In practice, of course, multiplets of protons A and X have usually not been identified in the regular one-dimensional spectrum, and exact values for the spin couplings involved are unknown. However, an approximate guess for those values is sufficient for fruitful use of the "mulitplet-selective filter", especially since acquisition times, AT, in the t_1 and t_2 dimensions usually have a duration of only one to several hundred milliseconds.

As an example, Figure 1 compares absolute value mode cross sections taken parallel to the F_1 axis at the F_2 frequency of proton H1 through three COSY spectra, all obtained from the same set of acquired data, for a sample of amphotericin B in Me$_2$SO-d_6. Figure 1a shows the cross section obtained if no digital filtering is used. The diagonal peak shows a broad base due to the absolute value mode and the in-phase nature of the unresolved multiplet components. The cross peak with Me38 is strong, but the cross peak with proton H2 has very low intensity. The noise in this trace is partly so-called t_1 noise[9,10] and arises from instabilities in the spectrometer system which cause some of the signal energy of the intense peaks (H1 and Me38) to be distributed over the entire trace. Figure 1b shows the trace that is obtained if the commonly used sine-bell function is applied in both dimensions. The line shape is improved and the diagonal peak (H1) is attenuated compared with Figure 1a, but the H1–Me38 cross peak is still a factor of about 60 stronger than the H1–H2 cross peak. Figure 1c shows the cross section that is obtained if the multiplet selection procedure, described earlier, is applied in order to emphasize the H1–H2 cross peak. The signal-to-noise ratio for the H1–H2 cross peak has improved dramatically, mainly because of the matched filtering in both dimensions but also because the intense resonances in this F_1 section, which are the major contributors to t_1 noise, are attenuated. Note that the use of the multiplet-selective filter introduces a broadening of the multiplet structure in both frequency dimensions.

The H1–H2 cross peak has been enhanced to within about a factor of 2 relative to the H1–Me38 cross peak. Both H1 and H2 are coupled to methyl groups, and this coupling is estimated to be 7 Hz. The H1–H2 coupling is unknown but is estimated at 5 Hz. The H2–H3 coupling is unknown and is not incorporated in the filtering function. The total filtering function, $G(t)$, used in both dimensions for a duration of the acquisition time, AT, is given by

$$G(t) = \cos (7\pi t)^3 \sin (5\pi t) \sin (\pi t/\text{AT}) \qquad (3)$$

The last factor of this function denotes a sine bell, added to the optimized filter in order to avoid truncation of the time domain data at the end of the FID.

We have shown that the relative intensity and sensitivity of cross peaks in homonuclear correlated spectra can be increased dramatically by use of digital filtering procedures optimized for this purpose. This approach is particularly important for the common case where small impurities are present in the sample, and low contour levels in a regular COSY spectrum show a jumble of corresponding cross peaks. Also, by trying a number of different filtering functions one is able to distinguish between cross peaks due to relatively large couplings and small long-range couplings. The method is also applicable in heteronuclear[11] and homonuclear relayed coherence transfer spectroscopy[12,13] and in proton double-quantum spectroscopy.[14]

In view of improvements in computer technology and incorporation of array processors in commercial spectrometers, we expect that the extra data processing time, needed for reprocessing the same set of time domain data several times, will not be a major factor in the near future.

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Fluoride Ion Induced Rearrangements of Chloromethyl-Substituted Silanes: Carbanionic Character of Groups Undergoing Migration

Robert Damrauer,* Stephen E. Danahey, and Vernon E. Yost

Chemistry Department
University of Colorado at Denver
Denver, Colorado 80202
Received July 2, 1984

We have discovered that chloromethyl-substituted silanes undergo alkyl- and aryl-group rearrangement induced by fluoride ion solubilized by 18-crown-6. This migration is largely controlled by the ability of the migrating group to bear the negative charge which develops in the transition state.

