Rate Constants for F^- Transfer from SF_6^- to Fluorinated Gases and SO_2. Temperature Dependence and Implications for Electrical Discharges in SF_6

L. Wayne Sieck*[†] and Richard J. Van Brunt[‡]

Chemical Kinetics and Electrosystems Divisions, National Bureau of Standards, Gaithersburg, Maryland 20899 *(Received: June 2, 1987; In Final Form: August 28, 1987)*

The reactivity of SF_6^- toward SO_2, SOF_2, SO_2F_2, SOF_4, SF_4, and SiF_4 has been investigated by using the technique of pulsed electron beam high-pressure mass spectrometry. These studies were initiated in order to probe the complex anionic chemistry occurring during electrical discharge in SF_6. Although no reaction of any type was observed with SOF_2 and SO_2F_2, efficient F^- transfer of the type $SF_6^- + A \rightarrow AF^- + SF_5$ was found in all of the other systems including the $SO_2F^- + SOF_4$ pair, which was studied separately. With the exception of the $SF_6^- + SiF_4$ reaction, all of the pairs exhibited a negative temperature coefficient in that the rate constants for F^- transfer decreased substantially with increasing temperature. The reaction $SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$ was found to proceed with a rate constant of $(5.6 \pm 0.8) \times 10^{-10}$ $cm^3/(molecule{\cdot}s)$ throughout the temperature range studied (298-510 K), which corresponds to a collision efficiency of unity. The other reactions were found to approach unit collision efficiency only at reduced temperatures (<300 K). The reactions studied were used to provide additional information concerning the gas-phase F^- affinity scale, and the F^- affinity of SiF_4 was defined as 2.2 ± 0.4 kcal/mol higher than SOF_4 via equilibria measurements. The placement of SF_5 within the F^- affinity scale indicates that SF_6^- is reactive toward several of the major stable byproducts generated during electrical breakdown in SF_6. This behavior was verified by direct observation of the temporal growth and decay profiles of the various anions produced after pulsed ionization of an SF_6 sample which had been subjected to prior partial decomposition in a negative corona discharge. Some comments are also included concerning the stability of the $SF_6^-{\cdot}SF_6$ dimer ion, and the implications of all of the present data with respect to mobility measurements in SF_6 are also discussed.

Introduction

Electrical breakdown in gaseous sulfur hexafluoride containing trace quantities of water vapor is known to lead to the formation of various stable oxyfluorides including SOF_2, SOF_4, and SO_2F_2, as well as SO_2, HF, and SF_4.[1-3] Additional end products such as SiF_4 are also produced during the SF_6/O_2 plasma etching of polysilicons.[4] The accumulation of decomposition products, even at very low levels, may be expected to affect the identity of the negative charge carriers during breakdown in SF_6 due to F^- exchange reactions of the type $SF_6^- + A \rightarrow AF^- + SF_5$. Reactions of this type have, in fact, been proposed as a sensitive technique for detection of some of the byproducts of electrically discharged SF_6 by Sauers,[5] who also reported estimated rate constants for several F^- exchange reactions measured in a uniform electric field with a drift cell-mass spectrometer. A comparison of the temperature and E/N (electric field to gas density) dependence of the rate for $SF_6^- + SOF_4 \rightarrow SOF^- + SF_5$ has also been reported by Van Brunt and co-workers.[3] Other rate constant determinations involving SF_6^- and likely decomposition products have been restricted to single-temperature measurements with the neutrals SiF_4,[6] SF_4,[7] and SO_2.[8] Streit, who investigated the reactivity of SF_6^- toward a variety of neutrals at room temperature using a flowing afterglow technique,[8] found that many exothermic reactions proceeded with collision efficiencies which were substantially less than unity. In cases such as these it has usually been found that the rate constants exhibit a negative temperature coefficient, and the interpretation of this general behavior has been the subject of a review by Kebarle.[9] More recently, the temperature dependence of the kinetics of electron transfer involving SF_6^- and several fluorocarbons has been considered in detail by Kebarle and co-workers,[10] and the results were interpreted in terms of an internal barrier to reaction in the transition states for $SF_6^-{\cdot}A$ collision complexes. The few measurements reported to date for the reactions of SF_6^- with products of discharged SF_6 have typically yielded rate constants below the collision limit, suggesting that the rates may also be temperature sensitive. The present study was initiated to provide a more quantitative kinetic base for modeling of the complex ion chemistry occurring during electrical breakdown in SF_6 containing trace impurities generated during decomposition. To this end we have investigated the temperature dependence of a number of individual F^- transfer reactions using the method of pulsed high-pressure mass spectrometry. The consecutive anionic mechanisms operative in SF_6 samples subjected to prior partial decomposition in a negative corona discharge were also characterized by using this technique via direct observation of the temporal growth and decay profiles of the various product/reactant ions. Some comments are also included concerning the gas-phase fluoride affinity scale.

Experimental Section

All of the kinetic measurements were carried out with the NBS pulsed electron beam high-pressure mass spectrometer system, which has been modified for negative ion operation as described previously.[11] Determinations of the rate constant (k) for the reaction $SF_6^- + A \rightarrow AF^- + SF_5$ at a given temperature were performed by exposing a premixed sample of SF_6 and A (usually 100:1), diluted with CH_4 as an inert carrier gas, to a short pulse (100-400 μs) of 1-keV electrons at total chamber pressures falling in the range 0.4-1.5 Torr. Under these conditions, SF_6^- is produced essentially instantaneously by associative attachment of thermalized secondary electrons to SF_6. The resultant ion signals from SF_6^- and AF^- were then recorded as a function of time following termination of the ionizing pulse. These signals were usually monitored for 3-10 ms, in channels of 10-20-μs width,

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[†] Chemical Kinetics Division.

