480 J. Am. Chem. Soc. 1981, 103, 480-481

Gas-Phase Reactions of Cyclic Silanes

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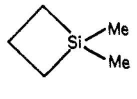
Received September 29, 1980

Pentavalent silicon anions are frequently postulated as intermediates in the reactions of organosilicon compounds with nucleophiles but under normal circumstances have lifetimes too short for study.[1,2] In view of the recent explosive growth in the use of organosilicon compounds as facilitators in organic synthesis,[3] it has become increasingly important to learn more about the mechanisms of organosilicon reactions and the energetics, structures, and reactivity of these elusive intermediates. We wish to report that in the gas phase, by using a flowing afterglow (FA) system,[4,5] a large number of organic pentavalent silicon anions, including silicon anions with five carbon substituents, can be generated cleanly by reaction of anions with substituted silanes. Of particular interest are the reactions of F^- with cyclic silanes **1–4**,[6] not only because they shed light on the stereochemistry and energetics of pentacoordinate anion formation but also because some novel cleavage reactions producing α-silylcarbanions occur.



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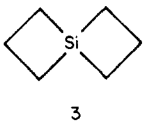

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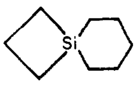

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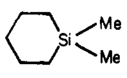

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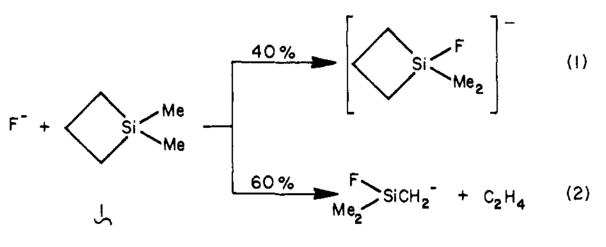
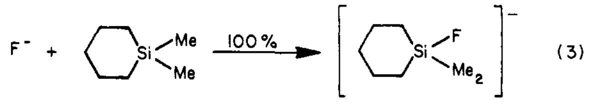
In our experiments, fluoride ion is produced by dissociative electron attachment to NF_3 and swept out of the ionizing region by a stream of helium (He flow velocity = 80 m s^{-1}, He pressure = 0.30 torr). The neutral silane reactants are added downstream after reagent ions have reached thermal equilibrium by collisions with He. Ionic products are sampled and analyzed by a quadrupole mass filter and detected by an electron multiplier.

Two major processes compete in the silacyclobutanes **1–3**, as exemplified by the reaction of 1,1-dimethylsilacyclobutane, **1** (eq 1 and 2), where approximate product distributions are given.[7,8] In contrast, 1,1-dimethylsilacyclohexane (**4**) reacts to form a single ion product (eq 3). Reactions 1 and 3 correspond to direct F^- adduct formation; these anions are formulated as pentacoordinate silicon species. The ionic products like **5** are α-silyl carbanions, formally produced by F^- addition to **1–3** followed by cleavage of the strained silacyclobutane ring and loss of ethylene.[9]



1 **5**



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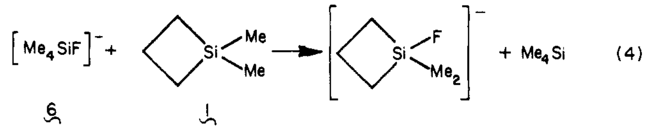
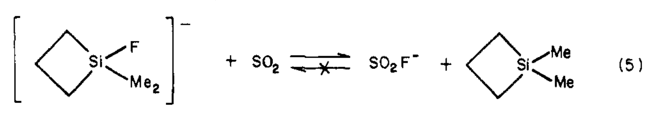
Adducts of $(CH_3)_4Si$, $(CH_3)_3SiF$, and several other organosilanes are also produced by direct F^- addition.[10] The F^- adduct of $(CH_3)_4Si$ (**6**) transfers F^- to all of the cyclic silanes **1–4** in a manner analogous to reaction 4. In such gentle F^- transfers, no ring cleavage is observed. The adducts of **1–4** readily transfer F^- to SO_2 in an irreversible reaction (eq 5).[11] When a series of such F^- transfer reactions is used, a semiquantitative F^- affinity scale can be determined as previously described for boron,[12] phosphorus,[13] and fluorinated silicon compounds.[14] We estimate the F^- affinities of **1–3** to be 40 ± 5 kcal/mol^{-1} with a qualitative ordering **1** $\simeq$ **2** < **3**. Equilibrium studies indicate that the F^- affinity of **1** is just 0.5 kcal/mol^{-1} less than that of $(CH_3)_3SiF$. In dramatic contrast is the F^- affinity of silacyclohexane **4** which, like that of $(CH_3)_4Si$ and other simple alkylsilanes, is less than 23 kcal/mol^{-1}, as bracketed by F^- transfer to H_2O.[15]



