K'=[R_nNH_{4-n}^+(cis\text{-}\mathbf{1})BF_4^-]/[R_nNH_{4-n}^+][BF_4][cis\text{-}\mathbf{1}]$ is the overall equilibrium constant for $R_nNH_{4-n}^+$(*cis*-**1**)BF_4^- formation, and k_I is the isomerization rate constant from $R_nNH_{4-n}^+$(*cis*-**1**)BF_4^- to the *trans* isomer.

$$-\frac{d[cis\text{-}\mathbf{1}]}{dt} = k_1[R_nNH_{4-n}^+(cis\text{-}\mathbf{1})BF_4^-]$$

$$= k_1K'[R_nNH_{4-n}^+][BF_4^-][cis\text{-}\mathbf{1}]$$

However, this equation does not straightly explain for the observeation of the second reaction order in $[R_nNH_{4-n}BF_4]_o$, unless we assumed that dissociation of $R_nNH_{4-n}BF_4$ in DMSO is extensive. This may be plausible due to strong hydrogen bond interactions between R_nNH_{4-n} BF_4 If the assumption is valid, each equivalent of $R_nNH_{4-n}BF_4$ would dissociate to give respectively one equivalent of $R_nNH_{4-n}^+$ and BF_4^-, and therefore $[R_nNH_{4-n}^+]$ and $[BF_4^-]$ are both equal to $[R_nNH_{4-n}BF_4]_o$. Substitution these into the above equation would give the following equation,

$$-\frac{d[cis\text{-}\mathbf{1}]}{dt} = k_f[R_nNH_{4-n}BF_4]_0^2[cis\text{-}\mathbf{1}]$$

where k_IK could be combined and denoted as the k_f. The second order kinetics in $[R_nNH_{4-n}BF_4]_o$ could then be explained.

2. Experimental

All reactions were performed under nitrogen. Acetonitrile was dried over CaH_2. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity plus (400 MHz). All 400 MHz ^1H NMR spectra were recorded in $CDCl_3$ deuterated acetonitrile (CD_3CN) and deuterated dimethylsulfoxide (DMSO-d_6) and are reported in ppm as δ. The kinetic experiments were carried out in DMSO-d_6. The ^1H NMR assignments for *cis*-**1** and *trans*-**1** were previously reported in literature.[7,8,13] Infrared spectra were obtained with KBr using Nicolet MAGNA-IR 550 spectrometer series type FT-IR and are reported in ν as cm^{-1}. Elemental analysis was performed by Heraeus CHN-O Rapid.

2.1. General procedure for the kinetic measurements

The kinetic measurements were performed by using ^1H NMR spectroscopy (Varian Unity plus (400 MHz)) with temperature control. Solution of *cis*-**1** and solution of the ammonium salt with known concentrations in DMSO-d_6 were prepared before measurement. Both solutions were pre-warmed to the desired temperature, mixed, and subjected to the NMR spectrometer for data collection. The concentrations of *cis*-**1** after mixing were set within the range of 8.48 to 25.5 mM. The concentrations of the ammonium salts were set within the range of 1.19 to 12.6 mM. The progress of the isomerization of *cis*-**1** to *trans*-**1** was monitored by taking the NMR spectrum for every 15 to 30 min. ^1H NMR of *cis*-**1** in DMSO-d_6 shows a singlet of methyl protons at δ 0.55 ppm, which is corresponding to the resonance of the methyl protons. On addition of the ammonium salt solution, two additional methyl singlets of the *trans*-isomer at δ 0.46 and 0.41 ppm gradually appeared. The ratio of [*trans*-**1**]/[*cis*-**1**] at a time could be determined on the basis of the methyl proton integrations. For the temperature variation experiments, the temperature range of 25–47 °C was used. The rate constant was determined according to the equation

$$\ln\left(\frac{[cis\text{-}\mathbf{1}]_t}{[cis\text{-}\mathbf{1}]_0} - \frac{1}{K+1}\right) = -k_f^{cat}\left(1+\frac{1}{K}\right)t + \ln\left(\frac{K}{K+1}\right)$$

By using linear least square fitting of $\ln([cis\text{-}\mathbf{1}]_t/[cis\text{-}\mathbf{1}]_o - (1/K+1))$ versus t, a slope of $-k_f^{cat}(1+1/K)$could be obtained. The value of k_f^{cat} could then be calculated.