[‡] Electrosystems Division.

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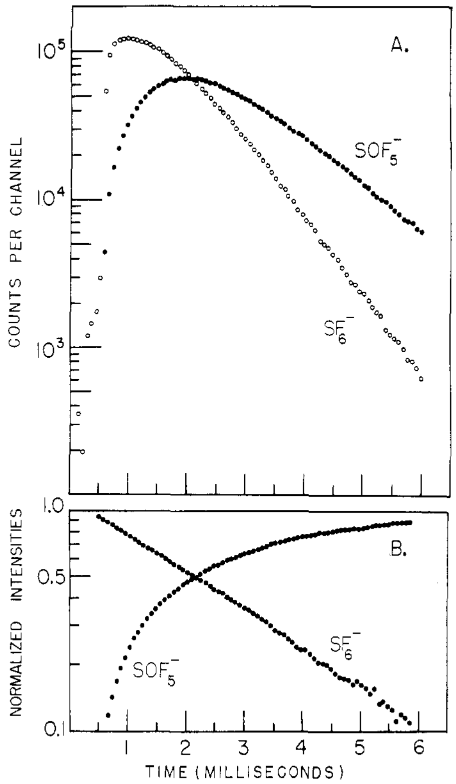

Figure 1. Raw data (A) and normalized data (B) obtained as a function of time following pulsed ionization of a CH_4–SF_6–SOF_4 mixture. Conditions given in Experimental Section.

and accumulated in a multichannel scalar serving as a signal averager. The collected data were fed into a minicomputer, which normalized the intensities at each reaction time. A standard irreversible kinetics program was used to evaluate the appropriate rate parameters. Specific details of these measurements and others, as well as some examples of experimental data, are given below. The chemicals used were of the highest purity commercially available and were used without further treatment.

SF_6/SOF_4 Mixtures. The SF_6^-/SOF_4 system was investigated from 262 to 433 K. Various concentrations of SOF_4, ranging from 1.9×10^{-5} to 6.7×10^{-5} mole fraction in CH_4, were studied at total chamber pressures from 0.4 to 1.4 Torr. Sample results are given in Figure 1, which shows raw and normalized data obtained from a mixture of 1.9×10^{-5} mole fraction SOF_4 in CH_4 containing 1.9×10^{-3} mole fraction SF_6 at a total pressure of 1.30 Torr at 344 K. Figure 1A displays the accumulated signals, in 15-μs-wide channels, for SF_6^- and SOF_5^- in every fifth channel for 6 ms following initiation of a 400-μs-wide electron pulse. The resultant time-resolved normalized intensities are shown in Figure 1B. For this particular measurement, k was evaluated from the relative ion signals recorded from 0.6 to 3.5 ms, which encompasses the data taken from the beginning of ion decay to the point at which the statistics become poor due to reduced signal levels. The slope of the normalized decay of SF_6^- corresponds to a k of 5.3×10^{-10} cm^3/(molecule·s) for the reaction $SF_6^- + SOF_4 \rightarrow SOF_5^- + SF_5$. No other reactions were detectable under our conditions. Note that the SF_6^- decay rate is considerably reduced during the ionization pulse due to ambipolar diffusion during the period of high electron flux, which greatly reduces the residence times of reactant ions. An additional initial delay occurs due to the time required for the first ions exiting from the sampling orifice to pass through the mass filter and reach the conversion dynode of the detector. Under the conditions of this particular measurement, the total transit time after exit for SF_6^- and SOF_5^-, which have nearly equal masses (146 and 143 daltons), was approximately 60 μs. The computer-generated analysis incorporates standard corrections for differences in flight times for ions of differing m/z values throughout the period of raw data accumulation.

SF_6/SO_2 Mixtures. The reaction $SF_6^- + SO_2 \rightarrow$ products was studied over the range 300–530 K. In this particular system three separate primary channels were observed:

$$\begin{aligned} SF_6^- + SO_2 &\rightarrow SO_2F^- + SF_5 \\ &\rightarrow SF_5^- + SO_2F \\ &\rightarrow SO_2F_2^- + SF_4 \end{aligned}$$

At longer reaction times, both SF_5^- and $SO_2F_2^-$ were found to react further with SO_2 via F^- transfer to yield SO_2F^- as the terminal ion. In order to evaluate the overall k for reason of SF_6^-, the individual intensities of SO_2F^-, SF_5^-, and $SO_2F_2^-$ were recorded as a function of time and summed in each channel prior to normalization with the time-resolved SF_6^- signal. Concentrations were varied from 2.1×10^{-5} to 4.2×10^{-5} mole fraction SO_2 in CH_4.

