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Turbulent Ion Flow Tube Study of the Cluster-Mediated Reactions of SF_6^- with H_2O, CH_3OH, and C_2H_5OH from 50 to 500 Torr

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Reactions of SF_6^- with H_2O, CH_3OH, and C_2H_5OH were studied at 298 K from 50 to 500 Torr in a newly constructed turbulent ion flow tube (TIFT). These reactions were found to be cluster-mediated reactions, where the reactants are in equilibrium with a stable association complex and then products are formed via a bimolecular reaction of the complex with a second neutral reactant. By use of known equilibrium constants, rate constants were derived for the reaction of the complex with the second solvent molecule. The rate constants for these reactions, which are essentially pressure-independent, are 3.2×10^{-14} cm^3 s^{-1}, 1.8×10^{-13} cm^3 s^{-1}, and 2.2×10^{-13} cm^3 s^{-1} for H_2O, CH_3OH, and C_2H_5OH, respectively. Primary product ions for the H_2O reaction include SOF_4^- and $F^-(HF)_2$, and primary products for the CH_3OH and C_2H_5OH reactions include $F^-(HF)(ROH)$ and $F^-(HF)_2$. The observed ions are frequently solvated. The product distributions for the alcohol reactions show pressure dependencies from 50 to 500 Torr. These results have implications for the modeling of low-temperature corona or glow-type discharges, as well as for the use of SF_6^- as a chemical ionization mass spectrometry agent in humid environments.

Introduction

It is well-known that the high-voltage gaseous dielectric, SF_6, reacts in the presence of trace oxygen or water vapor in electrical discharges to form neutral byproducts that include such species as SOF_2, SOF_4, SO_2F_2, SO_2, and HF.[1,2] A variety of ionic byproducts are also observed, including $H_3O^+(H_2O)_n$, $SF_5^+(H_2O)_n$, $SOF_3^+(H_2O)_n$, SOF_x^-, $F^-(HF)_n$, $OH^-(H_2O)_n$, $SF_6^-(HF)_n$, and $SF_6^-(H_2O)_n$. Some of the proposed reaction pathways for the formation of various negative ions involve SF_6^- reacting with either the impurities or the byproducts of neutral reactions. Unfortunately, kinetics for the fundamental ion reactions have not been thoroughly investigated in many cases. For example, there are numerous reports of SOF_4^- being observed in SF_6 discharges[1] and in the ion source of an atmospheric pressure mass spectrometer,[3] and it has been suggested that the ion results from the following reaction:

$$SF_6^- + H_2O \rightarrow SOF_4^- + 2HF \qquad (1)$$

However, the kinetics of reaction 1 has not been examined; only the thermochemistry of the clustering reaction between SF_6^- and H_2O has been reported.[4] This reaction also suggests a role for trace water vapor in the formation of HF, a species that attacks insulators once it is formed in the discharge.

Because H_2O is often present as an impurity in SF_6 discharges, a more thorough understanding of the reaction between SF_6^- and H_2O would have application to the modeling of low-temperature corona, partial discharges, or glow-type discharges. In addition, understanding the reaction of SF_6^- with H_2O is important for chemical ionization mass spectrometry (CIMS) because H_2O is present in large amounts (and is presumed to be unreactive) when SF_6^- is used as a CIMS agent in humid atmospheres.[5−8] This study clarifies the interaction of SF_6^- with H_2O at 298 K over the pressure range from 50 to 500 Torr. We have also examined the related reactions of SF_6^- with CH_3OH and C_2H_5OH over this pressure range.

A previous report by Knighton et al.[9] indicated that at 2−3 Torr the reaction of SF_6^- with methanol is a cluster-mediated reaction:

$$SF_6^- + CH_3OH \xleftrightarrow{K_{eq}} SF_6^-(CH_3OH) \xrightarrow{k_2[CH_3OH]} \text{products} \qquad (2)$$

where the reactants are in equilibrium with the association complex and then a bimolecular reaction of the stable cluster ion with another CH_3OH molecule yields products. A class of cluster-mediated reactions that includes the reactions of SF_6^- with H_2O, CH_3OH, and C_2H_5OH has been investigated in our laboratory. We report rate constants and product distributions for these reactions at 298 K over the pressure range from 50 to 500 Torr.