2.2. General procedure for the preparation of alkylammonium tetrafluoroborates

Following is a typical preparative procedure for alkylammonium tetrafluoroborates. Alkyl or phenyl ammonium tetrafluoroborates were prepared according to the literature procedures of Kukhar.[26] They were prepared by reaction of the corresponding alkylammonium chlorides with triethyloxonium tetrafluoroborate in acetonitrile. Since most of the salts are hygroscopic, they are collected under nitrogen, sealed and sent for microanalysis.

2.2.1. Octylammonium tetrafluoroborate (2). To a solution of 1-octylamine (10 mL, 56.9 mmol) in CH_2Cl_2 (20 mL) in an ice bath were slowly added concentrated hydrochloric acid (4.75 mL, 56.9 mmol). The mixture was

stirred for another 5 h. White suspension was collected by filtration and further purified by recrystallization from CH_2Cl_2. The crystals were collected under nitrogen and dried in vacuum to give colorless octylammonium chloride (6.69 g, 71%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (s, 3H), 2.70 (t, J=7.6 Hz, 2H), 1.55–1.50 (m, 2H), 1.35–1.20 (m, 10H), 0.84 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.7, 31.2, 28.5, 26.9, 25.9, 22.1, 14.0; IR (KBr) ν 3400–2700 cm^{-1} (NH_3^+, br, s). To a solution of octylammonium chloride (3 g, 18 mmol) in dried acetonitrile (18 mL) under nitrogen at room temperature was added triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$, 18 mmol). The solution was refluxed for 24 h until outgassing of alkyl chloride was no longer observed. In some occasion, the completion of reaction was traced by ^{1}H NMR. The solid obtained after evaporation of the solvent was further purified by recrystallization from ethyl acetate. The product was collected by filtration under nitrogen, and dried in vacuum to give colorless crystals. (2.76 g, 71%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 (s, 3H), 2.75 (t, J=7.6 Hz, 2H), 1.52–1.46 (m, 2H), 1.35–1.20 (m, 10H), 0.85 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 41.4, 32.5, 29.8, 29.7, 27.7, 26.9, 23.4, 14.4; IR (KBr) ν 3400–3200 cm^{-1} (NH_3^+, br), 1200–1000 cm^{-1} (B–F, br). Anal. calcd for $C_8H_{20}BF_4N$: C, 44.27; H, 9.29; N, 6.45. Found: C, 44.79; H, 9.42; N, 6.50.

2.2.2. 1,6-Hexanediammonium bistetrafluoroborate (3). 1,6-Hexanediammonium dichloride obtained was purified by washing with methanol and CH_2Cl_2 to give colorless solid (75%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (s, 6H), 2.73 (t, J=7.6 Hz, 4H), 1.57–1.53 (m, 4H), 1.31–1.28 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 39.2, 27.4, 26.0; IR (KBr) ν 3400–2700 cm^{-1} (NH_3^+, br). 1,6-Hexanediammonium bistetrafluoroborate obtained was recrystallized from acetonitrile to give colorless solid. (46%): ^{1}H NMR (400 MHz, CD_3CN) δ 5.82 (s, 6H), 2.95 (t, J=7.6 Hz, 4H), 1.66–1.59 (m, 4H), 1.41–1.31 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN) δ41.2, 27.3, 26.1; IR (KBr) ν 3300–3200 cm^{-1} (NH_3^+, br), 1200–1000 cm^{-1} (B–F, br). Anal. calcd for $C_6H_{18}B_2F_8N_2$: C, 24.69; H, 6.22; N, 9.60. Found: C, 25.02; H, 6.22; N, 9.43.