SO_2/SOF_4 Mixtures. The reaction $SO_2F^- + SOF_4 \rightarrow SOF_5^- + SO_2$ was studied in four-component mixtures. Since SF_6^- is reactive toward both SO_2 and SOF_4, an SO_2/SOF_4 ratio of 20:1 was maintained to minimize initial F^- transfer to SOF_4 from SF_6^-. As noted above, the primary reaction of SF_6^- with SO_2 yields three products, SO_2F^-, SF_5^-, and $SO_2F_2^-$, all of which are potentially reactive with SOF_4. However, due to the large excess of SO_2, conversion of SF_5^- and $SO_2F_2^-$ to SO_2F^- occurs rapidly, such that at longer reaction times only two ions are present, SO_2F^- and SOF_5^-, with SO_2F^- predominating. This sequence is shown in Figure 2, which displays raw data obtained from a mixture of 2.2×10^{-5} mole fraction SOF_4, 4.4×10^{-4} mole fraction SO_2, and 2.2×10^{-2} mole fraction SF_6 in CH_4 at a total pressure of 1.29 Torr at 379 K. Accumulated data are shown for every fifth channel (10-s width) for 3.5 ms following initiation of a 400-μs-wide ionizing pulse. (Note that the intensity of SO_2F^- has been reduced by a factor of 10 for display purposes.) Although it is evident from the growth and decay profiles that SF_5^- and $SO_2F_2^-$ are major ions at short reacton times, both quickly react out and essentially disappear from the composite spectrum after slightly more than a millisecond under these conditions of temperature and concentration. The rate constant for the reaction of interest, $SO_2F^- + SOF_4 \rightarrow SOF_5^- + SO_2$, was then determined from the normalized intensities of SO_2F^- and SOF_5^- between 1.1 and 3 ms. The data shown in Figure 2 correspond to a value of 3.6×10^{-10} cm^3/molecule·s) for F^- transfer at 379 K. This reaction was also studied at 296 and 329 K.

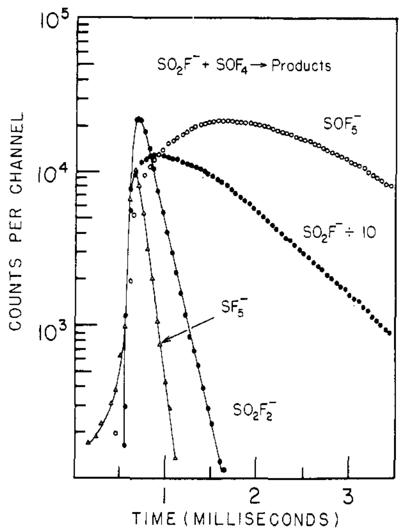

Figure 2. Raw data showing ion intensities as a function of time following pulsed ionization of a CH_4–SF_6–SO_2–SOF_4 mixture. Details given in Experimental Section.

SOF_4/SiF_4 Mixtures. We had originally intended to measure the k for the reaction $SOF_5^- + SiF_4 \rightarrow SiF_5^- + SOF_4$. However, in mixtures thought to be appropriate for such measurements (~20:1 in favor of SOF_4 and 1×10^{-5} mole fraction SiF_4 in CH_4), the equilibrium $SOF_5^- + SiF_4 \leftrightarrow SiF_5^- + SOF_4$ was established at relatively short reaction times, which precluded any evaluation of the k for F^- transfer from SOF_5^-. The equilibrium constant

was determined at six temperatures over the range 298–387 K, and the resultant van't Hoff plot gave $\Delta H° = 2.2 \pm 0.4$ kcal/mol and $\Delta S° = -3.2 \pm 1.0$ eu for the exchange reaction as written. The equlibrium constant at 298 K was 8.7.

Miscellaneous Measurements. The following reactions were studied under the stated conditions. (i) $SOF_5^- + SiF_4 \leftrightarrow SiF_5^- + SOF_4$: 299–387 K, 2.1×10^{-4} mole fraction SOF_4 and 1.1×10^{-5} mole fraction SiF_4. (ii) $SF_6^- + SOF_2, SO_2F_2 \rightarrow$ products: 298 and 450 K, 5.5×10^{-5} mole fraction of the oxyfluorides. (iii) $SOF_5^- + H_2O \rightleftarrows SOF_5^- \cdot H_2O$: 297 K, 4×10^{-5} mole fraction SOF_4, 6.3×10^{-3} mole fraction H_2O. (iv) $SF_6^- + SF_4 \rightarrow SF_5^- + SF_5$: 293–450 K, 3.2×10^{-5} to 7.0×10^{-5} mole fraction SF_4. (v) $SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$: 298–500 K, 1.7×10^{-5} mole fraction SiF_4.

Discharge-Decomposed SF_6. A sample of SF_6 was exposed to a continuous, direct current, negative point–plane corona discharge at a total pressure of 2 atm in a 3.7-L cell. The discharge was operated for 30.6 h at a current of 40 μA, corresponding to 4.4 C of net total charge transported. The specific techniques used, including product analysis, were identical with those described in ref 2. This treatment results in the generation of a mixture containing approximately 450 ppm of SOF_4, 350 ppm of SOF_2, and 180 ppm of SO_2F_2. Small quantities of SO_2, <10 ppm, are also produced directly during discharge, and this product may accumulate due to secondary reactions involving hydrolysis of oxyfluorides and other byproducts.[12] The influence of decomposition products on the identities of the negative ions formed in the gas was assayed by comparisons of time-resolved composite mass spectra obtained from the pure and discharged material.