Experimental Section

Measurements were made with the Air Force Research Laboratory's recently constructed turbulent ion flow tube (TIFT). This instrument has been described previously in detail.[10] For this study, SF_6^- reactant ions were formed and injected into the flow tube by coflowing a mixture of 1% SF_6 in helium, at a rate of approximately 1 cm^3 min^{-1}, with buffer gas (typically 60 L min^{-1}) into the flow tube through an in-line ionizer. An additional flow of buffer gas, typically 15 L min^{-1}, was introduced into the flow tube via another inlet in order to maintain turbulent flow. Most experiments utilized a nitrogen buffer gas, which was obtained from the gas delivery port of a high-pressure liquid N_2 dewar. Some experiments also required the use of a helium buffer (He, 99.997%), although the excessive flow rates needed to maintain turbulent flow limited the use of the helium buffer gas. Neutral reactants (absolute ethanol, U.S. Industrial Chemicals; 99.9% methanol, Fisher; and distilled

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water) were introduced into the flow tube through a bubbler system where nitrogen or helium carrier gas was passed through a sample of the reactant at a rate of up to 1 L min^{-1}. The reactant flow rate was derived from the known vapor pressure of the solvent along with the nitrogen flow rate and the total pressure in the bubbler; the reactant flow rate was roughly proportional to the square root of the nitrogen flow rate. The flow tube temperature was maintained at 298 K; the tube pressure was varied from 50 to 500 Torr by throttling the exhaust valve while keeping the flow rate constant. A small fraction of the gas in the tube flowed through a sampling orifice, and the reactant and product ions in this flow were mass-analyzed in a quadrupole mass filter and detected by a particle multiplier. Kinetics were measured by monitoring the reactant and product ion count rates as a function of the flow rate of the neutral reactant gas. The reaction times were determined from the neutral reactant inlet distance and from the ratio of the ion velocity to the buffer velocity, which has been characterized previously at 298 K by time-of-flight techniques as functions of both the Reynolds number and the tube pressure.

Results

Over the pressure range from 50 to 500 Torr, SF_6^- reacts with ROH (R = H, CH_3, C_2H_5) in a manner similar to the scheme reported by Knighton et al.[9] that is shown in reaction 2. The only primary product ions observed in these reactions are the stable association complexes, $SF_6^-(ROH)$. The fact that the reactants are in equilibrium is demonstrated by plotting

$$K' = \frac{[SF_6^-(ROH)]}{[SF_6^-][ROH]} \qquad (3)$$

as a function of the solvent concentration, as shown in Figure 1 for the H_2O and C_2H_5OH reactions at 300 Torr. Relative ion concentrations are provided by the measured ion intensities, while the neutral density is obtained from the derived reactant flow rate. The magnitude of K' is found to be essentially independent of the solvent concentration, except at very low concentrations, indicating that the reactants rapidly establish equilibrium with the association complex.

Evidence for the involvement of an additional solvent molecule in the overall reaction is provided by the kinetics data. For the complex mechanism shown in reaction 2, the integrated rate equation obtained by use of the equilibrium approximation is[11]

$$[SF_6^-] = [SF_6^-]_0 \exp(-K_{eq}k_2[ROH]^2t) \qquad (4)$$

under conditions where $[ROH] \gg [SF_6^-]_0$. If this mechanism is correct, the reaction is second-order with respect to the solvent concentration. Note that if products were to form instead via a unimolecular dissociation of the cluster complex, then the rate expression would be

$$[SF_6^-] = [SF_6^-]_0 \exp(-K_{eq}k_1[ROH]t) \qquad (5)$$

An example of the kinetics data for the reaction of SF_6^- with CH_3OH at 200 Torr is shown in Figure 2, plotted vs $[CH_3OH]$ in the top panel and vs $[CH_3OH]^2$ in the bottom panel. The data clearly demonstrate that the decays of SF_6^- are consistent with the involvement of two solvent molecules. The $[H_2O]^2$ dependence for the SF_6^- and H_2O reaction has recently been confirmed by Huey et al.[12]