Considerable recent activity has focused on the degree of anionic character associated with groups cleaved from silicon by nucleophiles, particularly in cases where the pK_a values of the groups undergoing cleavage are less than 37.[1] Such reactions are induced both by basic and fluoride ion catalysis, generally from trimethylsilyl-substituted derivatives.[1] A variety of correlations between substituent and acidity constants and rates or relative rates of cleavage has made it clear in such reactions that the cleaved carbon fragment has substantial carbanionic character.[1,2]

Quite recently we have measured the gas-phase acidities of some weakly acidic hydrocarbons by reaction of hydroxide ion with several trimethylsilyl-substituted alkanes.[3] Indeed, we have found a remarkable correlation between the gas-phase acidities of RH ($\Delta H°_{acid}$) and the product ratio (1/2) resulting from competitive cleavage producing CH$_3$H and RH in eq 1.

$$(\text{CH}_3)_3\text{SiR} \xrightarrow{\text{OH}^-} \underset{\textbf{1}}{(\text{CH}_3)_3\text{SiO}^-} + \text{R-H}$$
$$\rightarrow \underset{\textbf{2}}{(\text{CH}_3)_2\text{RSiO}^-} + \text{CH}_3\text{-H}$$

$$(1)$$

We report here on some solution-phase work involving the rearrangement of alkyl and aryl groups. This work is particularly important because it occurs in condensed phase with the migration of groups that are weakly acidic. Thus, it partially bridges a gap between the studies just discussed. We have found that (chloromethyl)trimethylsilane reacts with potassium or cesium fluoride in the presence of 18-crown-6 in aromatic hydrocarbon solvents to give exclusively dimethylethylfluorosilane (eq 2). Although

$$\underset{\textbf{3}}{(\text{CH}_3)_3\text{SiCH}_2\text{Cl}} \xrightarrow[\text{toluene}]{\overset{\text{18-crown-6}}{\text{KF or CsF}}} (\text{CH}_3)_2(\text{CH}_3\text{CH}_2)\text{SiF} \qquad (2)$$

related rearrangements of chloromethyl-substituted silanes under acidic conditions (e.g., aluminum chloride catalysis) have been reported and studied in detail,[4] only a few examples of base-induced reaction of chloromethyl-substituted silanes are known and these rarely involve the migration of a simple alkyl group.[5] Nevertheless, two reports of alkyl migration are relevant to this

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Table I. Product Ratios from the Reaction of Substituted Silanes, $(CH_3)_2RSiCH_2Cl$, with Fluoride Ion and Constants Used in Analysis

R	$(CH_3)_2(F)Si-$ CH_2R^a $(4)/CH_3(R)-$ $(CH_3CH_2)SiF$ (5)	ΔH°_{acid}	σ^* constant	σ_I constant
ethyl	1.5	421[b]	−0.10[c]	−0.055[g]
methyl	1.0	416.6[b]	0.00[c]	−0.046[g]
isopropyl	0.67	419[b]	−0.19[c]	−0.064[g]
cyclopropyl	7.0	412[b]	0.11[g]	
butyl	0.87	420[c]	−0.13[c]	−0.060[g]
vinyl	20	406[b]	0.56[f]	0.05[c]
phenyl	16	399[b]	0.60[c]	0.10[c]

^{a} Statistically corrected. These ratios are obtained early in the reaction before secondary reactions occur. ^{b} Reference 3. ^{c} Hine, J. "Structural Effects on Equilibrium in Organic Chemistry"; Wiley-Interscience: New York, 1975. ^{d} Brown, T. L. *J. Am. Chem. Soc.* **1958**, *80*, 6489–6491. ^{e} Estimated from ref 3. ^{f} Barlin, G. B.; Perrin, D. D. *Q. Rev., Chem. Soc.* **1966**, *20*, 77–101. Values greater than that of phenyl have also been reported (Hine, J.; Bailey, W. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 2075–2078). ^{g} Shorter, S. "Correlation Analysis of Organic Reactivity"; Research Studies Press: New York, 1982.

Table II. Correlation of log **4/5** with ΔH°_{acid}, σ^* Constants, and σ_I Constants

| reactn | slope (correlation coefficient) correlated with | | |
	σ^* constant	σ_I constant	ΔH°_{acid}
solution phase (eq 3)	1.81 (0.943)	9.06 (0.952)	−0.0674 (0.904)
gas phase (eq 1)	1.45 (0.858)	9.29 (0.826)	−0.0784 (0.999)

study: (1) Voronkov and co-workers have demonstrated low yields of alkyl migration in (chloromethyl)silanes reacting with KF at high temperature in polar solvents,[6] and (2) Hopper and co-workers have reported methyl migration in hot-tube reactions over solid KOMe.[7] Both examples demonstrate alkyl migration, but in neither case do the authors attempt to examine the migration in any detail.