Results and Discussion

Hydrolysis. Under certain conditions several of the systems were found to be sensitive to hydrolysis in the gas-handling manifold and sample inlet reservoir. No difficulties were encountered with samples containing SO_2, SOF_2, SO_2F_2, SOF_4, and SiF_4, provided that H_2O was not deliberately introduced into the mixture and the reaction chamber temperature was held below ~250 °C. (The sample inlet reservoir was maintained at 150 °C for all measurements.) However, at higher chamber temperatures in nominally dry samples containing SOF_4, as well as mixtures containing nominally dry SF_4 at any temperature, it was apparent that hydrolysis was occurring. (The term nominally dry is used to describe samples prepared directly from manufacturer-supplied components and not subjected to desiccation.) This situation was immediately evident after inspection of the time-resolved composite mass spectra of these mixtures, which showed SiF_5^- to be the terminal ion. SiF_5^- is produced by F^- transfer to SiF_4, which is generated by heterogeneous reactions of HF with silicon-containing components within our inlet system. Hydrogen fluoride is known to be one of the products of the hydrolysis of SOF_4 ($SOF_4 + H_2O \rightarrow SOF_2 + 2HF$), and among the sulfur oxyfluorides, SOF_4 is particularly labile toward attack by water vapor.[12] SF_4 is even more sensitive, with a room-temperature rate constant for gas-phase hydrolysis ($SF_4 + H_2O \rightarrow SOF_2 + 2HF$) which is 200 times higher than that for SOF_4.[13] In SF_4–SF_6–CH_4 samples the apparent k for the reaction $SF_6^- + SF_4 \rightarrow SF_5^- + SF_5$ was found to decrease as a function of time following preparation of the particular mixture under study. The hydrolysis rate depended, to some extent, upon the prior history of the gas-handling and inlet manifold, but even overnight baking at 350 °C under vacuum followed by preconditioning with SF_4 did not prevent slow destruction of the sample. Under our driest conditions repetitive determinations of the k for F^- transfer at 298 K over a 1-h period exhibited a decrease of ~15°/h from the initial value. In addition, some SiF_5^- was always present in the composite mass spectra of mixtures containing SF_4 immediately after sample makeup, indicating that some hydrolysis had already occurred in the manufacturer-supplied starting material. Therefore, the values of k quoted in Table I for the reaction $SF_6^- + SF_4$ should be considered lower limits.

TABLE I: Rate Constants

reaction	k_{298} ($\times 10^{10}$)[a]	k_{373} ($\times 10^{10}$)[a]
$SF_6^- + SF_4 \rightarrow SF_5^- + SF_5$	7.4	5.0
$SF_6^- + SO_2 \rightarrow SO_2F^-, SF_5^-, SO_2F_2^-$	10.6	8.1
$SF_6^- + SO_2F_2 \rightarrow$ products	nr[b]	nr[b]
$SF_6^- + SOF_2 \rightarrow$ products	nr[b]	nr[b]
$SO_2F^- + SOF_4 \rightarrow SOF_5^- + SO_2$	6.8	3.9
$SF_6^- + SOF_4 \rightarrow SOF_5^- + SF_5$	8.5	4.0
$SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$	5.6	5.6
$SOF_5^- + SiF_4 \rightarrow SiF_5^- + SOF_4$	see text	see text

[a] Units of cm^3/(molecule·s), error limits assumed as ±10%. [b] nr denotes no reaction ($k < 10^{-15}$). Electron exchange was also not detected.

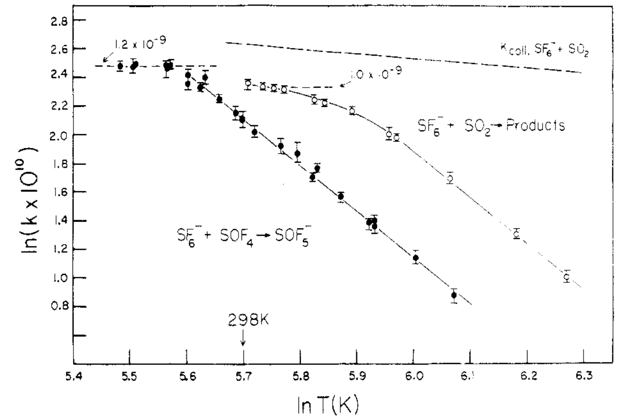

Figure 3. Temperature dependence of rate constants, plotted as ln ($k \times 10^{10}$), with units of k as $10^{-10} cm^3$/(molecule·s), versus ln T, in kelvin. Reactions as labeled. Theoretical limiting k(collision) for the $SF_6^- + SF_4$ pair shown as a broken line.

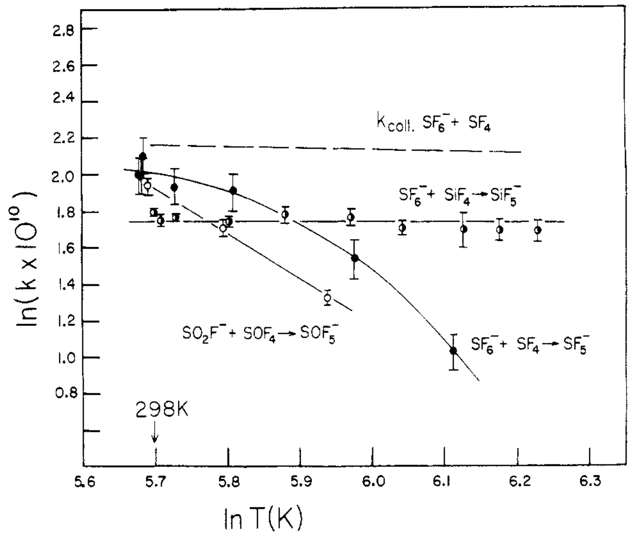

Figure 4. Temperature dependence of rate constants, plotted as ln T ($k \times 10^{10}$), with units of k as $10^{-10} cm^3$/(molecule·s), versus ln T, with T in kelvin. Reactions as labeled. Theoretical limiting k(collision) for the SF_6 + SF_4 pair shown as a broken line.