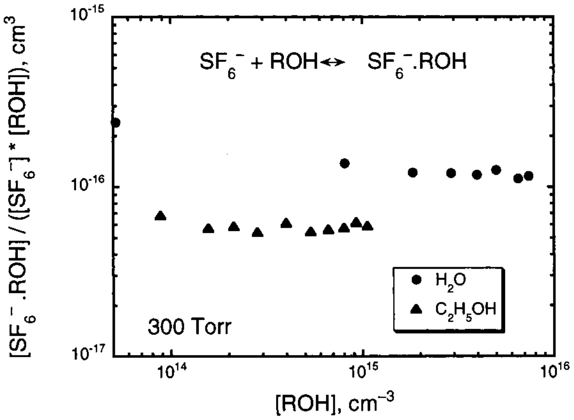

Figure 1. Demonstration of initial equilibrium for SF_6^- reacting with H_2O and C_2H_5OH at 300 Torr. $K' = [SF_6^-(ROH)]/\{[SF_6^-][ROH]\}$.

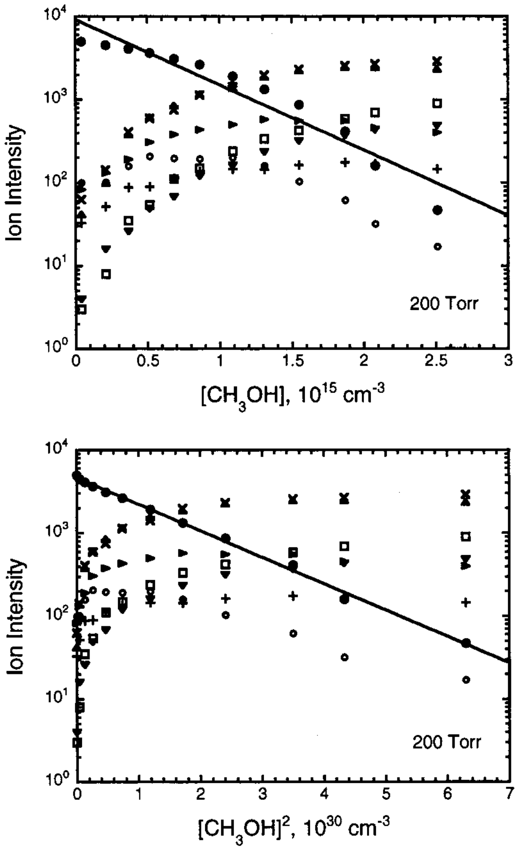

Figure 2. Example of data for reaction of SF_6^- with CH_3OH at 200 Torr plotted as (a, top panel) pseudo-first-order kinetics and (b, bottom panel) pseudo-second-order kinetics. The species are represented as follows: (●) SF_6; (○) $SF_6^-(CH_3OH)$; (arrowhead pointing right) $F^-(HF)_2$; (△) $F^-(HF)_2(CH_3OH)$; (▽) $F^-(HF)_2(CH_3OH)_2$; (+) $F^-(HF)(CH_3OH)$; (×) $F^-(HF)(CH_3OH)_2$; (□) $F^-(HF)(CH_3OH)_3$.

The applicable rate equation (eq 4) further indicates that if K_{eq} were known, then k_2 could be determined from the linear slope of the plot of ln $[SF_6^-]/[SF_6^-]_0$ vs $[ROH]^2$. Ideally, data such as that shown in Figure 1 could be used to determine equilibrium constants for these reactions. Unfortunately, the "equilibrium constants" obtained in this manner are not independent of the total buffer gas pressure; K' is found to increase with increasing buffer gas pressure from 50 to 500 Torr, as shown in Figure 3 for the H_2O reaction. This increase in K' is an experimental artifact that can be attributed to the formation of additional $SF_6^-(ROH)$ upon sampling the high-pressure flow tube gases into vacuum through an orifice 50 μm in diameter.

