they have relatively weak acidic properties but with $GeCl_4$ stronger than $SiCl_4$.[7,8,27] Thus the spectroscopic probe of the intact complex, Δa_N, seems to be measuring a somewhat different property than displayed in complex formation.

Although the groups attached to the tin atom of compound S make it an unusual Lewis acid, its study has afforded a direct comparison between R_2NO and a more conventional base. The ability of DTBN to compete favorably with THF (for compound S) but not with pyridine (for $SnCl_4$) established its Lewis base character within the framework of more ordinary chemical experience. Previous estimates of the basicity of R_2NO, obtained from measurement of ΔH_f for adducts of TMPN with H-bonding Lewis acids, indicate that TMPN is a stronger base than acetone.[24]

Comparing group IVb and IVa (Figure 5), we see than a_N for $TiCl_4$ is slightly greater than that for $SnCl_4$. Within group IVb, the great difference between Δa_N for $TiCl_4$ and $Ti(OPh)_4$ is perhaps somewhat surprising in view of the reported Mulliken electronegativities: Cl, 9.4; Br, 8.4; OPh, 8.5.[28] On the basis of these electronegatives and the fact that $\Delta a_N(TiCl_4) \gtrsim \Delta a_N(SnCl_4)$ one might predict that Δa_N for Ti(OPh) should be slightly greater than that for $SnBr_4$, whereas it is considerably less. This discrepancy may result from a sensitivity of the effective electronegativity of a group (*i.e.*, OPh) to the atom to which it is bonded. The use of a very sterically hindered reference base interacting with the relatively sterically hindered $Ti(OPh)_4$ may also serve to reduce Δa_N.

Although the results for nitroxide complexes with the group III trihalides have been previously detailed,[4] it is interesting to note in Figure 5 the large difference between Δa_N for this class of acids and for the group IV tetrahalides. We also see that even with the substantial reduction in Δa_N upon going from $AlCl_3$ to $Al(i\text{-}Bu)_3$[29] still $\Delta a_N(Al(i\text{-}Bu)_3) \approx \Delta a_N(SnCl_4)$.

Results for hydrogen-bonded, $R_2NO \cdot HOR$, adducts have been included primarily for illustrative purposes. These adducts form in the highly polar ROH, and thus the values of Δa_N may not be strictly comparable to those observed for the MX_n adducts. Nevertheless, it is interesting to note that the largest values of Δa_N produced by H bonding exceed those for the weaker acids of group IV. The Δa_N of the H-bonding Lewis acids ROH can be readily accounted for by the obvious differences in the electronegativities of the R groups.

We have studied R_2NO complexes with group IV Lewis acids and have compared our results with other measurements of their acceptor strengths as well as with the ordering of the group III Lewis acids. Changes in nitroxide ^{14}N hfs are a readily measured and convenient scale of relative acceptor strengths. Although in many cases the complexes are unstable at room temperature, they can usually be studied at low temperatures. This technique, applicable to the study of a wide variety of molecular Lewis acids in solution, can be further extended to the investigation of catalytically interesting surface acidic sites.[30]

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Registry No. $Ti(OPh)_4 \cdot$DTBN, 51202-21-2; $GeCl_4 \cdot$DTBN, 51176-02-4; $SiCl_4 \cdot$DTBN, 51176-03-5; S·DTBN, 51130-07-5; $SiF_4 \cdot$DTBN, 51176-04-6; $SnBr_4 \cdot$DTBN, 51176-05-7; $SnCl_4 \cdot$DTBN, 51176-06-8; $TiCl_4 \cdot$DTBN, 51176-07-9; DTBN, 2406-25-9; TMPN, 2564-83-2; $GeCl_4 \cdot$TMPN, 51176-08-0; $SiCl_4 \cdot$TMPN, 51176-09-1; $SiF_4 \cdot$TMPN, 51176-10-4; $SnCl_4 \cdot$TMPN, 51176-11-5.

