A New Mode of Fluoride-Ion Exchange Reactions between Tetracoordinate Silane and Pentacoordinate Fluorosilicate

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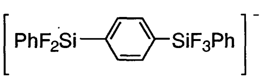
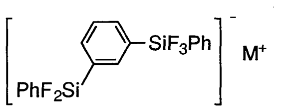
Intramolecular fluoride-ion donor-acceptor systems such as [*p*- and *m*-(difluorophenylsilyl)phenyl]trifluorophenylsilicates showed a new mode of fluoride-ion exchange reactions in solution, for which a concerted bimolecular exchange mechanism through cyclophane-like transition states was proposed on the basis of a dynamic ^{13}C NMR analysis of rates and activation parameters.

Although fluoride-ion exchange reactions between a tetracoordinate silane and the corresponding pentacoordinate fluorosilicate constitute an interesting class of atom-transfer self-exchange reactions at main-group metal centers,[1] the mechanism has been studied very scarcely. Marat et al. have previously investigated the rates of exchange between $RSiF_4^-$ and $RSiF_3$ by dynamic ^{19}F NMR spectroscopy; without determining the reaction order or the activation parameters, the exchange has been reported to proceed via a transition state having linear arrangement of [Si---F---Si].[2] A theoretical study has shown that SiH_nF_{4-n} (n = 1 - 3) forms a stable linear Si-F-Si bridge with $[SiH_nF_{5-n}]^-$ in the gas phase.[3] We have recently reported on the synthesis and structure of novel intramolecular fluoride-ion donor-acceptor systems, **1a** and **1b**, and related bissilicates,[4,5] where phenyltrifluorosilicate (D_f) and phenyldifluorosilyl (A_f) groups serve as a fluoride-ion donor and a fluoride-ion acceptor, respectively. We wish herein to report a new mode of fluoride-ion exchange reactions found in **1a** and **1b**. A dynamic ^{13}C NMR study has shown that the fluoride-ion exchange of **1a** and **1b** occurs mostly in bimolecular processes. The large negative activation entropies observed for the bimolecular exchange suggest that the reaction proceeds via a rather unusual fluorine-bridged cyclophane-like transition states.



1a

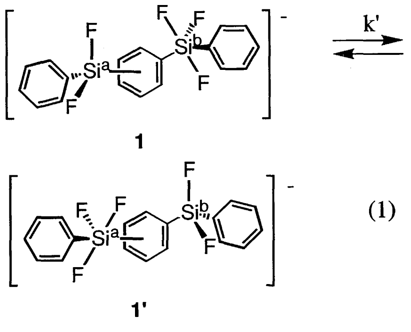


1b

$M^+ = K^+$(18-crown-6)

The ^{1}H, ^{13}C, ^{29}Si, and ^{19}F NMR spectra of these silicates showed significant temperature dependence. Although the ^{19}F NMR spectra of **1a** and **1b** were complicated by the additional Berry pseudo-rotation,[6] line widths of the ^{13}C NMR signals due to aromatic carbons of D_f and A_f were analyzed simply by assuming the exchange shown in Eq. 1. The apparent first-order rates (k') for the two-site exchange were determined by using the linewidths for the pertinent pairs of the ^{13}C NMR signals in the slow exchange region.[7] The rate constants k' showed linear dependence on the concentration of the silicates as shown in Figure 1. Rates of unimolecular- (k_1) and bimolecular fluoride-ion transfers (k_2) for **1** were determined from the intercepts and the slopes of the linear lines, respectively, after correcting the intrinsic NMR line widths.

Whereas the unimolecular exchange rates for **1a** in CD_2Cl_2 were negligible in the temperature range of measurements, the rate for **1b** in CD_2Cl_2 was estimated to be 36 s^{-1} at 273 K. Although the value is significantly beyond the limits of the experimental error, the detailed mechanism for the unimolecular exchange for **1b** remains open.



(1)

$$k' = k_1 + k_2[\mathbf{1}] \qquad (2)$$

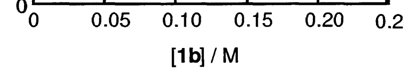


Figure 1. Temperature and concentration dependence of pseudo-first-order rate constants (k') of the fluoride-ion exchange reaction for **1b** in CD_2Cl_2 (■: 278 K, ▲: 273 K, ●: 268 K).

Discussion herein is concentrated on the mechanism for the bimolecular exchange. The second-order rate constants and activation parameters for the exchange are summarized in Table 1 as well as those for the exchange between a trifluorodiphenylsilicate **2** and the corresponding tetracoordinate silane **3** in CD_2Cl_2, as a prototypical bimolecular fluoride-ion exchange reaction (Eq. 3).

Whereas the theoretical calculations by Fujimoto et al.[3] suggest that the fluorine-bridged complex between **2** and **3** is more stable than the starting system, the situation would be modified by significant effects of solvent polarity. Actually, the complex between **2** and **3** was not observed as a stable species in solution by NMR. The linear fluorine-bridged structure would be taken to be a *transition state* or a *transient intermediate* for the exchange reaction between **2** and **3** (Eq. 3) as proposed by Marat et al.[2] Rather exceptionally, the $\Delta S^{\ddagger}$ for the exchange in the **2/3** system is even positive in spite of the bimolecular reactions between ions and neutral molecules. The results suggest that the loss of mobility of solvent molecules due to orientation to the solutes is much larger at the ground state than at the transition state in the **2/3** system, in other words, significant desolvation takes place with the progress of the reaction.

