Dissociation of SF$_6$, CF$_4$, and SiF$_4$ by Electron Impact

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The dissociation by electron-impact of SF$_6$, CF$_4$, and SiF$_4$ has been studied with a consolidated mass spectrometer. Data are also given on the appearance potentials of various ions in the mass spectra and measurements on the isotope abundance of sulfur, carbon, and silicon. The observed appearance potentials of the F$^+$ ion in SF$_6$ and CF$_4$, and the C$^+$ ion in CF$_4$ were found to be lower than the calculated value assuming formation of a positive atom ion and a free electron, but nearly equal to the calculated value assuming the formation of a positive atom ion and a negative fluorine ion. The large relative abundance of the SF$_4$$^{++}$ ion in SF$_6$ and the CF$_2$$^{++}$ ion in CF$_4$ is taken to indicate the formation of these ions by removal of two F$^-$ ions in the former and possibly an F$^-$ ion and a free electron in the latter case.

I. Introduction

The results reported in this paper are a part of a general study of the dissociation of volatile fluoro compounds by electron impact. Many of these compounds have been useful in isotope abundance studies of a number of the elements because of their relatively high vapor pressure and the monoisotopic character of fluorine. Apparently very little has been published, however, concerning the dissociation of such molecules by electron impact except to note in the isotope studies that dissociation, rather than formation of the molecular ion, is the more probable process. Kusch, Hustrulid, and Tate, [1],[1] and Baker and Tate [2] have shown that this is a property shared with the chlorides of phosphorous, arsenic, and antimony, as well as some halogen derivatives of methane namely, CCl$_4$, CHBrF$_2$, and CCl$_2$F$_2$. More recently, White and Cameron [3] have reported the critical potentials of various ions in the mass spectrum of UF$_6$. No value was listed for the UF$_6$$^+$ ion, presumably because of its very low intensity. No information was given as to the relative abundance of the various dissociated ions. In view of considerable interest in these compounds, therefore, we wish to report in detail the dissociation patterns for several fluorocompounds as well as the appearance potentials of various ions in the mass spectra. Data are also given on the isotope abundance of sulfur, carbon,

[1] Figures in brackets indicate the literature references at the end of this paper.

and silicon for purposes of comparison with value previously obtained for these elements using other types of mass spectrometers and other compounds.

II. Experimental Procedure

Pertinent details of the Consolidated mass spectrometer and the methods used to obtain the reported data have been described in detail in previous reports [4, 5]. The voltage scale of the appearance potential measurements was corrected using the observed value of the argon A$^+$ ion compared to the spectroscopic value [6]. The mass spectra were obtained at ionizing electron energies of 50, 70, and 100 volts. The most abundant ion in each 50-volt spectrum is assigned a value of 100 percent. The other ions are evaluated according to their abundance relative to the most abundant ion. The isotope abundance measurements were made at several different values of ion accelerating voltage and of electron energy and current. Whenever possible, the ratios were checked using different ions in the same mass spectrum. The fact that no significant variation in the isotope abundance ratios was observed under these conditions was assumed to indicate minimum discrimination in the ion source.

The SF$_6$ was obtained from the high voltage laboratory of the Massachusetts Institute of Technology and was a portion of a sample submitted to the Temperature Measurements Section of the Bureau for test purposes. Mass spectro-

metric analysis indicated an approximate purity of 99 percent with small amounts of fluorocarbons as impurities. It was used without further purification. The CF$_4$ was obtained from the Jackson laboratory, E. I. du Pont de Nemours Co., and used without further purification. Mass spectrometric analysis showed a total impurity of about 2 percent, principally CClF$_3$, N$_2$, and CO$_2$. Several samples of SiF$_4$ were prepared by Howard W. Bond [2] by reacting H$_2$SO$_4$ and CaF$_2$ in the presence of SiO$_2$ from various sources. These samples were also used without further purification. The mass spectrometer indicated a purity $>$99 percent. The principal impurity was CO$_2$.