6 **1**



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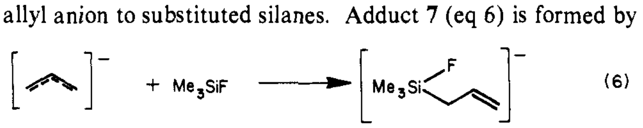
We have also observed several instances of direct addition of allyl anion to substituted silanes. Adduct **7** (eq 6) is formed by



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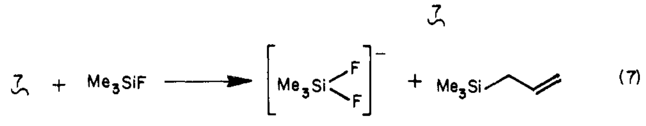

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[7] Product distributions are determined by extrapolating ion densities to zero flow of added neutral reactant. This excludes contributions from secondary reactions. Care has been taken to minimize mass discrimination. Values are reproducible up to ~5%.

[8] Product distributions (adduct/ring cleavage) for reaction of F^- with **2** and **3** are 61%/39% and 24%/76%, respectively.

[9] A referee has suggested that F^- may attack the α-carbon of **1**, giving concerted elimination of C_2H_4 and $FCH_2SiMe_2^-$. This is an alternative formulation which seems possible, although not as probable to us.

[10] DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012–5015.

[11] SO_2F^- is produced by dissociative electron attachment to SO_2ClF. The fluoride affinity of SO_2, or the bond strength $D(SO_2\text{–}F^-)$, is estimated to be 45 ± 5 kcal/mol on the basis of F^- transfer reactions in: Sullivan, S. A.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *28*, 69–80.

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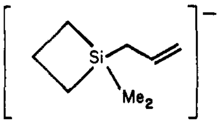
addition of allyl anion to $(CH_3)_3SiF$. The subsequent reaction (eq 7) of **7** with the fluorinated silane clearly indicates that Si–C bond formation occurs in adduct **7** and is consistent with the expected higher F^- affinity of $(CH_3)_3SiF$ compared to $(CH_3)_3SiC_3H_5$. Allyl anion also adds to **1** giving adduct **8**, which we believe is the first report of a silicon anion bearing five carbon substituents.



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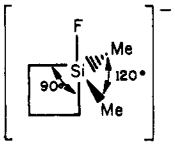
Our results are consistent with the trigonal-bipyramidal (tbp) geometry for these pentavalent silicon anions in which strain in the four-membered ring is relieved by allowing it to span one equatorial and one apical position (see structure **9**). The results



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are also in accord with the enhanced reactivity of strained cyclosilanes in nucleophilic reactions in solution[1,16] for which a similar explanation has been given and lend support to the intermediacy of such ions in chemical reactions of silanes. We had expected that **3** would have a much higher F^- affinity than either **1** or **2** because strain could be relieved in both rings; it turns out, however, that these F^- affinities are quite close to each other (probably <3 kcal/mol). We suggest that this is because F in the adduct of **3** must take an equatorial position if both silacyclobutanes are to span equatorial and apical positions. This is not a favorable orientation for F, whose apicophilicity is large.[17]