Therefore, to explore the nature of this reaction in detail, we prepared or obtained ethyl, isopropyl, cyclopropyl, phenyl, *n*-butyl, and vinyl compounds of the type $(CH_3)_2RSiCH_2Cl$. These were each reacted with fluoride ion as in eq 3. When the log of the

$$(CH_3)_2RSiCH_2Cl \xrightarrow[\text{toluene}]{\substack{\text{18-crown-6}\\ F^-}}$$
$$(CH_3)_2SiFCH_2R + CH_3RSiFCH_2CH_3 \quad (3)$$
$$\mathbf{4} \qquad\qquad \mathbf{5}$$
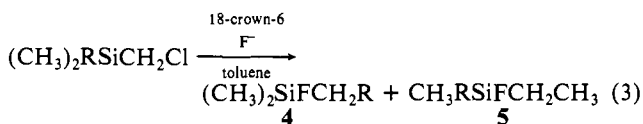
ratio of products (**4/5**) is plotted vs. (1) the gas-phase acidities,[3] (2) σ^* constants, or (3) σ_I constants, roughly linear correlations were obtained, a comparable fit being found for σ^* and σ_I (the correlation coefficients are 0.943 and 0.952, respectively), a poorer fit for ΔH°_{acid} (correlation coefficient 0.904). The gas-phase data correlate only with ΔH°_{acid} (correlation coefficient 0.999). Tables I and II summarize these data. There is a definite correspondence between the gas- and solution-phase data when plotted against ΔH°_{acid}, indicating that eq 1 and 3 are sensitive to substituent properties in a similar way. A more focused look at these data, however, reveals some interesting differences. In solution the data are better accommodated by solution parameters while in the gas phase, gas-phase parameters work best. If the solution reaction behaved exactly like the gas-phase one and if these data more perfectly correlated with σ^* and σ_I constants, then ethyl and vinyl would migrate less readily than methyl and phenyl. That they do not may be the result of solvent interactions that we presently do not understand. What is clear is the similarity between the gas- and solution-phase experiments, resulting because substituents

tend to stabilize the negative charge localized on the migrating group. The rough correlation with σ^* suggests that the amount of negative charge localization is modest (Taft ρ^*).

A consistent mechanistic model for reaction of fluoride ion and these chloromethyl-substituted silanes (eq 4) involves the formation
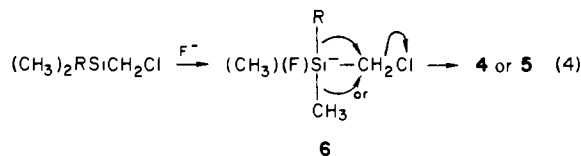
of a pentacoordinate adduct (**6**), where CH_3 and R migrate competitively to displace chloride ion. The driving force for pentacoordination is the high fluoride affinity of silanes demonstrated both in solution and the gas phase;[8] the migratory efficiency is controlled largely by anion stability.

In conclusion, we report a new reaction of chloromethyl-substituted silanes, one whose mechanism we have briefly explored. Our data suggest that fluoride ion induces alkyl and/or aryl migration through a pentacoordinate intermediate where the ease of migration correlates with the ability of the migrating group to stabilize the negative charge which is developed in the transition state.

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Transition-State Structure and the Temperature Dependence of the Kinetic Isotope Effect

Bo Anhede and Nils-Åke Bergman*

Department of Organic Chemistry University of Göteborg and Chalmers University of Technology, S-412 96 Göteborg, Sweden

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The temperature dependence of the kinetic hydrogen isotope effect (KIE) as a mechanistic criterion has attracted great attention during recent years.[1] In particular, a temperature-independent KIE coupled with an anomalous A_H/A_D ratio has been taken as a probe of a nonlinear transition state for the hydrogen transfer. This simple rule has already come into common use[2–4] despite some published results which indicate that there might be limitations to its usefulness.[5]

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