III. Results and Discussion

Sulfur hexafluoride.—Table 1 shows the mass spectrum of SF$_6$ at three different ionizing voltages. No correction has been made in this or following mass spectrum tables for the contribution of the ion accelerating field to the electron energy. No SF$_6^+$ ion was observed. Its abundance is estimated to be less than 2/10,000 of the abundance of the SF$_5^+$ ion. The most probable dissociation process is loss of one fluorine atom from the molecular ion. In the formation of ions requiring further dissociation, however, the subsequent loss of three fluorine atoms from the molecular ion is more probable than the loss of 2 atoms. For example, the abundance of the SF$_3^+$ ion is greater than that of the SF$_4^+$ ion, and the SF$^+$ ion is more abundant than the SF$_2^+$ ion. The doubly charged ions S^{++}, SF^{++}, SF$_2^{++}$, SF$_3^{++}$, and SF$_4^{++}$ were observed. The ions F^{++}, SF$_5^{++}$, and SF$_6^{++}$ were not found and are estimated to be less than 0.02 percent of the SF$_5^+$ peak. It is of interest that for 100-volt electrons, the abundance of the SF$_2^{++}$ ion and SF$_4^{++}$ ion is greater than the abundance of the corresponding singly charged ions. The peak at m/e=91.8 is a metastable ion that has undergone dissociation after traversing the ion accelerating field [7]. It can be ascribed to the transition

$$SF_5^+ \rightarrow SF_4^+ + F.$$

If m_a is the apparent mass, m_i and m_f, the initial and final masses, respectively, $m_a = (m_f)^2/m_i = (108)^2/127 = 91.8$.

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[2] Now at the National Institute of Health, Bethesda, Maryland.

TABLE 1. *Mass spectrum of SF$_6$ for 50, 70, and 100-volt electrons*

m/e	Ion	Relative intensities		
		50 volts	70 volts	100 volts
16	S^{++}	0.03	0.06	0.09
19	F$^+$	3.37	5.63	9.11
25.5	SF^{++}	--------	0.76	1.97
32	S$^+$	5.60	9.96	13.5
33	S$^+$	0.06	0.09	0.11
34	S$^+$	.27	.47	.60
35	SF$_2^{++}$	1.36	6.80	13.3
35.5	SF$_2^{++}$	--------	0.10	0.10
36	SF$_2^{++}$	0.07	.33	.62
44.5	SF$_3^{++}$	0.38	1.26	2.17
45.5	SF$_3^{++}$	--------	0.07	0.11
51	SF$^+$	8.66	11.0	11.6
52	SF$^+$	0.07	0.09	0.11
53	SF$^+$	.40	.51	.64
54	SF$_4^{++}$	4.05	11.0	17.6
54.5	SF$_4^{++}$	--------	0.09	0.11
55	SF$_4^{++}$	0.23	.54	.78
70	SF$_2^+$	5.74	6.39	6.46
71	SF$_2^+$	0.04	0.07	0.09
72	SF$_2^+$	.27	.30	.27
89	SF$_3^+$	27.6	33.5	35.7
90	SF$_3^+$	0.20	0.26	0.24
91	SF$_3^+$	1.22	1.48	1.56
91.8	SF$_5^+ \rightarrow$SF$_4^+$+F	0.21	0.26	0.24
108	SF$_4^+$	8.98	10.8	11.5
109	SF$_4^+$	0.07	0.11	0.10
110	SF$_4^+$	.41	.47	.51
127	SF$_5^+$	100.	113	117
128	SF$_5^+$	0.92	1.14	1.15
129	SF$_5^+$	4.30	4.89	4.87
131	SF$_5^+$	0.04	0.04	0.04

