Cluster-Assisted Decomposition Reactions of the Molecular Anions of SF₆ and C₇F₁₄

W. B. Knighton, D. R. Zook, and E. P. Grimsrud

Department of Chemistry, Montana State University, Bozeman, Montana, USA

The cluster ions formed by the attachment of dimethylsulfoxide (DMSO) and methanol to the molecular negative ions of C₇F₁₄ and SF₆ have been studied by a pulsed e-beam high pressure mass spectrometer (PHPMS) and by an atmospheric pressure ionization mass spectrometer (APIMS). The free energy change (ΔG°) for the clustering equilibria reaction, $M^- + S \rightleftharpoons M^-S$, at 35 °C are found to be -7.7 and -7.2 kcal/mol for $S = \text{DMSO}$ and $M^- = \text{C}_7\text{F}_{14}^-$ and SF_6^- , respectively, and -6.4 and -4.5 kcal/mol for $S = \text{methanol}$ and $M^- = \text{C}_7\text{F}_{14}^-$ and SF_6^- , respectively. While the cluster ions formed by DMSO are found to be stable against side reactions, those formed by methanol undergo decomposition processes in which the central core ion is fragmented. At 35 °C, the rate law for the decomposition of the $\text{SF}_6^-(\text{CH}_3\text{OH})_1$ ion is second-order, involving the $M^-(\text{CH}_3\text{OH})_1$ cluster ion and another methanol molecule. While the $\text{C}_7\text{F}_{14}^-(\text{CH}_3\text{OH})_1$ ion also decomposes through this second-order process, a competing unimolecular mechanism is also operative at 35 °C. With increases in the PHPMS ion source temperature to 150 °C, the unimolecular decomposition process becomes progressively dominant for both of the $M^-(\text{CH}_3\text{OH})_1$ cluster ions of C₇F₁₄ and SF₆. Methanol cluster ions of the type M^-S_2 are not observed under any of the conditions examined here. When methanol or water partial pressures of a few torr or higher are present in the buffer gas of the APIMS ion source, the decomposition reactions are very fast and only the fragment ions produced by these reactions are observed in the electron-capture (EC)-APIMS spectra of C₇F₁₄ and SF₆. Also, in the methanol-containing APIMS ion source, the course of the SF₆⁻ decomposition reaction is altered so that fragment ions of the type $F^-(S)_n$ dominate the EC-APIMS spectrum of SF₆ at all ion source temperatures. For C₇F₁₄, fragment ions of the type $F^-(S)_n$ become dominant at lower ion source temperatures. These previously unknown reactions are expected to be important in the analysis of perfluorinated compounds by mass spectrometric methods that utilize ionization by electron capture or negative chemical ionization. The nature of the fragment ions produced in these cluster-assisted reactions may also provide a new source of information concerning the structures of the molecular negative ions of SF₆ and C₇F₁₄. (*J Am Soc Mass Spectrom* 1990, 1, 372-381)

Perfluorinated compounds (PFCs) generally possess high chemical stability and for this reason have been put to many practical uses. This stability also accounts for their great persistence once released into the environment. In sharp contrast to their general lack of chemical reactivity, however, is their behavior in the presence of low energy electrons; many of the PFCs have demonstrated extraordinary reactivity with thermalized electrons with which they readily react to form negative ions [1]. This facility for electron capture (EC) makes some of the PFCs ideal for use as a dielectric fluid in high-voltage transformers; for a long time, they will effectively inhibit electrical discharges. Some of the most sensitive methods of detecting PFCs at trace levels in the environment are also based on their fast EC reactions. These instruments are the EC detector [2] for gas chromatography and high pres-

sure negative ion mass spectrometers [3]. Some of the methods that have shown promise for removing PFCs from waste and drinking water have also been based on the EC reactions of these compounds [4].

For the above and other reasons, the gas-phase negative ion chemistry of several of the PFCs have been studied extensively. In these studies, unusual and interesting behavior has often been revealed. For example, while SF₆ (sulfur hexafluoride) and C₇F₁₄ (perfluoromethylcyclohexane) have been shown [1, 5, 6] to undergo resonance EC (reaction 1) extremely rapidly,

both of these molecules, M , and their molecular negative ions, M^- , have been shown to react extremely slowly in electron transfer (reaction 2),

with various electron donors, A⁻, or electron acceptors, A, even when reaction 2 in either direction is exoergic by several kcal/mol [7-9]. Exoergic reactions of this type normally proceed with collision frequencies [9].