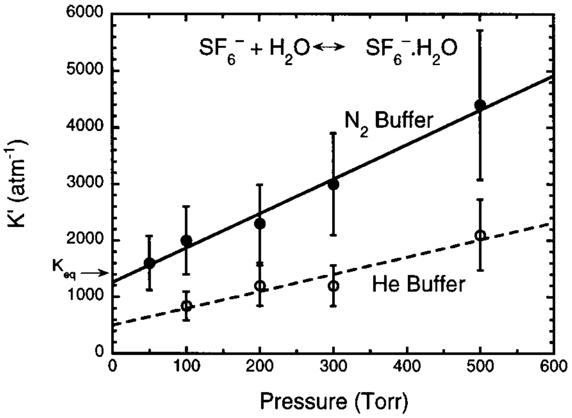

Figure 3. Pressure dependence of K' for H_2O reaction, shown for both N_2 and He buffers. Actual K_{eq}, as determined by Sieck,[4] is shown on y-axis.

TABLE 1: Rate Constants, k_2, and Product Distributions from 50 to 500 Torr for the Reactions of $SF_6^-(ROH)$ with an Additional ROH Molecule[a]

		product distributions		
pressure (Torr)	k_2[b] (10^{-13} cm^3 s^{-1})	$F^-(HF)_2$-$(ROH)_n$	$F^-(HF)$-$(ROH)_n$	SF_4O^--$(ROH)_n$
		H_2O		
50	0.37	0.21		0.79
100	0.26	0.14		0.86
300	0.31	0.16		0.84
500	0.33	0.16		0.84
		CH_3OH		
50	2.6	0.39	0.61	
100	1.3	0.50	0.50	
200	1.5	0.56	0.44	
300	2.2	0.60	0.40	
500	1.7	0.65	0.35	
		C_2H_5OH		
50	1.5			
100	1.6	0.20	0.80	
200	2.4	0.57	0.43	
300	2.6	0.71	0.29	
500	2.9	0.73	0.27	

[a] Collisional rate constants for H_2O, CH_3OH, and C_2H_5OH reactions are 2.2×10^{-9} cm^3 s^{-1}, 1.8×10^{-9} cm^3 s^{-1}, and 1.6×10^{-9} cm^3 s^{-1}, respectively. [b] k_2 was determined from K_{eq} values of 1400, 3225, and 5320 atm^{-1} for the reactions of SF_6^- with H_2O, CH_3OH, and C_2H_5OH, respectively, as reported in ref 4.

To illustrate this effect, several experiments were also carried out with helium buffer gas, which should result in less cluster formation upon sampling.[13] As expected, a significantly smaller increase in K' is observed with the helium buffer gas. The value of K' is also affected by the fact that clusters may dissociate upon sampling. These sampling complications make it impossible to accurately determine equilibrium constants in this instrument at this time. However, the sampling problems should not affect rate constant or primary product determinations. Clustering of the products with the solvent molecules is affected by this problem.

Actual equilibrium constants, K_{eq}, measured by high-pressure mass spectrometry have been reported by Sieck[4] for the reactions of SF_6^- with H_2O, CH_3OH, and C_2H_5OH. Use of Sieck's values for K_{eq} now allows k_2 to be determined from the present kinetics measurements made at 50−500 Torr. These results are shown in Table 1. The reaction rate constant for $SF_6^-(H_2O)$ reacting with another H_2O is pressure-independent, within our experimental uncertainty, and is approximately 3.2 (±1.3) × 10^{-14} cm^3 s^{-1}. The rate constants for both alcohol reactions also appear to be pressure-independent and are larger than that for the H_2O reaction, 1.8 (±0.7) × 10^{-13} cm^3 s^{-1} and 2.2 (±0.9) × 10^{-13} cm^3 s^{-1} for CH_3OH and C_2H_5OH, respectively. The reported errors represent the combined uncertainties in the equilibrium measurements and the current rate measurements. All the measured reaction rate constants are significantly smaller than the collisional rate constants calculated from the parametrized trajectory model of Su and Chesnavich;[14,15] for H_2O, CH_3OH, and C_2H_5OH, the collisional rate constants are 2.2×10^{-9} cm^3 s^{-1}, 1.8×10^{-9} cm^3 s^{-1}, and 1.6×10^{-9} cm^3 s^{-1}, respectively.