Table 2 lists the appearance potentials of various ions in the mass spectrum of SF$_6$. A complete analysis of the appearance potential data is not possible because of the lack of necessary spectroscopic or thermochemical data. However, from the relation

$$D(SF_6) = Q(SF_6) + 3D(F_2) + L(S),$$

where $Q(SF_6)$ is the energy of formation of SF$_6$, $D(F_2)$ is the dissociation energy of molecular fluorine, $L(S)$ is the heat of sublimation of sulfur, and the thermochemical data of Bichowsky and Rossini [8] the energy of dissociation of the process SF$_6$— S+6F, is calculated to be 516 kcal/mole or 22.4 electron volts. It follows that the minimum energy required to produce an S$^+$ ion and a free electron will be $D(SF_6)$ plus the ionization poten-

tial (10.3 volts) [6] of sulfur (22.4+10.3=32.7 volts). The observed appearance potential of the S^+ ion is 37.3 volts. This is 4.6 volts in excess of the calculated minimum energy required to produce an S^+ ion and a free electron. It is concluded that the production of S^+ gives considerable kinetic energy to the seven dissociation fragments; namely 4.6 volts if a free electron is removed. If it is assumed that one of the fluorine atoms combines with the electron to form an F^- ion in the ionization process, the excess energy is increased to 8.6 volts by the value of the electron affinity (4.0 volts) [9] of fluorine. One could also assume that one or two pairs of fluorine atoms combined in the ionization process to form molecular fluorine with an energy of 2.7 volts per molecule of F_2, but this seems to be an improbable process in spontaneous dissociation.

TABLE 2. *Appearance potentials of various ions in the mass spectrum of* SF_6

m/e	Ion	Appearance potential
		v
19	F^+	35.8 ± 1
32	S^+	37.3 ± 1
35	SF_2^{++}	46.5 ± 0.5
51	SF^+	$31.3\pm\ .3$
54	SF_4^{++}	$40.6\pm\ .5$
70	SF_2^+	$26.8\pm\ .3$
89	SF_3^+	$20.1\pm\ .3$
91,8	$SF_5^+ SF_4^{+}+F$	$20\ \ \pm1$
108	SF_4^+	18.9 ± 0.2
127	SF_5^+	$15.9\pm\ .2$

An F^+ ion could conceivably be found in any process in which SF_6 is dissociated. However the appearance potential of F^+ (35.8 volts) is higher than the appearance potential of any of the polyatomic singly charged ions. This suggests that F^+ occurs from complete dissociation like the S^+ ion. From the same dissociation process, the minimum energy required to produce an F^+ ion and a free electron is 22.4+18.6⁶=41.0 volts. The observed appearance potential of F^+ (35.8 volts) is insufficient to produce F^+ and a free electron. The minimum energy required to produce an F^+ and an F^- from SF_6, however, is 37.0 volts. The observed value (35.8 volts) is close enough to leave little doubt that this is the actual process involved.

Table 3 gives the observed isotope abundance of sulfur. Also given in table 3 are the results re-

ported by Nier [10] from a study of SO_2 using a specially designed mass spectrometer. The disagreement of the S^{36} abundance is greater than the estimated experimental error whether calculated from the SF_5^+ ion, the SF_4^+ ion or the SF_2^+ ion. Other ions were not usable because of low intensity or interference by the metastable ion or doubly charged ions. From the isotopic masses listed by Pollard [11] (assuming same packing fraction for S^{34} and S^{36}) and the conversion factor 1.000275, the authors' values give a chemical weight of 32.065. The accepted value by chemical methods is 32.066 [12].

Carbon Tetrafluoride.—Table 4 shows the mass spectrum of CF_4 at several energy values of the ionizing electrons. The most probable dissociation process is again the loss of one fluorine atom to produce the CF_3^+ ion. The abundance of the CF_4^+ ion is estimated to be less than 1/1,000 relative to the CF_3^+ ion. The relatively large abundance of the CF_2^+ ion is unusual by analogy with other halogenated molecules (see, for example, [1] and [2], and tables 1 and 7). Doubly charged

TABLE 3. *Isotope abundance of sulfur*

	m/e			
	32	33	34	36
Mean	95.03	0.76	4.17	0.035
Average deviation	±0.02	±.01	±0.01	±.003
Nier [10]	95.1	.74	4.2	.016

TABLE 4. *Mass spectra of* CF_4 *for 50, 70 and 100-volt electrons and* CH_4 *for 50-volt electrons*