2.2.3. Hexadecylammonium tetrafluoroborate (4). Hexadecyl-ammonium chloride obtained was recrystallized from $CHCl_3$ to give colorless solid (79%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (s, 3H), 2.72 (t, J=7.6 Hz, 2H), 1.53–1.48 (m, 2H), 1.35–1.15 (m, 26H), 0.84 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.7, 31.4, 29.1, 29.1, 29.0, 28.9, 28.8, 28.6, 27.0, 25.9, 22.2, 14.1; IR (KBr) ν 3200–2700 cm^{-1} (NH_3^+, br). Hexadecyl ammonium tetrafluoroborate was recrystallized from THF to give colorless solid (53%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 (s, 3H), 2.7 (t, J=7.6 Hz, 2H), 1.51–1.45 (m, 2H), 1.36–1.18 (m, 26H), 0.84 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.9, 31.3, 29.1, 29.0, 28.9, 28.8, 28.6, 27.1, 25.8, 22.2, 14.1; IR (KBr) ν 3300–3100 cm^{-1} (NH_3^+, br), 1200–1000 cm^{-1} (B–F, br). Anal. calcd for $C_{16}H_{36}BF_4N$: C, 58.36; H, 11.02; N, 4.25. Found: C, 58.68; H, 11.00; N, 4.26.

2.2.4. *tert*-Butylammonium tetrafluoroborate (5). *tert*-Butylammonium chloride was crystallized from ethanol to give colorless solid. (69%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 51.2, 27.4; IR (KBr) ν 3200–2900 cm^{-1} (NH_3^+, br, m). *tert*-Butylammonium tetrafluoroborate was recrystallized from acetonitrile to give colorless solid (39%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 51.7, 27.7; IR (KBr) ν 3300–3100 cm^{-1} (NH_3^+, br), 1300–1000 cm^{-1} (B–F, br). Anal. calcd for $C_4H_{12}BF_4N$: C, 29.85; H, 7.51; N, 8.70. Found: C, 29.79; H, 7.65; N, 8.43.

2.2.5. Benzylammonium tetrafluoroborate (6). Benzylammonium chloride obtained was crystallized from MeOH to give colorless solid (87%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.46 (s, 3H), 7.50–7.36 (m, 5H), 3.99 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 134.1, 128.9, 128.5, 128.4, 42.1; IR (KBr) ν 3200–2700 cm^{-1} (NH_3^+, br), 1600 cm^{-1} (C=C). Benzylammonium tetrafluoroborate obtained was crystallized from acetonitrile to give colorless solid (75%): ^{1}H NMR (400 MHz, CD_3CN) δ 7.48–7.43 (m, 5H), 6.46 (s, 3H), 4.15 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 133.1, 130.4, 130.4, 130.1, 44.9; IR (KBr) ν 3300–3100 cm^{-1} (NH_3^+, br), 1615 cm^{-1} (C=C), 1200–1000 cm^{-1} (B–F). Anal. calcd for $C_7H_{10}BF_4N$: C, 43.12; H, 5.17; N, 7.18. Found: C, 43.44; H, 5.15; N, 7.24.

2.2.6. Diethylammonium tetrafluoroborate (7). Diethylammonium chloride obtained was recrystallized from acetonitrile and followed by washing with hexane and ether to give colorless solid (68%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 2H), 2.90–2.81 (m, 4H), 1.17 (t, J=7.6 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 41.2, 10.9; IR (KBr) ν 3300–2700 cm^{-1} (NH_2^+, br). Diethylammonium tetrafluoroborate obtained was recrystallized from ethyl acetate to give colorless solid (44%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (s, 2H), 3.02 (q, J=7.2 Hz, 4H), 1.15 (t, J=7.6 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 42.0, 11.7; IR (KBr) ν 3200–2900 cm^{-1} (NH_2^+, br), 1300–900 cm^{-1} (B–F, br). Anal. calcd for $C_4H_{12}BF_4N$: C, 29.85; H, 7.51; N, 8.70. Found: C, 29.83; H, 7.67; N, 8.58.

2.2.7. Triethylammonium tetrafluoroborate (8).[27] Triethylammonium chloride prepared was recrystallized from acetonitrile to give colorless solid (48%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.60 (s, 1H), 3.06–3.00 (m, 6H), 1.19 (t, J=7.6 Hz, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 45.2, 8.4; IR (KBr) ν 3200–2900 cm^{-1} (NH^+, br). Triethylammonium tetrafluoroborate obtained was precipitated from ethyl acetate to give colorless solid (38%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 1H), 3.08 (q, J=7.2 Hz, 6H), 1.16 (t, J=7.6 Hz, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ46.0, 8.9; IR (KBr) ν 3200–2900 cm^{-1} (NH^+, br), 1300–900 cm^{-1} (B–F, br). Anal. calcd for $C_6H_{16}BF_4N$: C, 38.13; H, 8.53; N, 7.41. Found: C, 38.30; H, 8.73; N, 7.37.