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Reactions of Gaseous Inorganic Negative Ions. V. Dissociative Electron Capture and Ion-Molecule Reactions in Methylfluorosilanes[1]

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The negative ion mass spectra of methylfluorosilanes $(CH_3)_nSiF_{4-n}$ ($n = 4$–1) measured at low pressure and at low electron energies are characterized by the loss of atomic hydrogen and atomic fluorine from the parent molecule negative ion. The dominant ions are those formed by loss of hydrogen atoms. Elimination of neutral HF is a characteristic reaction of the $(P - H)^-$ ion where $(P - H)^-$ represents parent molecule ion minus a hydrogen atom. Negative ion-molecule reactions of the methylfluorosilanes with SF_6^- involve fluoride ion transfer. Rate constants and reaction cross sections have been measured as a function of primary ion energy. The reaction cross section shows a dramatic decrease in magnitude as fluorine is replaced by methyl groups in the series of compounds. The magnitude of the reaction cross section among the series of compounds varies in a manner similar to the known stability of the pentavalent methylfluoro anions in condensed phases.

Introduction

Primary and secondary negative ion formation in nonmetal fluorides has been studied by several investigators.[2,3] The investigations have had as their goal the characterization of negative ion formation processes, evaluation of ionic heats

(1) Presented in part at the 21st Meeting of the American Society for Mass Spectrometry, San Francisco, Calif., May 1973.

(2) T. C. Rhyne and J. G. Dillard, *Int. J. Mass Spectrom. Ion Phys.*, 7, 371 (1971); *Inorg. Chem.*, 10, 730 (1971); *J. Amer. Chem. Soc.*, 91, 6521 (1969).

of formation, and the measurement of rate constants and reaction cross sections. Several studies of the negative ions formed in silicon compounds have been published.[4-7]

The negative ions in methylchlorosilanes and the reactions of the silanes with SF_6^- and O^- have been reported by Jager and Henglein.[6] The primary processes for ion formation at low pressures occur by C-H and Si-C bond cleavage reactions. In the ion-molecule reactions with SF_6^- the most important process is collisional dissociation producing Cl^-. Reactions with O^- also yield secondary ions produced predominantly by dissociative charge transfer, although in some instances O^- impact eliminates neutral chlorine atoms producing the species $[(CH_3)_nSiCl_{3-n}O]^-$.

Pentacoordinate anions of methylfluorosilanes have been studied[8] in solution using ^{19}F nmr to examine the behavior and probable structure of the anions. The spectra are consistent with a trigonal-bipyramidal geometry. In the presence of fluoride ion rapid intermolecular exchange occurs according to

$$RSiF_4^- + F^{*-} \rightleftharpoons RSiF_3F^{*-} + F^- \qquad (1)$$

The purpose of the present study was to characterize the negative ions formed at low pressures, to elucidate the ion-molecule reactions occurring with SF_6^- and the methylfluorosilanes, and to discover the variation in reaction cross section with changes in the substituent groups attached to silicon.

Experimental Section

The methylfluorosilanes CH_3SiF_3, $(CH_3)_2SiF_2$, and $(CH_3)_3SiF$ were purchased from PCR Inc. Low-voltage positive ion mass spectra indicated that no significant (<2%) impurities were present, so the compounds were used without additional purification. Tetramethylsilane (nmr grade) was purchased from Alfa Inorganics, and SF_6 from Matheson Gas Products. Silane was prepared according to procedures in the literature.[9]

The mass spectrometer used in this study was a Hitachi Perkin-Elmer RMU-6 single-focusing instrument. The ion source envelope is pumped by a high-speed diffusion pump so that pressures in the region remain below 5×10^{-6} Torr for a typical source pressure of 20 μ. The ion source, data acquisition procedures, and methods of obtaining and evaluating data have been described previously.[2] Low-pressure mass spectra (10^{-7}–10^{-6} Torr) and dissociative capture processes were studied using an RMU-7 mass spectrometer described earlier.[10]

For the methylfluorosilanes, the source-conditioning time[2] was less than 1 hr. In each case however the sample was admitted to the instrument for at least 1 hr before any ion current or ionization efficiency curve measurements were carried out.