		Carbon tetrafluoride			Methane	
m/e	Ion	Relative intensities at—			Ion	Relative intensities at 50 volts
		50 volts	70 volts	100 volts		
12	C^+	6.72	10.1	11.0	C^+	2.40
13	C^+	0.08	0.11	0.12		
15.5	CF^{++}	----------	.06	.15		
19	F^+	3.09	5.95	8.14	H^+	3.21
25	CF_2^{++}	1.51	5.93	11.0		
25.5	CF_2^{++}	----------	0.06	0.13		
31	CF^+	3.67	4.85	6.17	CH^+	7.91
34.5	CF_3^{++}	----------	2.04	3.92		
50	CF_2^+	12.4	15.4	15.6	CH_2^+	15.9
51	CF_2^+	0.13	0.17	0.17		
69	CF_3^+	100	120	133	CH_3^+	84.6
70	CF_3^+	1.16	1.31	1.46	CH_4^+	100

ions CF^{++}, CF_2^{++}, and CF_3^{++} were observed. No metastable ions were observed. The mass spectrum of methane is also included in table 4 for comparison. No doubly charged or metastable ions are observed in methane.

Table 5 lists the appearance potentials of various ions in the mass spectrum of CF_4. A complete analysis of the appearance potential data is impossible due to the lack of sufficient thermochemical or spectroscopic data. From Bichowsky and Rossini [8] the energy of dissociation into atoms $CF_4 \rightarrow C + 4F$ is calculated to be 458 kcal/mole, or 19.9 electron volts. The minimum energy required to produce a C^+ ion and a free electron is $19.9 + 11.2^6 = 31.1$ volts. The minimum energy to give F^+ and a free electron with complete dissociation is $19.9 + 18.6^6 = 38.5$ volts. The observed appearance potentials of both ions are less than these values, and it must be assumed that in both cases F^- ions are formed in the ionization process and not free electrons. The process $CF_4 \rightarrow C^+ + F^- + 3F$ requires $31.1 - 4.0 = 27.1$ volts compared to the observed appearance potential of 27.5 ± 1 volts. The process $CF_4 \rightarrow C + F^+ + F^- + 2F$ requires $38.5 - 4.0 = 34.5$ volts compared to the observed appearance potential of 35.5 ± 1 volts.

TABLE 5. *Appearance potentials of various ions in the mass spectrum of* CF_4

m/e	Ion	Appearance potential
		v
12	C^+	$27.5 \pm 1.$
19	F^+	$35.5 \pm 1.$
25	CF_2^{++}	44.3 ± 0.5
31	CF^+	$29.8 \pm .3$
34.5	CF_3^{++}	$43.8 \pm .5$
50	CF_2^+	$21.8 \pm .3$
69	CF_3^+	$15.9 \pm .2$

The C^{12}/C^{13} ratio as measured from the CF_3^+ and the CF_2^+ ions was 89.9 ± 1.7, compared with the value of 90 ± 2 reported by Nier and Gulbranson [13], using carbon dioxide from the air.

Silicon Tetrafluoride.—Table 6 shows the mass spectrum of SiF_4 for 50, 70, and 100-volt electrons. The removal of one fluorine atom to form the SiF_3^+ ion is again the most probable process. In contrast to SF_6 and CF_4, however, the molecular ion has an appreciable abundance. Further dissociation to SiF_2^+, SiF^+, and Si^+ follows the general pattern of halogenated molecules, i. e., the

abundance of ions with an odd number of halogen atoms is greater than the abundance of those with an even number. The doubly charged ions SiF^{++}, SiF_2^{++}, and SiF_3^{++} were observed. The SiF_2^{++} ion becomes more abundant than the singly charged ion above 50 volts. No metastable ions are observed.

