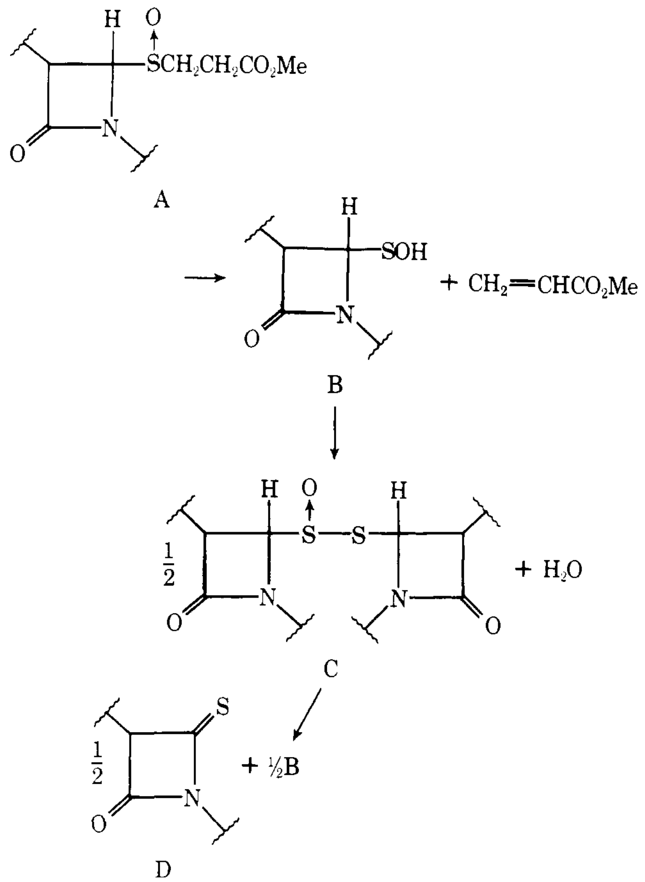
Scheme I



matic); ν_{max} (CHCl$_3$) 1830, 1785, and 1730 cm^{-1}; mass spectrum *m/e* (M$^+$ 446, 390, 334, 203, and 187). Presumably, the formation of these azetidin-2-oxo-4-thiones involves the sequence shown in Scheme I.[10] Methyl acrylate is eliminated from the carbomethoxyethyl sulfoxide A with concomitant formation of the sulfenic acid B which undergoes self-condensation to the thiolsulfinate ester C. Fragmentation of C results in the formation of the azetidin-2-oxo-4-thione D and the sulfenic acid B which is recycled.

Like in the penicillins and in the cephalosporins, the strained four-membered ring in **11** and in **12** is highly substituted by heteroatoms, and as judged from its high C=O stretching frequency, the amide bond lacks the normal amide resonance stabilization to an even more pronounced degree than in the bicyclic β-lactam antibiotics.[11] These structural features are expected to impart to the azetidin-2-oxo-4-thiones a high and versatile chemical activity which is now being investigated.

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Mario D. Bachi,* Jacob Vaya
Department of Organic Chemistry
The Weizmann Institute of Science
Rehovot, Israel

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Extensive Redistribution of Fluorine and Hydrogen in the Reaction of CF_3^+ with SiH_4[1]

Sir:

In a study of the reaction of CF_3^+ with SiH_4 in the gas phase, we have observed a very extensive redistribution of fluorine and hydrogen between carbon and silicon centers which must occur within a single collision complex.

CF_3^+ ions were formed from either CF_4 or CF_3Cl in an electron-impact ion-source, separated from the other ions, that were simultaneously produced, by a quadrupole mass filter, and injected at barycentric energies of 0.3–10 eV into a collision cell containing SiH_4 at a pressure of 1.0×10^{-3} Torr. In related experiments SiH_3^+ ions were formed by electron impact on SiH_4 and reacted with CF_3H in the collision chamber. The ions produced by the collisions were mass analyzed by a second quadrupole mass filter and detected by an electron multiplier. The details of the apparatus have been described previously.[2]

^{28}Si monoisotopic mass spectra for several relative kinetic energies of reactants are shown in Table I, the intensities of all ions having been corrected for contributions due to the naturally occurring ^{29}Si(4.7%) and ^{30}Si(3.1%) isotopes. Identification of the product ions was confirmed by observation of the mass shifts, if any, that resulted when SiH_4 was replaced by SiD_4.

At all three relative kinetic energies of the reactants the predominant product ion is SiH_3^+. On the basis of available thermochemical data[3-5] the only electrically neutral product that is energetically feasible at 1.3 eV is CF_3H and hence the predominant reaction must be written as in eq 1.

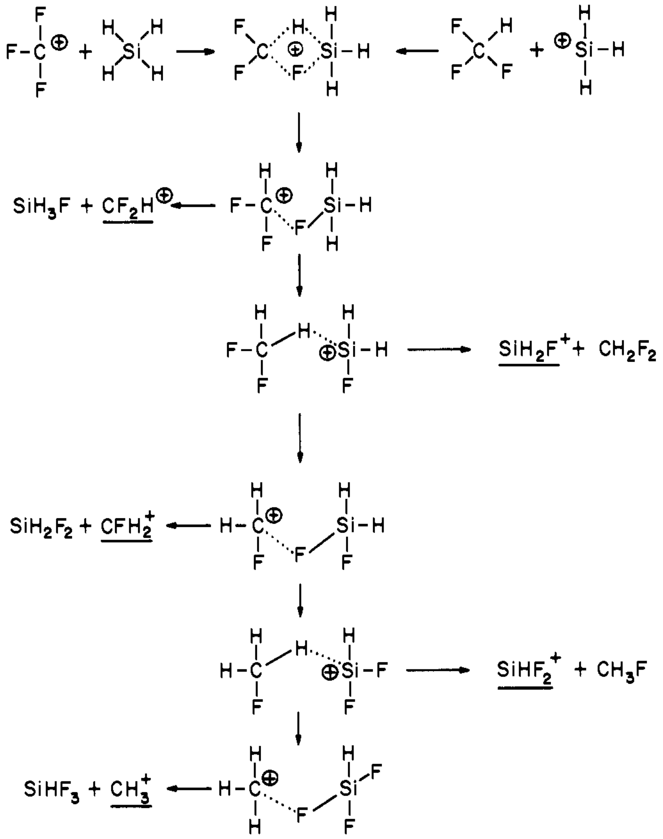
$$CF_3^+ + SiH_4 \rightarrow CF_3H + SiH_3^+ \qquad (1)$$