2.2.8. (1,1-Diphenylmethyl)ammonium tetrafluoroborate (9). (1,1-Diphenylmethyl)ammonium chloride obtained was recrystallized from ethanol to give colorless solid (91%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 3H), 7.56 (d, J=7.2 Hz, 4H), 7.40 (t, J=7.6 Hz 4H), 7.33 (t, J=7.6 Hz, 2H), 5.61 (s, 1H);^{13}C NMR (100 MHz, DMSO-d_6) δ 138.8, 129.2, 128.7, 127.8, 57.6; IR (KBr) ν

3300–2600 cm^{-1} (NH_3^+, br), 1610 cm^{-1} (C=C, s). (1,1-Diphenylmethyl)ammonium tetrafluoroborate obtained was recrystallized from CH_2Cl_2 to give colorless solid (57%): ^1H NMR (400 MHz, CD_3CN) δ 7.49–7.26 (m, 10H), 7.26 (s, 3H), 5.69 (s, 1H);^{13}C NMR (100 MHz, CD_3CN) δ 137.2, 130.3, 130.3, 128.4, 60.0; IR (KBr) ν 3300–3100 cm^{-1} (NH_3^+, br), 1597 cm^{-1} (C=C), 1200–900 cm^{-1} (B–F, br). Elemental analysis suggested that the salt is a monohydrate. Anal. calcd for $C_{13}H_{14}BF_4N\cdot(H_2O)$: C, 54.01; H, 5.58; N, 4.85. Found: C, 54.87; H, 5.38; N, 4.92.

2.2.9. L-Phenylalanine methyl ester ammonium tetrafluoroborate (10). To a solution of L-phenylalanine (5.0 g, 29.8 mmol) in distilled MeOH (50 mL) under nitrogen at at 0 °C was added distilled thionyl chloride (3.28 mL, 44.7 mmol) dropwise. After addtion, the mixture was stirred at room temperature for 24 h. The reaction was followed by TLC, using BAW (butanol–acetic acid–H_2O=4:1:1) as the mobile phase. After completion of the reaction, methanol was removed by distillation. Ether (400 mL) was added to precipitate the product. The solid product was collected by suction filtration under nitrogen, followed by washing with iced ether, and dried under vacuum to give L-phenylalanine methyl ester ammonium chloride (5.91 g, 91%): ^1H NMR (400 MHz, DMSO-d_6) δ 8.53 (s, 3H), 7.35–7.23 (m, 3H), 7.22 (d, J=6.8 Hz, 2H), 4.28 (t, J=6.8 Hz, 1H), 3.66 (s, 3H), 3.14 (dd, J=14.0, 6.0 Hz, 1H); 3.06 (dd, J=13.8, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.1, 134.4, 129.2, 128.4, 127.1, 53.2, 52.5, 35.9; IR (KBr) ν 3300–2700 cm^{-1} (NH_3^+, br), 1766 cm^{-1} (C=O). 1600 cm^{-1} (C=C). L-phenylalanine methyl ester ammonium tetrafluoroborate obtained was precipitated from CH_2Cl_2 to give colorless solid. (18%): ^1H NMR (400 MHz, DMSO-d_6) δ 8.33 (s, 3H), 7.37–7.22 (m, 3H), 7.21 (d, J=6.8 Hz, 2H), 4.32 (t, J=6.8 Hz, 1H), 3.68 (s, 3H), 3.12–3.02 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.5, 134.5, 129.4, 128.7, 127.4, 53.2, 52.7, 36.0; IR (KBr) ν 3300–2800 cm^{-1} (NH_3^+, br), 1747 cm^{-1} (C=O), 1609 cm^{-1} (C=C), 1200–900 cm^{-1} (B–F, br). Anal. calcd for $C_{10}H_{14}BF_4NO_2$: C, 44.98; H, 5.28; N, 5.25. Found: C, 44.78; H, 5.25; N, 5.32.

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