Results and Discussion

Low-Pressure Mass Spectra. The primary ions detected in three of the silanes investigated, CH_3SiF_3, $(CH_3)_2SiF_2$, and $(CH_3)_3SiF$, are summarized in Table I. The relative abundance of each ion measured at the maximum in the resonance-capture process and a probable process for ion formation are given in the table. The abundance represents the monoisotopic abundance which has been corrected for the silicon-29 and -30 isotopes and for carbon-13. Although no attempt was made to compare accurately the abundances of ions from one compound to another, the intensity and total ion current varied in the manner $CH_3SiF_3 > (CH_3)_2SiF_2 > (CH_3)_3SiF$. When spectra were measured at the same ion source pressure, the total ion current varied by approximately a factor of 10 from CH_3SiF_3 to $(CH_3)_3SiF$.

The most abundant ions in each compound are those formed by cleavage of the C-H bonds. With the exception of CH_3SiF_3 the $(P - H)^-$ $[(\text{parent} - H)^-]$ ion is the most abundant species at low energies. Even so, the abundance of $CH_2SiF_3^-$ is rather large (28%) at low energies. At 50 eV, the most abundant ion is the $(P - H)^-$ species for all three methylfluorosilanes. Other important ions are those formed by loss of hydrogen and the methyl group. For dimethyl- and trimethylfluorosilanes the loss of HF from the $(P - H)^-$ ion is an important reaction and the elimination of HF represents a favorable process for cleavage of the SiF bond. The intensity of the $[(P - H) - HF]^-$ ion from CH_3SiF_3 was too low (<1%) to measure precisely its ionization efficiency curve. The most important process for cleavage of the Si-F bond in CH_3SiF_3 is *via* loss of fluorine atom yielding $CH_3SiF_2^-$.

The fragmentation processes producing silicon-containing ions for the methylfluorosilanes are similar to those reported[6] for the methylchlorosilanes in that C-H and Si-C bond cleavage reactions are important processes. In contrast, however, the most abundant ion at low energies in the chlorosilane derivatives is Cl^-. As noted in Table I, F^- is formed in low abundance while the $(P - H)^-$ and $(P - H_2)^-$ ions are intense in the methylfluorosilanes. The factors which contribute to this difference must include the greater electronegativity of fluorine in the fluorosilanes and the lower silicon-chlorine bond energy for chlorosilanes.

The dissociative capture processes are characterized by a single maximum with the exception of *m/e* 67, $HSiF_2^-$ in $(CH_3)_2SiF_2$. In the compounds the capture processes occur above 5 eV with no ions detected below 5 eV. The presence of more than one maximum in the $HSiF_2^-$ ion current curve is evidence that this rearrangement ion may be formed from two different precursor ions or from different states of a single ion.

No parent molecule negative ions were detected at any electron energy in any of the compounds. Measurements were carried out at *m/e* values corresponding to ^{28}Si for the P^- ion which is also $(P - H)^-$ for ^{29}Si. A resonance capture curve, over the energy range from near zero to 10 eV, identical with that for $(P - H)^-$ (^{28}Si) was obtained in each case. This result is expected since parent molecule negative ions at higher energies would be formed *via* secondary processes. At near zero eV the $(P - H)^-$ ions are not formed, so no interference from these ions occurs and identification of parent molecule ions would be facilitated. Mass spectra were determined at *m/e*'s for the parent molecule ions at near thermal electron energies and no parent molecule ions were detected. If formed, the relative abundance of the parent molecule ions must be less than about 0.01%. The important point is that no ions from the methylfluorosilanes are formed at low electron energies where SF_6^- and SF_5^- are formed in SF_6.

Because of the rather low intensities of the negative ions no metastable ions were noted so that processes suggested in Table I are deemed the most reasonable based on the energetic measurements.