Table I. ^{28}Si Monoisotopic Mass Spectra of CF_3^+ + SiH_4 Reaction

m/e	Ion	Relative intensity at barycentric energy 1.3 eV	3.2 eV	9.5 eV
12	C^+	—	—	3
13	CH^+	—	0.5	14
14	CH_2^+	—	0.5	3
15	CH_3^+	18	17	3
29	SiH^+	11	24	215
30	SiH_2^+	15	49	150
31	SiH_3^+	1000	1000	1000
33	CFH_2^+	17	*a*	*a*
47	SiF^+	6	12	135
49	SiH_2F^+	69	262	438
50	CF_2^+	40	54	244
51	CF_2H^+	283	307	250
67	$SiHF_2^+$	*b*	*b*	*b*

[a] Definitely present but obscured by isotopic contribution of $^{30}SiH_3^+$. [b] Definitely present but not measurable quantitatively due to proximity of CF_3^+ reactant ion.

Scheme I



As the kinetic energy of the reactants is increased there is an enhanced formation of other products, including those such as SiH_2^+, SiH^+, CH_2^+, CH^+, and C^+ which are formed in endothermic processes.

The fact that eq 1 is the major reaction in CF_3^+-SiH_4 collisions is not surprising, since it is well documented that the major reaction of silanes with positive ions is hydride transfer.[6-9] Furthermore, kinematic studies of the H^- transfer from silanes have shown that the reaction proceeds mainly by a direct stripping-type mechanism as contrasted to the formation of a long-lived intermediate complex.[11] The surprising feature of the reaction is that at low kinetic energies ions such as CH_3^+, CH_2F^+, and $SiHF_2^+$, which represent extensive redistribution of H and F atoms, are formed.

The surprising feature alluded to arises from the fact that, at the pressures used, the mean free path in the collision cell is ~30 times longer than the ion path and, hence, all products must result from a *single collision* of CF_3^+ and SiH_4. Thus to form CH_3^+, for which only the neutral products $SiHF_3$ (or SiF_2 + HF) are possible, a collision complex must be formed which holds together long enough for six (or seven) bonds to be broken and six bonds to be formed. In view of the tendencies of positive carbon centers to abstract hydride from silanes[6-9] and of positive silicon centers to abstract fluoride from fluorocarbons,[12] and on the basis of the known bridging properties of hydrogen and fluorine in inorganic[13] and organosilicon[14] chemistry, we propose the mechanism shown in Scheme I. In this mechanism the necessary long-lived complex is held together by alternating hydrogen and fluorine bridges that arise as hydride and fluoride are successively exchanged and the center of positive charge alternates between carbon and silicon. As the redistribution proceeds, the complex is pictured as passing continually through double-bridged structures, the first of which is shown at the top of Scheme I. Stable product ions may be formed by random unimolecular break-up of the complex at various stages and those ionic products actually observed are underlined. The rate constant for the total reaction of CF_3^+ with SiH_4 at 1.3 eV is 6.5×10^{-10} cm³/s.

In confirmation of the mechanism proposed in Scheme I is the fact that the same extensive redistribution products are formed in SiH_3^+ collisions with CF_3H, a system which results in the same intermediate collision complex and presumably the same mechanism. The entrance into the mechanistic sequence from these reactants is shown in the upper right of Scheme I. It is interesting that the extensive redistribution products are definitely not observed in collisions of SiH_3^+ with CF_4.

The fall-off in yield of CH_3^+ and CH_2F^+ at the higher energies (Table I) is in accord with a shorter complex lifetime and the existence of more energetically feasible reaction channels, as the internal energy of the complex is increased.

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J. R. Krause, F. W. Lampe*
Davey Laboratory, Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

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Deuterium Labeling Studies of Bicyclo[3.1.0]hexatriene

Sir:

We had previously reported preliminary results which were compatible with the intermediacy of bicyclo[3.1.0]hexatriene (I) when *exo,exo*-4,6-dibromobicyclo[3.1.0]hex-2-ene (II) was treated with potassium *tert*-butoxide.[1] A priori, the conversion of II to 6-*tert*-butoxyfulvene (III) in high yield resulted either from two HBr eliminations accompanied by the addition of *t*-BuOH or an HBr elimination followed by the substitution of *tert*-butoxide for bromide. III was accompanied by two minor side products, 6-bromofulvene and bromobenzene, which clearly arose by different mechanistic pathways. To further substantiate our initial claim, we examined the deuterium isotope effect on product distribution.

By labeling the halogens at C_4 and C_6 we demonstrated that bromobenzene was formed by loss of the C_4 hydrogen and C_6 halogen. The 6-bromofulvene presumably was the result of a cis 1,4 HBr elimination generating 6-bromobicyclo[3.1,0] hexa-1,3-diene (IV) which then underwent a disrotatory