Rate Constants. Rate constants derived for the various reactions at 298 and 373 K (100 °C) are summarized in Table I. The variation of k with temperature (T) for five reaction pairs is shown in Figures 3 and 4. The error bars indicate the repoducibility of replicate measurements at a given T. With the exception of the $SF_6^- + SiF_4$ pair, all of the systems exhibit a negative T coefficient in that k decreases with increasing temperature. This type of behavior has been observed previously in several classes of reactions involving cations, and in every case a plot of ln k versus

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ln T yields a straight line with a negative slope when the reaction efficiency becomes much less than unity. A detailed description of the various factors which are thought to influence the kinetics in those systems has been presented by Kebarle.[9] Both the SF_6^- + SOF_4 and SF_6^- + SO_2 pairs exhibit an asymptotic approach to limiting values at lower temperatures. Although this approach is gradual in the SF_6^- + SO_2 system, an abrupt change in slope appears to occur for the SF_6^- + SOF_4 reaction at approximately 270 K (ln T = 5.6). Sharp transitions of this type have been reported previously for hydride transfer[14] and alkylation reactions[15] as the collision efficiency approaches unity. Unfortunately, the polarizibility and dipole moment of SOF_4 are unknown; consequently, it is not possible to verify that the lower T value of 1.2×10^{-9} cm^3/(molecule·s) indicated in Figure 3 corresponds to k(collision) for SF_6^- and SOF_4. On the other hand, both the polarizibility (3.8×10^{-24} cm^3) and dipole moment (1.61 D) of SO_2 are known, and application of the parametrization formalism for ion–polar molecule collisions of Su and Chesnavich[16] to the SF_6^- + SO_2 pair yields a calculated k(collision) of 1.4×10^{-9} cm^3/molecule·s) at 300 K. The experimental value at 300 K is $\sim 1.0 \times 10^{-9}$, corresponding to a reaction efficiency of 0.7. However, the contour of the plot (Figure 3) for this pair indicates that k is still increasing at the lowest experimental temperature (300 K); i.e., the limiting value has not been reached. Above 370 K, the variation of k with T may be expressed as $k = 0.114 \exp(-3.16 \ln T)$ cm^3/(molecule·s). For the SF_6^- + SOF_4 reaction the analogous equation is $k = 0.124 \exp(-3.3 \ln T)$, which is applicable above 270 K. Lindinger et al.[17] have investigated the kinetic energy (KE) dependence of the SF_6^- + SO_2 reaction at 300 K using a flow drift technique. Three product ions were found (SO_2F^-, SF_5^-, and $SO_2F_2^-$), and a value for k of 1.0×10^{-9} cm^3/(molecule·s) was measured for reaction of thermal ions (0.04-eV KE), in quantitative agreement with the present results. The reaction was also found to exhibit a negative energy dependence analogous to the negative T dependence observed here, with k decreasing to $\sim 1 \times 10^{-10}$ cm^3/(molecule·s) at a KE of 0.5 eV. Streit[8] has also reported a k of $(1.0 \pm 0.3) \times 10^{-9}$ cm^3/(molecule·s) for this reaction at room temperature (thermal ions).

The variation of k with T for $SF_6^- + SF_4 \rightarrow SF_5^- + SF_5$ is shown in Figure 4. Measurements for this pair were complicated by hydrolysis and by the fact that some SF_5^- is also produced by dissociative electron attachment of SF_6 ($\sim$2.5% of the SF_6^- signal) during the ionization pulse. Taken together, these factors induce a greater uncertainty than is characteristic of the other systems studied. However, it is clear from Figure 4 that this reaction pair also exhibits a negative T coefficient, and the contour of the plot indicates a smooth transition to a limiting low T value similar to that found for the SF_6^- + SO_2 reaction. The value of k at 298 K is approximately 7.4×10^{-10} cm^3/(molecule·s), which is nearly equal to the collision k at this temperature (8.5×10^{-10}). The latter can be calculated directly since values for the dipole moment (0.632 D) and polarizibility (6.02×10^{-24} cm^3) are available.[7]

The reaction $SO_2F^- + SOF_4 \rightarrow SOF_5^- + SO_2$ also shows a negative T dependence, with no indication of a transition to a limiting value over our experimental range of 298–379 K (Figure 4). Again, the ln k versus ln T plot appears to give a straight line, with $k = 8.06 \times 10^{-5} \exp(-2.05 \ln T)$$cm^3$/(molecule·s). The last system studied as a function of T was the SF_6^- + SiF_4 pair. In this case no variation in reactivity was observed over the experimental range of 298–508 K (Figure 4). Within these limits F^- transfer to produce SiF_5^- was found to proceed with a k of $(5.6 \pm 0.8) \times 10^{-10}$ cm^3/(molecule·s), which corresponds to a collision efficiency of unity since the Langevin capture rate constant for this pair is 5.5×10^{-10} cm^3/(molecule·s). (SiF_4 has no dipole moment.) The negative temperature coefficients observed for the various F^- transfer reactions cannot be interpreted rigorously due to the lack of accurate thermochemical information. However, the only system not showing a negative T dependence is the SF_6^- + SiF_4 pair, and this is also the only combination in which the neutral reactant has no permanent dipole moment. It is expected that the reactivity of ions with polar molecules will decrease slightly as T increases. This results from the fact that the total k(collision) is expected to exhibit a rather complex inverse T dependence.[16] The effect of T on the predicted k(collsion) is quite gradual, however, and is shown in Figure 3 for the SF_6^- + SO_2 pair and in Figure 4 for the SF_6^- + SF_4 pair. Comparison of the experimental k's with k(collision) demonstrates that the observed decreases are substantially in excess of those predicted simply on the basis of variations in the capture rate constants. The presence of a permanent dipole in the colliding neutral (A) can influence the alignment within (SF^-·A) collision complexes, resulting in an internal chemical barrier to F^- transfer (low entropy transition state). When this situation occurs, a negative temperature coefficient is often observed in particle-transfer reactions.[9] We should note, however, that the overall process $SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$ is also the most exothermic reaction of any of those studied (see section on Fluoride Affinities), creating a condition which may tend to overwhelm any special properties of the (SF_6^-·SiF_4) collision complex which are common to the other pairs studied. Therefore, the relationship which appears to exist between a negative T dependence and dipole moment may be coincidental.