Ion-Molecule Reactions. The reactions of negative ions from SF_6, namely, SF_6^- and SF_5^-, at low electron energies with CH_3SiF_3, $(CH_3)_2SiF_2$, $(CH_3)_3SiF$, $(CH_3)_4Si$, and SiH_4 were investigated. In these studies SF_6 pressure was nominal-

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Table I. Negative Ions Formed in Methylfluorosilanes at Low Pressures and at Low Electron Energies

Silane	Ion	Rel abund	Onset, eV	Max, eV	Process
CH_3SiF_3	F^-	8.2		11.5	$CH_3SiF_3 + e^- \rightarrow F^- + CH_3SiF_2$
	$CH_3SiF_2^-$	22	9.6	11.5	$\rightarrow CH_3SiF_2^- + F$
	SiF_3^-	12	7.7	10.1	$\rightarrow SiF_3^- + CH_3$
	$CSiF_3^-$	3.2	9.7	12.3	$\rightarrow CSiF_3^- + H_2 + H?$
	$CHSiF_3^-$	100	8.6	11.1	$\rightarrow CHSiF_3^- + H_2$
	$CH_2SiF_3^-$	28	7.9	10.6	$\rightarrow CH_2SiF_3^- + H$
$(CH_3)_2SiF_2$	F^-	10		17.2	$(CH_3)_2SiF_2 + e^- \rightarrow F^- + (CH_3)_2SiF$
	CH_2SiF^-	38	5.5	6.7	$\rightarrow CH_2SiF^- + CH_3 + HF?$
	SiF_2^-	19	5.3	6.7	$\rightarrow SiF_2^- + 2CH_3?$
	$HSiF_2^-$	1	5.7	6.6	$\rightarrow HSiF_2^- + ?$
	$HSiF_2^-$	2	7.8	10.3	$\rightarrow HSiF_2^- + ?$
	$(CH_2)_2SiF^-$	11	5.5	9.1	$\rightarrow (CH_2)_2SiF^- + H + HF$
	$CH_3SiF_2^-$	47	5.5	6.8	$\rightarrow CH_3SiF_2^- + CH_3$
	$C_2H_3SiF_2^-$	2	7.9	9.8	$\rightarrow C_2H_3SiF_2^- + H_2 + H?$
	$(CH_2)_2SiF_2^-$	57	7.1	9.8	$\rightarrow (CH_2)_2SiF_2^- + H_2$
	$(CH_3)(CH_2)SiF_2^-$	100	6.0	8.7	$\rightarrow (CH_3)(CH_2)SiF_2^- + H$
$(CH_3)_3SiF$	F^-	5	7.2	9.5	$(CH_3)_3SiF + e^- \rightarrow F^- + (CH_3)_3Si$
	$(CH_2)_2CH_3Si^-$	5	6.3	7.8	$\rightarrow (CH_2)_2CH_3Si^- + H + HF$
	$(CH_2)_2SiF^-$	5	6.2	7.8	$\rightarrow (CH_2)_2SiF^- + H_2 + CH_3?$
	$(CH_2)_3SiF^-$	5	7.0	10.2	$\rightarrow (CH_2)_3SiF^- + H + H_2?$
	$(CH_2)_2CH_3SiF^-$	20	7.2	9.5	$\rightarrow (CH_2)_2CH_3SiF^- + H_2$
	$(CH_2)(CH_3)_2SiF^-$	100	5.4	8.0	$\rightarrow (CH_2)(CH_3)_2SiF^- + H$

ly 3.0 μ and the pressure of the silane was varied from 0.5 to 20.0 μ. The important reaction in the binary mixtures is fluoride ion transfer from SF_6^-. In Figure 1 a comparison of the ionization efficiency curves for SF_6^-, SF_5^-, and $(CH_3)_2SiF_3^-$ recorded at a repeller voltage of 2.0 V indicates that the primary ion is SF_6^-. The fluoride ion transfer reaction from SF_6^- (reaction 2) appears to be the dominant

$$SF_6^- + (CH_3)_nSiF_{4-n} \rightarrow (CH_3)_nSiF_{5-n}^- + SF_5 \qquad (2)$$

reaction at least to repeller potentials of 4.0 V. The ionization efficiency curves at repeller potentials from 1.5 to 4.0 V are similar to that shown in Figure 1. At the higher repeller potentials there is some slight broadening of the $(CH_3)_2SiF_3^-$ ionization efficiency curve, but the energy maximum and shape correspond most closely with that of SF_6^-. Similar behavior was observed for the other methylfluorosilanes.