$$\underset{\mathbf{2}}{[Ph_2Si^aF_3]^-} + \underset{\mathbf{3}}{Ph_2Si^bF_2} \rightleftharpoons [Ph_2F_2Si^a\text{---}F\text{---}Si^bF_2Ph_2]^-$$

$$\rightleftharpoons \underset{\mathbf{3'}}{Ph_2Si^aF_2} + \underset{\mathbf{2'}}{[Ph_2Si^bF_3]^-} \quad (3)$$

Table 1. Rate Constants (k_2) and Activation Parameters of Fluoride-Ion Exchange Reactions of **1** and between **2** and **3**

reaction system[a]	solvent	k_2 at 273 K	$\Delta H^{\ddagger}$/ ($kJ \cdot mol^{-1}$)	$\Delta S^{\ddagger}$/($J \cdot mol^{-1} \cdot K^{-1}$)
1a	CD_2Cl_2	1760[b]	21.3	-104
1b	CD_2Cl_2	445	27.8	-91.9
	acetone-d_6	2390[b]	35.0	-51.2
2/3	CD_2Cl_2	33600[b]	46.7	13.6

a. Countercation; K^+(18-crown-6). b. Calculated by using activation parameters.

Interestingly, the activation parameters for the exchange reactions of **1a** and **1b** are quite different from those for the **2/3** system; the former reactions are characterized by large negative $\Delta S^{\ddagger}$ (ca. -100 $J \cdot mol^{-1} \cdot K^{-1}$) and small $\Delta H^{\ddagger}$ values. The transition states for the exchange reactions of **1a** and **1b** should be much more restricted than that for the **2/3** system. On the basis of the extremely large $-\Delta S^{\ddagger}$ values for the second-order exchange reactions of **1a** and **1b**, it is proposed that the reactions proceed concertedly through fluorine-bridged cyclophane-like transition states (Eq. 4).[8] As shown in Table 1, significant solvent effects were observed on the rates and activation parameters for the reaction of **1b**; the $-\Delta S^{\ddagger}$ value in acetone-d_6 [dielectric constant (ε) for acetone,[9] 20.7] was smaller than that in less polar CD_2Cl_2 (ε for CH_2Cl_2,[9] 8.93), while the $\Delta H^{\ddagger}$ value was larger in acetone-d_6. The observed solvent effects are compatible with the present transition-state model, since a part of the oriented solvents at the ground states are expected to be released at the transition states, like the exchange in the **2/3** system, and the extent will be larger in acetone-d_6 than in CD_2Cl_2.[10,11] Related works are in progress.

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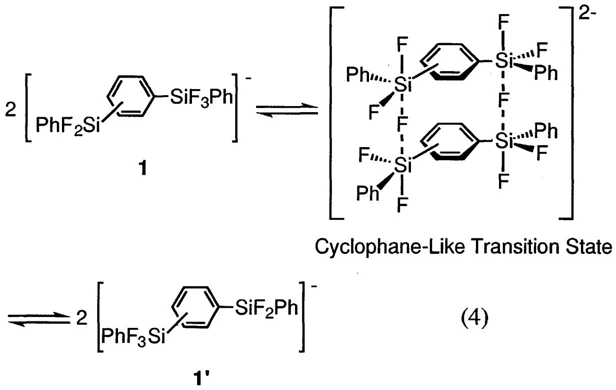

(4)

References and Notes

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5 In contrast to **1a** and **1b**, the *o*-isomer has been shown to have a fluorine atom bridging between two adjacent silicon atoms in the ground state: K. Tamao, T. Hayashi, Y. Ito, and M. Shiro, *J. Am. Chem. Soc.*, **112**, 2422 (1990); K. Tamao, T. Hayashi, Y. Ito, and M. Shiro, *Organometallics*, **11**, 2099 (1992).

6 R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

7 The pseudo first-order rate constants were determined by simulating the experimental ^{13}C signals recorded on a Bruker AC-300P NMR spectrometer by using a program DNMR2 (QCPE#140), G. Binsch and D. A. Kleiev (1969), or by analyzing half-widths of the signals. L. M. Jackman and F. A. Cotton, "Dynamic Nuclear Magnetic Resonance Spectroscopy," Academic Press: New York, 1975. The temperature was controlled with a AC–TBL temperature controller within ±0.1 K.

8 There are several possible conformations for the transition state for **1b**, whereas the syn conformation of the two phenylene rings is shown in Eq. 4.

9 S. L. Murov, "Handbook of Photochemistry," Marcel–Dekker, Inc., New York, 1973.

10 Unfortunately, the rates of the exchange reactions of **1a** and the **2/3** system were unable to measure in acetone because of the poor solubility.

11 Several interesting features are found in Table 1, as pointed out by a referee. The exchange of the **2/3** system is much faster than the bimolecular exchange of **1a** and **1b**. The stepwise exchange reactions of **1a** and **1b** via similar transition states to the reaction of the **2/3** system should be severely endothermic, because the former reactions give unfavorable pairs of D_f–C_6H_4–D_f and A_f–C_6H_4–A_f as intermediates, and therefore, they will be much slower than the prototypical exchange. The present results suggest that the possible stepwise exchange of **1a** and **1b** is less favorable than the concerted fluoride-ion exchange, where the cyclophane-like transition states would be stabilized electronically by a push-pull mechanism, while they accompany a large entropy loss. The k_2 for **1a** is significantly larger than that for **1b**. Whereas further works are required, the origin may be attributed to the different efficiency of the push-pull mechanism for stabilization of the transition state.