Hydration of SOF_5^-. A $\Delta G°$ of −5.1 kcal/mol was measured for the equilibrium $SOF_5^- + H_2O \leftrightarrow SOF_5^-\cdot H_2O$ at 297 K. Combining this value with an estimated $\Delta S°$ of 21 ± 2 eu, which is typical of $\Delta S°$ values for monohydration of inorganic anions,[18] gives a $\Delta H°$ for the $SOF_5^-\cdot H_2O$ association ion of −11.3 ± 0.6 kcal/mol. For comparison, the $\Delta H°$ (binding enthalpy) in $SF_6^-\cdot H_2O$ is −10.5 kcal/mol,[17b] indicating that $SOF_5^-\cdot H_2O$ is a slightly more stable complex. We should mention that slow hydrolysis of SOF_4 was noted during the course of this determination. This condition did not affect the equilibrium measurement due to the large excess of H_2O (see Experimental Section) and the fact that a knowledge of the concentration of SOF_4 is not required for evaluation of the equilibrium constant. That hydrolysis was occurring in these wet samples was evident from the composite mass spectra, which showed SiF_5^- and SOF_5^-·HF as terminal ions (see section on Hydrolysis).

Fluoride Affinities. The vapor-phase fluoride affinities of a variety of organic and inorganic molecules have been reported in a series of articles[19] by Larson and McMahon (F^- affinity defined as $\Delta H_D°$ for the dissociation $AF^- \rightarrow A + F^-$). Using ICR spectroscopy, they have established an extensive absolute affinity scale based on $\Delta G°$ measurements for numerous interlocking equilibria of the type $A_1F^- + A_2 \leftrightarrow A_2F^- + A_1$ and incorporating calculated $\Delta S°$ values for each reaction pair. For sulfur-containing molecules pertinent to this study, the following F^- affinities were reported (kcal/mol): SO_2F_2, 35.8; SOF_2, 37.4; SF_4, 43.8; and SO_2, 43.8. Bracketing experiments also gave an estimated value of 62 ± 4 kcal/mol for $\Delta H_D°(SiF_4–F^-)$. The present work supports this ordering and establishes the sequence SOF_2, SO_2F_2 < SF_5 < SF_4 < SO_2 < SOF_4 < SiF_4. The difference in F^- affinities between SOF_4 and SiF_4 was also determined here to be 2.2 ± 0.4 kcal/mol via direct equilibrium measurements. The relative positioning of SF_5 within our ladder results from the fact that no reaction of SF_6^- was found with either SOF_2 or SO_2F_2, while F^- transfer to SF_4 was found to proceed efficiently. According to the scale of Larson and McMahon, this places $\Delta H_D°(SF_5–F^-)$ within the range 37.4–43.8 kcal/mol. The F^- affinity of SF_5 can be estimated independently from the overall enthalpy change associated with the reaction $SF_5 + F^- \rightarrow SF_6^-$, providing all of the necessary heats of formation are available. A value for $\Delta H_f°(SF_6^-)$ can be calculated from the relationship $SF_6 + e^- \rightarrow SF_6^- + EA$. (EA denotes electron affinity.) Combining the recent value[10a] of EA (SF_6) = 24.2 ± 2 kcal/mol with

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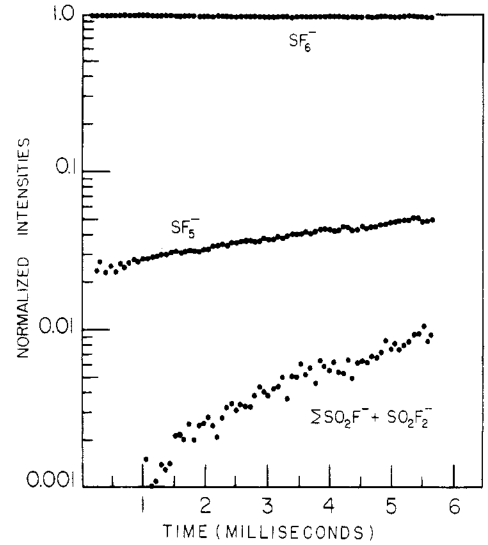

Figure 5. Normalized ion intensities observed as a function of time following pulsed ionization at 293 K of a sample of 0.1 mole fraction SF_6 in CH_4 prior to decomposition of the SF_6 in a negative corona discharge. Total pressure is 1.25 Torr. Data are displayed for every fifth channel.