In the mixture of SF_6 and $(CH_3)_4Si$ a very weak ion at *m/e* 107 was easily noted at 50 eV and barely discernible at low electron energies corresponding to the maximum in the SF_6^- ionization efficiency curve. Unfortunately accurate measurement of the *m/e* 107 ion current was not practical at low electron energies due to the presence of the broad *m/e* 110.4 metastable transition ($SF_6^- \rightarrow SF_5^- + F$). At the sensitivities required to detect $(CH_3)_4SiF^-$, the ion current was barely discernible on the low mass portion of the *m/e* 110.4 metastable species. Only an upper limit to the reaction cross section of about 3×10^{-18} cm^2/molecule at 2.0-V repeller can be reported. No attempt was made to measure the ionization efficiency curve for $(CH_3)_4SiF^-$, so it is assumed that the primary reactant ion was SF_6^-.

In the SF_6-SiH_4 mixture no evidence for SiH_4F^- was obtained at high electron energies (50-100 eV) where the SF_6^- ion current is large due to secondary electron-capture processes. The SiH_4F^- ion also was not detected at low electron energies corresponding to the maximum in the SF_6^- ionization efficiency curve. An upper limit for the reaction cross section of about $(0.5-1.0) \times 10^{-18}$ cm^2/molecule may be established for the fluoride ion transfer reaction of SF_6^- with SiH_4.

Parent molecule negative ions arising from charge-transfer reactions at low electron energies involving SF_6 negative ions (SF_6^- and SF_5^-) were not detected. In addition, collison-induced dissociative processes were not observed at low electron energies and for the ion energies studied. Upper limits for the cross section for the nonobserved reactions may be placed at about 10^{-18} cm^2/molecule.

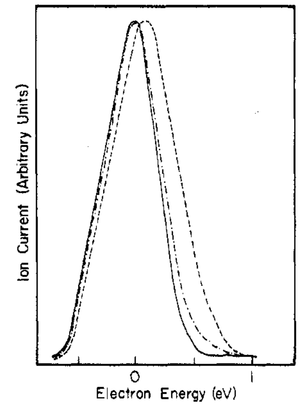

Figure 1. Ionization efficiency curves for SF_6^- (——), SF_5^- (- - - - -), and $(CH_3)_2SiF_3^-$ (- · - · -) in mixtures of SF_6 and $(CH_3)_2SiF_2$.

The phenomenological reaction cross sections and rate constants for the reactions of SF_6^- with the three methylfluorosilanes are presented in Tables II and III, respectively. The cross sections were measured for average SF_6^- ion energies from 0.56 to 1.5 V. With the exception of $(CH_3)_3SiF$ the cross sections show a decrease in magnitude with increasing ion energy, a behavior characteristic of an exothermic process. The values for $(CH_3)_3SiF$ are less accurate than those for the dimethyl- and methylfluorosilanes because the ion current was measured at high sensitivities of the mass spectrometer detection system. In addition, the *m/e* 111 peak intensity at low $(CH_3)_3SiF$ pressure and high repeller potentials was difficult to measure due to the metastable peak ($SF_6^- \rightarrow SF_5^- + F$) at *m/e* 110.4. The precision of the measurement was about 20-30% under these conditions for $(CH_3)_3SiF_2^-$ ion formation.

The magnitude of the cross section for each compound is of importance in correlating fluoride ion acceptor ability with molecular structure. The effective electronegativity, α, of substituents on silicon has been evaluated by Jensen[11] using ^{29}Si-H coupling constants in a series of halosilanes.

[11] M. A. Jensen, *J. Organometal. Chem.*, **11**, 423 (1968).