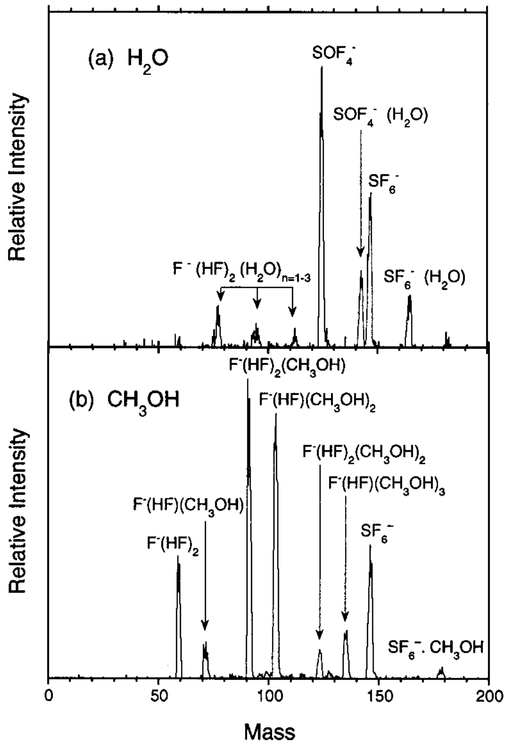

Figure 4. Mass spectra for reactions of SF_6^- with (a) H_2O and (b) CH_3OH at 100 Torr.

The final products of these cluster-mediated reactions are illustrated in the mass spectra shown in Figure 4. For the H_2O reaction (top panel), product ions include $SOF_4^-(H_2O)_n$ and $F^-(HF)_2(H_2O)_n$. For the CH_3OH reaction (bottom panel), products include $F^-(HF)(CH_3OH)_n$ and $F^-(HF)_2(CH_3OH)_n$. The reaction of SF_6^- with C_2H_5OH is analogous to that of CH_3OH, yielding $F^-(HF)(C_2H_5OH)_n$ and $F^-(HF)_2(C_2H_5OH)_n$. The primary product ions that are formed in the bimolecular reaction of $SF_6^-(ROH)$ with another solvent molecule are SOF_4^-, $F^-(HF)_2$, and $F^-(HF)(ROH)$. Subsequently, these product ions become further solvated by (a) additional reactions with the solvent [most of which are in equilibrium, as evidenced by plots such as that shown in Figure 1, where the ratio $[A^-(ROH)]/([A^-][ROH])$ remains constant with increasing solvent concentration] and by (b) sampling the high-pressure flow tube gas into vacuum. Thus, to determine product branching fractions, it is necessary to sum the solvated and unsolvated forms of each product ion. Branching fractions are determined by recording the product ion count rates as a function of the neutral reactant flow rate. To account for the effects of additional reactions between the product ions and the neutral reactants, the reported branching fractions are determined by extrapolating the measured branching fractions to a neutral reactant flow rate of zero as shown in Figure 5 for both H_2O and C_2H_5OH reactions. Product distributions determined in this manner are reported in Table 1. In addition to yielding the product branching fractions, these plots further demonstrate that, for CH_3OH and C_2H_5OH,

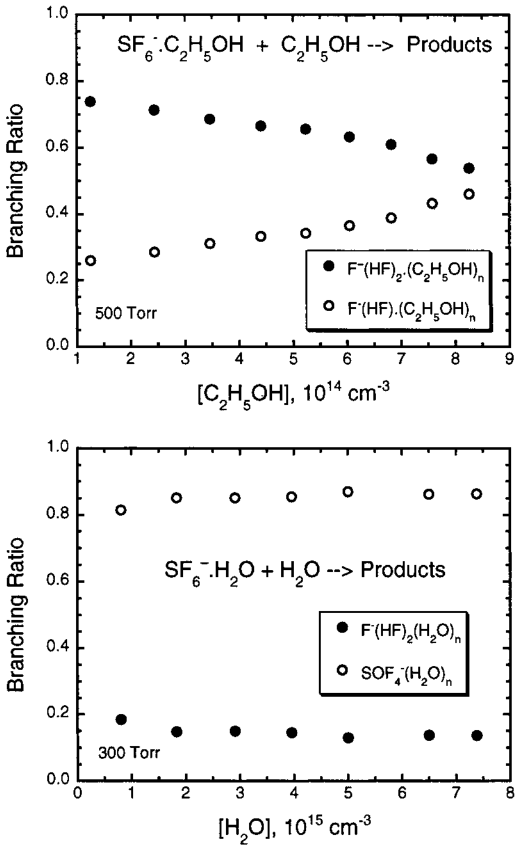

Figure 5. Product plot for (a, top panel) C_2H_5OH reaction at 500 Torr and (b, bottom panel) H_2O reaction at 300 Torr.