TABLE 6. *Mass spectrum of SiF_4 for 50, 70 and 100-volt electrons*

m/e	Ion	Relative intensities at—		
		50 volts	70 volts	100 volts
19	F^+	1.18	2.26	3.10
23.5	SiF^{++}	0.10	0.87	1.82
24	SiF^{++}	------------	.05	0.09
24.5	SiF^{++}	------------	.02	.05
28	Si^+	2.89	4.99	6.27
29	Si^+	0.18	0.28	0.38
30	Si^+	.11	.18	.21
33	SiF_2^{++}	1.35	4.56	7.48
33.5	SiF_2^{++}	0.08	0.23	0.38
34	SiF_2^{++}	.06	.16	.25
42.5	SiF_3^{++}	.46	1.37	2.13
43	SiF_3^{++}	.06	0.10	0.16
43.5	SiF_3^{++}	-------- ------	.04	.05
47	SiF^+	3.57	4.67	4.22
48	SiF^+	0.20	0.24	0.23
49	SiF^+	.15	.17	.17
66	SiF_2^+	.66	.79	.66
67	SiF_2^+	.06	.07	.07
68	SiF_2^+	.03	.04	.03
85	SiF_3^+	100.	122.	133.
86	SiF_3^+	5.01	6.10	6.86
87	SiF_3^+	3.34	4.08	4.53
104	SiF_4^+	1.79	2.14	2.39
105	SiF_4^+	0.10	0.12	0.12
106	SiF_4^+	.06	.07	.08

The appearance potentials of several ions in the mass spectrum of SiF_4 are given in table 7.

The relative abundance of the isotopes of silicon have recently been measured by several investigators. The results of Ney and McQueen [14], Inghram [15], and Williams and Yuster [16], together with the authors' values are given in table 8. The agreement between the present work and the previously reported values is within the experimental uncertainty. The chemical weight calculated from the isotopic masses listed by Pollard [11] is 28.09 compared to the accepted chemical value of 28.06 [12].

TABLE 7. *Appearance potentials of several ions in the mass spectrum of SiF_4*

m/e	Ion	Appearance potential
		v
66	SiF_2^+	27.5 ± 0.5
85	SiF_3^+	$16.1\pm.2$
104	SiF_4^+	$16.9\pm.5$

TABLE 8. *Isotope abundance of silicon*

	m/e		
	28	29	30
Mean	92.32	4.58	3.10
Average deviation	±0.03	±0.03	±0.02
Ney and McQueen [14]	92.24	4.69	3.07
Inghram [15]	92.28 ± 0.08	4.67 ± 0.05	3.05 ± 0.03
Williams and Yuster [16]	92.27	4.68	3.05

IV. Conclusions

In a few cases in which appearance potentials could be computed from thermochemical and spectroscopic data, it was found that the observed appearance potential was considerably less than the computed potential required to give an atom ion and a free electron, but nearly equal to the calculated potential required to give a positive atom ion and a negative fluorine ion. This was observed for F^+ ion from SF_6 and CF_4, and for the C^+ ion from CF_4. The mass spectra support the hypothesis that for these molecules, removal of a F^- ion rather than an electron is the most probable process in production of the positive ions. This would also explain the absence of the parent ions SF_6^+ and CF_4^+. In the case of SF_6, the heaviest doubly charged ion is SF_4^{++}, which indicates that two F^- ions are removed to form the double positive charge. The fact that SF_4^{++} is more abundant than SF_4^+ at 100 volts is not surprising if this is the mechanism of ionization. In the case of CF_4, a CF_3^{++} ion is observed although the CF_2^{++} ion is more abundant. This indicates that it is possible to ionize CF_4 by removing either two F^+ ions or one F^- ion and a free electron. The appearance potentials for these two processes are nearly the same.

In the case of SiF_4, the molecular ion is observed although its abundance is less than 2 percent of the SiF_3^+ ion. The appearance potential of the former is actually somewhat greater than the latter, which again indicates that the SiF_3^+ ion is formed by removal of an F^- ion from SiF_4. Consider the other possibility; i. e., the SiF_3^+ ion arises from the removal of a free electron and a fluorine atom. This is the same as removing a fluorine atom from the SiF_4^+ ion, and consequently must require work. Therefore, the appearance potential of SiF_3^+ must be higher than SiF_4^+ by that amount of work unless a negative ion is formed in the process.

V. References

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