Table II. Reaction Cross Section for the Formation of Secondary Ions as a Function of Repeller Voltage

Repeller voltage, V	Cross section × 10^{16}, cm^2/molecule		
	$CH_3SiF_4^-$	$(CH_3)_2SiF_3^-$	$(CH_3)_3SiF_2^-$
1.5	49.6	15.8	0.398
2.0	38.3	15.3	0.549
2.5	31.7	12.6	0.396
3.0	30.5	11.6	0.464
3.5	26.8	7.57	0.596
4.0	26.2	7.37	0.590

Table III. Rate Constants for the Formation of Secondary Ions as a Function of Repeller Voltage

Repeller voltage, V	Rate const × 10^{10}, cm^3/(molecule sec)		
	$CH_3SiF_4^-$	$(CH_3)_2SiF_3^-$	$(CH_3)_3SiF_2^-$
1.5	2.14	0.681	0.0172
2.0	1.91	0.761	0.0273
2.5	1.76	0.701	0.0220
3.0	1.86	0.707	0.0283
3.5	1.76	0.498	0.0392
4.0	1.84	0.519	0.0415

The value of α for fluorine is −2.67 eV; that for CH_3 is 0.36 eV. If the sum of the various group electronegativities is taken and the value of the sum used as an indication of the positive charge on silicon in the methylfluorosilanes, it is evident that the charge on silicon varies as $CH_3SiF_3 > (CH_3)_2SiF_2 > (CH_3)_3SiF > (CH_3)_4Si$. From the data in Table II, the cross section for fluoride ion transfer varies just in the same order for the compounds. A more definitive illustration of the variation in the reaction cross section is shown in Figure 2. In the figure the reaction cross section at a particular ion energy (0.94 eV, 2.5-V repeller) is plotted *vs.* the sum of the effective electronegativity. The cross section data for SiF_4[2b] are also included for comparison. The variation in cross section follows a straight line although there is no theoretical reason for expecting this behavior. The representation provides a means for predicting the variation in cross section as a function of substituent electronegativity. The significant point is that if the reaction cross section for fluoride ion transfer is an indication of the relative acidities of silanes in the gas phase,[2] the acidity varies directly with the negative of the sum of the electronegativities for the substituents attached to the central atom. These data are consistent with the previously noted behavior of nonmetal fluorides.

The relative stabilities of pentacoordinate alkyl-substituted silicon anions in solution have been predicted to be $CH_3SiF_4^- > (CH_3)_2SiF_3^- > (CH_3)_3SiF_2^-$ from fluoride ion exchange studies.[8] It has been suggested that $(CH_3)_2SiF_3^-$ would be largely dissociated at room temperature and that the likelihood of $(CH_3)_3SiF_2^-$ formation in solution would be small. Such predictions put forth based on solution measurements compare favorably with the gas-phase results obtained in this study. The very small cross section for $(CH_3)_3SiF_2^-$ formation in the gas phase is no doubt due to the weak acceptor properties of $(CH_3)_3SiF$.

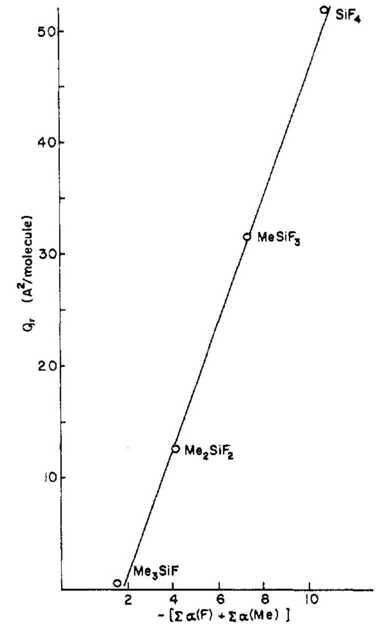

Figure 2. Variation of reaction cross section, Q_r, with the sum of effective electronegativity for substituents on silicon in $(CH_3)_nSiF_{4-n}$ compounds.