the $F^-(HF)_2(ROH)_n$ product ions undergo additional ligand switching, e.g.

$$F^-(HF)_2(C_2H_5OH)_n + C_2H_5OH \rightarrow F^-(HF)(C_2H_5OH)_{n+1} + HF \quad (6)$$

No ligand switching was found in the H_2O reactions. The rate constants for the switching reactions are much lower than the collision rate constants, and the reactions are most likely endothermic since ligand switching is generally rapid for exothermic reactions.[16] Comparing the reactant ion signal loss to the sum of the product ion signals yields a maximum absolute uncertainty in the branching fractions of 25%.

Unlike the reaction rate constants, the product distributions for the reactions of $SF_6^-(ROH)$ with an additional ROH molecule are pressure-dependent, as shown in Figure 6. The H_2O reaction produces mainly SOF_4^-. The product distribution has at most a weak pressure dependence. In contrast, the alcohol reactions, which yield predominately $F^-(HF)_2$ at higher pressures, are pressure-dependent over the entire range studied. The C_2H_5OH reactions were found to have a more significant pressure dependence than the CH_3OH reactions.

Discussion

Qualitatively, reactions of SF_6^- with the protic solvents H_2O, CH_3OH, and C_2H_5OH appear to behave according to the scheme first outlined for methanol by Knighton et al.,[9] where the formation of product ions is mediated by the initial formation of a stable solvent complex. The present measurement of the rate constant for the reaction of $SF_6^-(CH_3OH)$ with CH_3OH is in relatively good agreement with the previous measurement of 3.3×10^{-13} cm^3 s^{-1} made at 35 °C in a CH_4 buffer at 2−3 Torr. However, given the range of the present data, it is difficult to reconcile the product distributions that were reported previously, 72% $F^-(HF)_2(CH_3OH)_n$ and 28% $F^-(HF)(CH_3OH)_n$, with the current measurements. This difference remains unexplained.

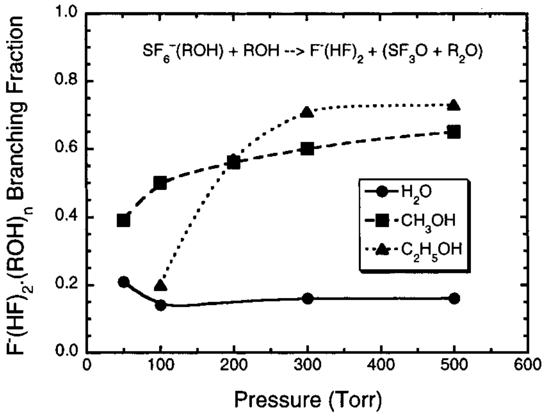

Figure 6. Pressure dependence of the product distributions. Only the $F^-(HF)_2(ROH)_n$ product channel is shown. The remaining products are $SF_4O^-(H_2O)_n$ for the H_2O reaction and $F^-(HF)(ROH)_n$ for the C_2H_5OH and CH_3OH reactions.

For all three solvents, the rate constants for the bimolecular reactions that ultimately lead to products are significantly less than the collisional rate constant. The small rate constants are not surprising given that products must form from rather complex reaction mechanisms involving numerous bonds being broken and re-formed. In a previous study, Huey et al.[5] proposed a mechanism for the reaction of SF_6^- with a number of atmospherically important neutrals ($ClNO_3$, HOCl, HCl, N_2O_5, and HNO_3). Their suggested mechanism involved the formation of an ion−molecule collision complex, with a sufficient lifetime to allow extensive rearrangement within the complex, followed by unimolecular dissociation of the complex to the observed product ions. The kinetics data presented here indicate clearly that this is not the case for the reaction of SF_6^- with the protic solvents water, methanol, and ethanol. At 298 K, these reactions require two solvent molecules to form product ions other than the association complexes.