A simple mechanistic description of the reactions of F^- with silacyclobutanes would be a competition between the unimolecular fragmentation of an excited F^- adduct and the stabilization of that adduct by nonreactive collisions with He carrier gas. It is expected that direct anion addition will result in adducts which have excess energy due to Si–F bond formation. This mechanism predicts that the product distribution (adduct vs. ring cleavage) in reactions like (1) and (2) will be dependent on He pressure. We find that the reaction of F^- with **1** proceeds on approximately every collision with $k_{exp} = (2.1 \pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.[18] Both k_{exp} and the product distribution of this reaction remain constant over the pressure range 0.20–0.50 torr. Similar experiments with argon as the carrier gas gave identical kinetic results. Apparently this simple mechanism does not adequately describe the reactions reported. One possible explanation is that in these reactions adduct formation and ring cleavage proceed through energetically or structurally different intermediates.

We are presently continuing our studies of the kinetics and energetics of the formation of pentacoordinate silicon anions as well as further mechanistic studies of gas-phase anion reactions with silanes.

Acknowledgment. This work was supported by The Council on Research and Creative Work of the University of Colorado Graduate School and grants from the National Science Foundation, the Army Research Office, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. R.D. expresses thanks to the University of Michigan, Chemistry Department, for the hospitality extended during sabbatical leave.

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(18) The collision rate is calculated by using the Langevin model $k = 2\pi q(\alpha/\mu)^{1/2}$. For the reaction of F^- with **1**, $k_{collision} = 1.97 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} when an estimated α of 11.3 Å^3 is used, based on comparison to similar compounds.

Thermodynamics of Solution of Nonpolar Gases in a Fused Salt. "Hydrophobic Bonding" Behavior in a Nonaqueous System

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Received July 14, 1980

Water is frequently considered to be a unique liquid. Its crucial role in biochemical systems is surely without parallel. It is often considered that its biochemical primacy derives from its abiliy to promote aggregation of the nonpolar chains of many amphipathic molecules, such as phospholipids, to produce biomembranes. This relationship of their organizing ability in biochemical systems to the unusual thermodynamics of solution of nonpolar compounds in water has been articulated persuasively by a number of authors, particularly Kauzman[1] and Tanford,[2] following the seminal paper of Frank and Evans[3] which drew attention to the peculiar thermodynamic situation and attempted to relate it to changes in the three-dimensional structure of water evoked by the introduction of nonpolar solutes.

In this preliminary report we will show thermodynamic properties of solution which are highly reminiscent of their behavior in water for several nonpolar gases in pure, anhydrous ethylammonium nitrate—a fused salt which is liquid down to 12 °C. Table I compares the Henry's law constant, standard free energy, enthalpy, and entropy for solution of krypton, methane, ethane, and *n*-butane in the fused salt (FS) and corresponding values for solution in water and cyclohexane (CX). The derived properties for transfer to CX from FS and H_2O are also listed in parentheses. Clearly, the magnitudes of the three principal thermodynamic properties are closely parallel in both polar media and are sharply differentiated from those in the nonpolar one. Although the range of free energies is slightly larger for solution in water than in FS, the range of enthalpies and entropies is larger for solution in the salt, and it is these latter properties which are often considered to be the primary manifestations of hydrophobic effects.[1-3] Other important thermodynamic properties for transfer demonstrate that the familar pattern of a large loss of free energy dominated by an increase in entropy which is associated with the transfer of nonpolar solutes from water to nonpolar solvents is recapitulated for transfer from FS to CX. The entropy and enthalpy changes are smaller for the fused-salt solutions, and the Barclay–Butler $\Delta S°_s/\Delta H°_s$ slope, which originally served to differentiate aqueous solutions[3] from those in other media, is intermediate for FS, between those in CX and H_2O.

Clear evidence for micelle formation has also been obtained from the observation of critical micelle concentrations of several surfactants (including CTAB) in FS, by both surface tension and light scattering measurements.[4]

We do not as yet have information comparing these properties with those for solution in other fused salts. It would be rash to speculate at this time on what structural or physical factors are behind the similarities in behavior of the aqueous and FS systems. In addition to the presumed high polarity and internal pressure,

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