Table IV. Heats of Formation of Gaseous Neutral and Ionic Species

M(g)	ΔH_f, kcal/mol	M(g)	ΔH_f, kcal/mol
SF_6	−289[12]	$(CH_3)SiF_4^-$	−279.6[a]
SF_6^-	−289[3]		
SF_5	−234[3]	$(CH_3)_2SiF_3^-$	−200.4[a]
SF_5^-	−304[3]		
F	18.88[12]	$(CH_3)_3SiF_2^-$	−121.3[a]
SiF_4	−385.9[12]		
CH_3SiF_3	−294.6[13]	$(CH_3)_4SiF^-$	−42.2[a]
$(CH_3)_2SiF_2$	−215.4[a]		
$(CH_3)_3SiF$	−136.3[a]		
$(CH_3)_4Si$	−57.2[12]		

[a] Upper limits for ΔH_f; see text.

The nature of the reactions of SF_6^- with the methylfluorosilanes is in contrast to dissociative charge-transfer processes noted for methylchlorosilanes.[6] The dominant secondary ion reported is Cl^- in the SF_6^- reaction with $(CH_3)_nSiCl_{4-n}$ (n = 0-3). In $SiCl_4$, some $SiCl_3^-$ is observed, but the intensity is about a factor of 5 less than that for Cl^-. That Cl^- is the dominant secondary ion is no doubt due to the availability of a favorable reaction channel at low ion energies. By comparison there are no low-energy dissociative channels available for the methylfluorosilanes, so only fluoride ion transfer from SF_6^- occurs at low ion energies. The investitation of fluoride ion transfer processes at higher ion energies has not been carried out in this study.

The variation of the reaction cross section with average ion energy can be evaluated for CH_3SiF_3 and for $(CH_3)_2SiF_2$ from the reaction cross section data in Table II. Since both molecules have finite dipole moments, it might be expected that the cross section would vary as E^{-1} at the ion energies of this study, 0.56-1.5 eV. Examination of the cross section with ion energy indicates that the variation is approximately $E^{-0.67}$ for CH_3SiF_3 and $E^{-0.66}$ for $(CH_3)_2SiF_2$. This variation is intermediate between the $E^{-1/2}$ behavior expected for the ion-induced dipole and the E^{-1} variation expected for the ion-dipole model. For SiF_4 the approximate $E^{-1/2}$ variation is expected for a nonpolar molecule. That the variation of the cross section for the methylfluorosilanes is greater than $E^{-1/2}$ may indicate that the excess internal energy in the primary SF_6^- ion masks any variation due to ion-dipole interactions. Also since no data at thermal ion energies are available, it is not known what the behavior at lower ion energies would be. It is possible that at low ion energies the ion-dipole attraction would be sufficient to alter the cross section behavior. Because of the scatter in the cross section data for $(CH_3)_3SiF$ it is not reasonable to discuss the cross section variation with ion energy.

The ionic heats of formation calculated, assuming that at the ion energies studied the reactions are exothermic, are summarized in Table IV. The heats of formation of $(CH_3)_2SiF_2$ and $(CH_3)_3SiF$ were estimated from the known heats of formation of gaseous SiF_4,[12] CH_3SiF_3,[13] and $(CH_3)_4Si$.[12] From the available thermochemical data the replacement of a methyl group by a fluorine atom was estimated to lower the heat of formation by 79.1 kcal/mol. The heats of formation of other species are collected in the table. There are no available data with which to compare the calculated ionic heats of formation. The values reported in Table IV represent upper limits to the heats of formation since excess energy has not been measured or included in the calculations.

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Registry No. CH_3SiF_3, 373-74-0; $(CH_3)_2SiF_2$, 353-66-2; $(CH_3)_3SiF$, 420-56-4; $(CH_3)_4Si$, 75-76-3; SiH_4, 7803-62-5; SF_6^-, 25031-39-4; $(CH_3)SiF_4^-$, 44244-53-3; $(CH_3)_2SiF_3^-$, 51108-60-2; $(CH_3)_3SiF_2^-$, 51202-29-0; $(CH_3)_4SiF^-$, 51108-61-3.