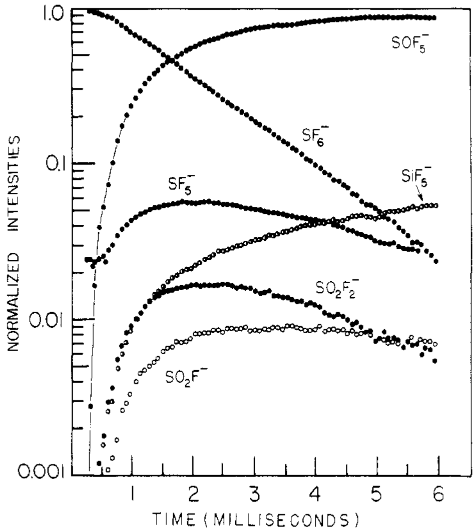

Figure 6. Normalized ion intensities observed as a function of time following pulsed ionization at 293 K of a sample of 0.05 mole fraction SF_6 in CH_4 after decomposition of the SF_6 in a negative corona discharge. Total pressure is 1.25 Torr. Data are displayed for every fifth channel.

Herron's[20] recommended $\Delta H_f°$ of 291.7 ± 0.2 kcal/mol for SF_6, it follows that $\Delta H_f°(SF_6^-)$ is −315.9 ± 2 kcal/mol based on currently available information. Since $\Delta H_f°(F^-)$ is well-defined as −59.5 ± 0.9 kcal/mol,[21] and taking $\Delta H_f°(SF_5)$ as −218.1 ± 3.2,[20] a F^- affinity for SF_5 of 38.3 ± 3.9 kcal/mol results from the calculated energy requirement for the dissociation $SF_6^- \rightarrow SF_5 + F^-$ (±3.9 kcal/mol is the simple propagated error). Considering the possible uncertainty in the EA value, which was obtained from ion–molecule equilibria measurements, as well as the number of individual heats of formation required for the various neutrals, the agreement between the independent value of 38.3 ± 3.9 and the experimental limits $37.4 \leq \Delta H_D°(SF_5\text{–}F^-) \leq 43.8$ kcal/mol apparently imposed by the measurements of Larson and McMahon is gratifying and certainly within the possible uncertainty introduced by combining calculated $\Delta S°$ values with direct $\Delta G°$ measurements to generate a $\Delta H°$ in the ICR studies (quoted as ±2 kcal/mol).

Sequential Negative Ion Chemistry in Discharged SF_6. In order to probe the identities of the successive negative charge carriers present during electrical discharge in SF_6, a sample previously exposed to partial corona decomposition was subjected to pulsed-kinetic analysis. Figure 5 shows the time-dependent ion profiles observed in the starting material (conditions listed in figure legends). Trace quantities of SO_2 were apparently present, as indicated by the low level formation of SF_5^-, $SO_2F_2^-$, and SO_2F^- at longer reaction times. Otherwise, the composite spectrum was found to be clean in that no other ions exceeding 0.1% of total ionization were detected up to 20-ms analysis time. The fractional yields of SF_5^-, $SO_2F_2^-$, and SO_2F^- at 5 ms equate to a concentration of 2 ppm of SO_2 based on the measured k for $SF_6^- + SO_2 \rightarrow$ products of 1×10^{-9} cm^3/(molecule·s) at 300 K. This same sample was subjected to slow decomposition in a negative point–plane corona discharge as described in the Experimental Section. The major discharge byproduct under these conditions is expected to be SOF_4, with smaller quantities of SO_2, SOF_2, SO_2F_2, and hydrolysis products such as HF. The yields of stable di- and polysulfur-containing compounds have not been determined, but are expected to be minimal. Figure 6 shows the initial anionic ion–molecule sequence occurring after pulsed ionization of the partially decomposed sample. Conditions were identical with those used to generate the data shown in Figure 5 except for an increase of a factor of 2 in the dilution factor. The accumulation of discharge byproducts and their subsequent chemistry induce a complex, but predictable, change in the temporal ion profiles. Three major features are evident: (i) SF_6^-, the only significant ion produced initially, is replaced as the dominant charge carrier by SOF_5^- after a few milliseconds; (ii) the fractional yields of SO_2F^-, $SO_2F_2^-$, and SF_5^- are significantly increased over the undischarged sample, although remaining at low relative levels; and (iii) among all of the ions present, only SiF_5^- and SOF_5^- show fractional increases at longer diffusion times. The rapid disappearance of SF_6^- from the composite spectrum can be mainly ascribed to reaction with SOF_4. The yields of the minor ions SF_5^-, $SO_2F_2^-$, and SO_2F^- result from F^- transfer to small quantities of SO_2 and SF_4 produced in the discharge. Consistent with the F^- affinity scale, all of these intermediate ions react further with the major oxyfluoride present, SOF_4, to yield SOF_5^-.