Unusual behavior has also been observed in electron photodetachment (PD) studies of SF₆⁻ and C₇F₁₄⁻. Drzaic and Brauman [10] observed no PD for SF₆⁻ for photon energies up to 4.0 eV, in spite of the fact that the electron affinity of SF₆ is thought to be about 1.0 eV [8]. In our laboratory, we recently began PD studies of negative ions at atmospheric pressure [11] and found [12] that the onset of PD for C₇F₁₄⁻ occurs with photon energies of about 3.4 eV, which is also much higher than the 1.0 eV [8] electron affinity of C₇F₁₄. These PD results suggest that the structures of the molecular anions of SF₆ and C₇F₁₄ differ considerably from those of the corresponding neutral molecules [13]. It has even been suggested [10] that SF₆⁻ is possibly an ion-molecule complex, which might be more appropriately written as (SF₅)F⁻, rather than a discrete molecular anion of octahedral geometry. These structural effects may also be responsible for the slow rates of electron transfer (reaction 2) that have been observed when C₇F₁₄ or SF₆ is involved as one of the reacting pair.

In this article we report additional measurements of the negative ion chemistry of C₇F₁₄ and SF₆ in which the cluster ions formed by the attachment of dimethyl sulfoxide (DMSO) and methanol molecules to C₇F₁₄⁻ and SF₆⁻ have been studied. Most significantly, the methanol clusters of these ions will be shown to be unstable against decomposition reactions in which the core ions are fragmented. These cluster-assisted decomposition reactions will be shown to be particularly important in determining the negative ion mass spectra of C₇F₁₄ and SF₆ in an atmospheric pressure ion source when either of the protic solvents, methanol or water, are present in the buffer gas. The possibility that these fragment ions provide evidence concerning the structures of the SF₆⁻ and C₇F₁₄⁻ molecular negative ions is considered.

Experimental

Two mass spectrometers were used in this study; an atmospheric pressure ionization mass spectrometer (APIMS) and a pulsed e-beam high pressure mass spectrometer (PHPMS). The APIMS has a relatively simple ⁶³Ni-based ion source of about 1.5-cc internal volume and has been described in considerable detail elsewhere [14, 15]. The ion-sampling aperture of the APIMS ion source is 50 μm in diameter. The buffer gas is technical grade nitrogen that was passed through oxygen- and water-removing traps (Alltech, Dearfield, IL). Small quantities of C₇F₁₄ and SF₆ were introduced to the APIMS ion source by a gas chromatograph. A specific partial pressure of DMSO, methanol, or water was added to the nitrogen buffer gas by use of a

Figure 1. Ion source of the PHPMS: a-rectangular stainless-steel source block, b-gas entrance port, c-repeller plate, d-ion exit flange, e-electron entrance flange, f-electron focusing lenses, g-filament, h-high conductance stainless screen, i-skimmer lens, j-support bracket, k-vacuum envelope flange.

temperature-controlled bubbler, which has been described elsewhere [15, 16].

The PHPMS was recently constructed in our laboratory and, with several variations of our own, was modeled after basic designs previously reported by Kebabian [17]. As this is our first use of this instrument, a thorough description of it will be provided. The ion source of the PHPMS, shown in Figure 1, was machined from a rectangular stainless block, 5 × 5 × 5.7 cm. Two large circular holes were drilled into this block; an axial hole 1.9 cm in diameter by 4.0 cm deep and another 1.60 cm in diameter extends from one side to the center. A sample inlet line and an electrical feedthrough for the repeller plate pass through the rear of the source block. Two hat-shaped flanges, each with a single 1.0-mm hole in its center, were inserted and sealed with gold O-rings into the bored channels. Along with the repeller plate shown in Figure 1, these flanges define the internal dimensions of the source. Razorblade slits were spot-welded across the 1.0-mm holes of both flanges to limit the gas conductance through the source, while allowing electron entrance and ion exit from the source. The razorblade slits were set to a width of 30 μm. For the experiments reported here, the side flange was placed flush with the internal wall of the channel providing an interior source diameter of 1.9 cm. The interior length of the ion source, as defined by the distance between the repeller plate and front ion exit flange, was 1.8 cm. The interior volume of the source is about 5.0 cm³. The repeller plate was held at ground potential along with the entire ion source block.