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Spectra and Structure of Organogermanes. XVI.[1] Microwave Spectrum of Trimethylcyanogermane

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The rotational spectrum of trimethylcyanogermane has been recorded from 26.5 to 40.0 GHz. The ground-state rotational constants have been determined for 12 different isotopic species and r_s values of 1.155 ± 0.002 and 1.947 ± 0.006 Å have been determined for the CN and $Ge\overline{CN}$ distances, respectively. With these values and an assumed structure for the methyl group, the following two structural parameters were obtained: $r(GeC) = 1.930 \pm 0.006$ Å and $\angle CGe\overline{CN} = 106.2 \pm 0.1°$. The determined structural parameters are compared to the corresponding ones for other methyl-substituted germanes. The infrared spectrum in the 2100-cm^{-1} region indicates the presence of approximately 5% of the isocyanide in the sample.

Introduction

A systematic elongation of the C-X bond in $(CH_3)_3CX$ compounds in which X = H,[2a] Cl,[2b] C≡CH,[3] and C≡N,[3] in contrast to the similar bond in CH_3X, has been found. A similar situation is also found as one compares the SiBr bond distance (2.24 ± 0.02 Å) in trimethylbromosilane,[4] $(CH_3)_3SiBr$, with the similar distance in silyl bromide (2.209 ± 0.001 Å).[5] The GeCl bond distance (2.170 ± 0.001 Å) in trimethylchlorogermane,[6] $(CH_3)_3GeCl$, was determined to be 0.022 Å longer than the corresponding distance in germyl chloride[7] (2.148 ± 0.003 Å). Recently, we completed microwave studies of trimethylgermane[8] and trimethylbromogermane[9] and found additional examples of the general elongation effect in the trimethylgermyl compounds. As a continuation of our studies on the spectra and structure of organogermanes,[6,8,9] we have carried out a microwave investigation of trimethylcyanogermane. Isotopic species studied included $(CH_3)_3Ge^{12}C^{14}N$, $(CH_3)_3Ge^{13}C^{14}N$, and $(CH_3)_3Ge^{12}C^{15}N$ along with four of the naturally abundant isotopic species of the germanium atom. This experimental information should allow the determination of the r_s structure of Ge-C≡N and the r_0 structure of the trimethylgermyl moiety which, in turn, could be compared with corresponding distances in germyl cyanide.[10] We were also interested in the possibility of the presence of isocyanide in the sample of trimethylcyanogermane as a comparison to the case of trimethylsilyl cyanide in which some of the isocyanide has been found to coexist.[11]

Experimental Section

The $(CH_3)_3Ge^{12}C^{14}N$, $(CH_3)_3Ge^{13}C^{14}N$, and $(CH_3)_3{}^{12}C^{15}N$ molecules were prepared by the addition of AgCN containing the desired isotopes of carbon and nitrogen to $(CH_3)_3GeCl$.[12] The ^{13}C and ^{15}N isotopes were obtained from the British Oxygen Co. in the form of KCN. The $(CH_3)_3GeCl$ was purchased from Ventron Inorganics.

A 1-g KCN sample was treated with an equimolar quantity of $AgNO_3$, filtered, and dried in a vacuum desiccator for 24 hr in the dark. The resulting AgCN was suspended in benzene and allowed to react with $(GH_3)_3GeCl$; the mixture was refluxed for 24 hr. The AgCl was then removed by filtration and the benzene was removed by distillation at atmospheric pressure to concentrate the product. When the volume of the solution approached 5 ml, it was transferred to a ministill and the remaining benzene removed under vacuum. The remaining material was a slightly discolored product. This product was then vacuum distilled and collected in a receiver cooled with Dry Ice. The resulting white crystals were stable if not exposed to the air or elevated temperatures.

The microwave spectrum of trimethylcyanogermane was investigated in the R-band frequency range (26.5–40.0 GHz) by the use of a Hewlett-Packard Model 8460A MRR spectrometer. The Stark cell

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