The appearance of SiF_5^- as one of the terminal ions was not unexpected. As stated earlier, the hydrolysis of decomposition byproducts such as SF_4, SOF_4, SOF_2, SO_2F_2, etc., involving trace levels of water vapor results in the concurrent generation of HF. Other rapid reactions occurring within the active discharge zone, such as $F + H_2O \rightarrow OH + HF$, also yield HF directly.[22] The net result is the gradual production of an otherwise stable product which reacts heterogeneously in turn with any silicon-containing material present in the discharge container to form SiF_4, which eventually diffuses into the active region. We cannot identify with certainty the source of SiF_4 in the present measurements. The reaction cell used for the corona-induced decomposition has a small internal quartz insulator but was otherwise free of silicon-containing components or contaminants (lubricants), as was the transfer line used for collection of the samples. Although the inlet system used for pulsed kinetic analysis does have additional sources of silicon (see section on Hydrolysis), there was no evidence that the fractional yield of SiF_5^- depended significantly upon the time interval between analysis and introduction of the discharged material into the mass spectrometer sample reservoir. On this basis it seems probable that the majority of the SiF_4 was slowly generated during the period in which the sample was contained in the discharge cell (120 h total, including 30.6 h of discharge). The long-term effect of trace SiF_4 on the composition of the negative charge carriers is shown in Figure 7. This sample of the discharged material, the same as shown in Figure 6, was not diluted with CH_4 in order to increase the rates of ion–molecule reaction with low-level products and more clearly identify the terminal ions (see conditions in figure legend). It is apparent from

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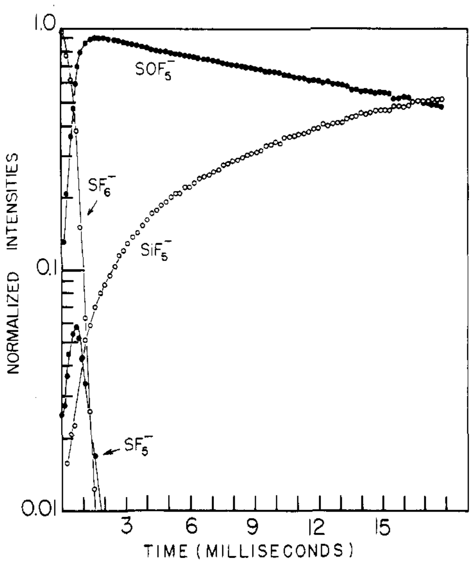

Figure 7. Normalized ion intensities observed as a function of time following pulsed ionization at 293 K of the same sample of SF_6 for which data are shown in Figure 6, but undiluted by CH_4. Pressure is 0.9 Torr. Data are displayed for every fifth channel.

the profiles that SiF_5^- will dominate the composite spectrum at analysis times beyond those possible with our instrumentation. As reported in the Experimental Section equilibrium was observed for the SOF_5^- + SiF_4 pair with a K_{eq} of 9 expected at 293 K for the F^- exchange $SOF_5^- + SiF_4 \leftrightarrow SiF_5^- + SOF_4$. The raw data of Figure 7 indicate that equilibrium was not attained in the partially decomposed sample under our pulsed analysis conditions since the SiF_5^-/SOF_5^- ratio was still slowly increasing at the longest reaction times. Combining the fact that the fractional intensities of SOF_5^- and SiF_5^- were equal at ~17 ms with a K_{eq} of 9 suggests that the concentration of SiF_4 was greater than 10% of the SOF_4 concentration in the discharged material since the limiting SiF_5^-/SOF_5^- ratio will certainly be greater than unity at reaction times sufficient to reach equilibrium under the conditions of Figure 7.

We must emphasize that this sample was subjected to moderate-to-heavy decomposition, with the total yield of detectable decomposition products approaching 1000 ppm of the starting material. These conditions were chosen in order to demonstrate the role of accumulated products in modifying the identify of the negative charge carriers during electrical breakdown. However, the yields of the various oxyfluorides and other byproducts are essentially linear with total discharge current[1a] and are expected to affect the anionic chemistry even at very low conversion levels. For example, assume the following set of conditions: SF_6 at a pressure of 200 kPa (2 atm) and 300 K, only 10 ppm of reactive impurities either present in the starting material or generated by partial decomposition, and an average k for reaction of SF_6^- of 2×10^{-10} cm^3/(molecule·s), which we suggest is typical for low E/N (field strength) situations involving SF_6 as the bulk component.[3] Using these values, solution of the standard second-order rate expression indicates that 90% of the SF_6^- produced initially will be replaced by other anions via reaction after only 20 μs of transit time. It is clear from this straightforward calculation that the identity of the negative charge carrier(s) in measurements incorporating SF_6 cannot be defined with certainty in the absence of direct analysis of the composite kinetic mass spectrum. Particularly sensitive toward impurity involvement would be systems operating at elevated pressures (long diffusion times), such as drift cell experiments designed to provide information on mobilities and ion transport. The total particle density is material only in that diffusion times are pressure dependent and that reactive impurities will be of greater importance when ion transport is slow (low E/N). Our previous studies[3] of SOF_4 production from corona discharges in various gas mixtures containing SF_6 indicates that deviations of the SOF_4 yield curves from linearity can be accounted for by destruction of SOF_4 via the reaction $SF_6^- + SOF_4$. However, other unidentified processes also appear to rapidly deactivate or consume SF_6^- in the discharge gap. The present study suggests that the reaction $SF_6^- + SiF_4$ would be a significant competing destruction process at higher SiF_4 concentrations. At low levels, SiF_4 plays and indirect protective role by converting SOF_5^- already produced into SOF_4 via the equilibrium $SOF_5^- + SiF_4 \leftrightarrow SiF_5^- + SOF_4$ (a situation analogous to that shown in Figure 7).

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Registry No. SF_6^-, 25031-39-4; SO_2, 7446-09-5; SOF_2, 7783-42-8; SO_2F_2, 2699-79-8; F_4OS, 13709-54-1; SF_4, 7783-60-0; SiF_4, 7783-61-1; F^-, 16984-48-8.