The fact that multiple solvent molecules play an essential role in a reaction is not without precedent; a dramatic example is the reaction of SO_3 with H_2O to form H_2SO_4. Morokuma and Muguruma[17] reported that the energetically most favorable transition state along the reaction pathway is actually a six-centered cyclic transition state involving two water molecules. Their proposed mechanism involves two water molecules concertedly transferring their hydrogen-bonding protons to the proton acceptor oxygen atoms, while a new S−O bond is formed between the newly generated hydroxyl group and SO_3. This implies the formation of H_2SO_4 from SO_3 and H_2O should be second-order with respect to the H_2O pressure, which is consistent with the experimental findings.[18−20]

In the case of SF_6^- reactions with alcohols, the ionic products of the cluster-mediated reactions include $F^-(HF)_2$ and $F^-(HF)(ROH)$:

$$\begin{aligned} SF_6^-(ROH) + ROH \rightarrow\ & F^-(HF)_2 + (SF_3O_2 + R_2) \\ & F^-(HF)(ROH) + (SF_3O + RF) \quad (7) \end{aligned}$$

The neutral products of these reactions, shown in parentheses, are not characterized in this experiment; they are assumed, on the basis of most favorable energetics.[21,22] Given that SF_6^- might be more appropriately represented as $(SF_5)F^-$ rather than as a discrete molecular anion of octahedral geometry,[23] perhaps the reaction mechanism involves complexation of $(SF_5)F^-$ and ROH(s) and new S−O bond(s) being formed as protons from one and two solvent molecules are transferred to form $F^-(HF)(ROH)$ and $F^-(HF)_2$, respectively. The pressure dependence in the product distributions may indicate that the operative mechanism involves a two-step process (i.e., a double-well potential surface). At higher pressures, some of the first intermediate that is formed via a single proton transfer undergoes collisions with the buffer, thereby cooling the complex. The cooler complex then lives longer, allowing more time for the second proton transfer, resulting in a larger percentage of the reaction proceeding to form $F^-(HF)_2$.

In the reaction of SF_6^- with water, the $F^-(HF)(ROH)$ product ion is not observed; rather, the major product ion at all pressures is SOF_4^-, undoubtedly driven by the favorable energetics involved with forming two HF molecules:

$$SF_6^-(H_2O) + H_2O \rightarrow SOF_4^- + 2HF + H_2O \qquad \Delta H \sim -300\ \mathrm{kJ\ mol^{-1}} \quad (8)$$

The estimated exothermicity of reaction 8 is based upon $\Delta_f H°[SF_6^-(H_2O)] = -1418$ kJ mol^{-1}, as obtained from the thermochemical data,[4,22] and upon $\Delta_f H°[SOF_4^-] \sim -1175$ kJ mol^{-1}, as estimated from trends in $\Delta_f H°[SO_mF_n^-]$ and $\Delta_f H°[SO_mF_n]$.[21,22] If reaction 8 produces HF molecules in two discrete steps, one might expect to observe a $SOF_4^-(HF)$ intermediate. While there is a weak feature in the mass spectrum corresponding to that mass, it can be attributed largely to the ^{34}S isotope peak of $SOF_4^-(H_2O)$. However, we cannot rule out the possibility that very trace amounts of $SOF_4^-(HF)$ are produced.

This present study indicates only some of the negative ions observed in SF_6 discharges that are currently attributed to H_2O impurities result from the reaction with SF_6^-. As suspected, SOF_4^- originates from SF_6^- reacting with H_2O, although the reaction mechanism is much more complicated than previously presumed. Other anions such as $OH^-(H_2O)_n$ and SOF_5^- that have also been attributed to water impurities in the discharge must result from reactions with ions other than SF_6^-. The study also demonstrates that $F^-(HF)_2$ ions result from reactions with H_2O or other protic solvents and are not necessarily products solely of HF reactions, as previously assumed.

SF_6^- has been proposed as a chemical ionization agent for detection of atmospheric trace neutrals,[5] and it is currently being used as such in the dry environment of the South Pole.[12] The present measurements allow a determination to be made regarding the water concentration that can be present before the reaction of SF_6^- with H_2O begins to interfere with trace neutral detection, a value that depends on a number of factors related to the individual CIMS instrument and the specific application.

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