The source block was heated by six resistive heaters that were inserted into 1/8" holes in the source block. The temperature was controlled by a Watlow model 804 temperature controller (Watlow, Winona, MN) using an iron-constantan thermocouple. Several additional thermocouples were also attached to various

parts of the source block in order to ensure uniformity of heating.

Gas samples of desired composition were prepared in a heated gas handling plant. The heart of the gas handling plant is a 5-L glass reservoir in which gaseous samples were prepared and stored during measurements. This reservoir is connected to the mass spectrometer and to an all-metal valving system by glass-to-metal seals and conflat flanges. The stainless valving system allows connection of the reservoir to a 2" diffusion pump, a buffer gas inlet, and a capacitance manometer [MKS (Andover, MA) model 221A, 0 to 1000 torr]. Chemicals were introduced to the 5.0-L glass reservoir by syringe through a teflon-backed septum affixed to the reservoir. Prepared gaseous mixtures were leaked to the mass spectrometer through a stainless-steel needle valve and a 1/4" stainless steel transfer line. The entire gas handling plant was enclosed in an insulated box maintained at 90 °C.

All chemicals were reagent grade and used as received from commercial suppliers. The buffer gas was ultrahigh purity methane (Matheson, Secaucus, NJ) and was passed through water- and oxygen-removing traps (Alltech) enroute to the gas handling plant.

With gas flowing to the mass spectrometer, the pressure in the ion source was measured using an MKS model 315BA (0-10 torr) capacitance manometer that was connected to the flow system by a tee in the transfer line. With use of the razorblade slits described above, ion source pressures up to about 4 torr were possible without causing excessive manifold pressure. At these source pressures, the differentially pumped source and quadrupole manifolds could be maintained at pressures below 3×10^{-4} and 3×10^{-6} torr, respectively. Most experiments were done at 3 torr ion source pressure.

The electron gun used for the pulsed experiments is shown in Figure 1. Its filament is displaced by about 5 cm from the electron entrance slit. The electron gun was controlled by a master clock that enables a short pulse, typically 40 μ sec, of 3000 eV electrons to irradiate the electron entrance slit once every 100 msec. Some of the ions that pass through the ion exit slit pass through the skimmer lens and into a second vacuum region where they are analyzed by a quadrupole mass filter [Extrel (Pittsburgh, PA), model C-50] and a channeltron electron multiplier [Galileo (Sturbridge, MA) model 4870E], which was operated in the ion counting mode. The temporal variations of any selected ion with respect to the firing of the e-beam is recorded and displayed by an IBM PC AT computer equipped with an Ortec (Oak Ridge, TN) ACE-MCS 913 multichannel scaling card. This device accumulates the number of counts for a given ion as a function of time for typically about 1,000 repetitions (100 s total measurement time) of the pulsed experiment.

The high pressure electron capture mass spectra (HPECMS) to be reported here were obtained by slowly scanning the full mass range of the quadrupole

mass filter while allowing the e-gun of the PHPMS to function in the pulsed mode.

Results and Discussion

HPECMS Spectra

HPECMS of C_7F_{14} obtained in 3.0 torr methane at an ion source temperature of 35 °C is shown in Figure 2a. The molecular anion, $C_7F_{14}^-$, is clearly dominant; no other ions of relative intensity larger than 1% are observed. In Figure 2b and c, the effects of adding 2.1 mtorr DMSO and 10.9 mtorr methanol, respectively, on the HPECMS spectrum of C_7F_{14} are shown. At this source temperature, cluster ions of the type M^-S (where M^- is the core molecular negative ion and S is either DMSO or methanol) are observed in spectra 2b and c along with the molecular $C_7F_{14}^-$ ion. The M^-S cluster ions are expected [18] and have been observed in previous studies of the solvation of other molecular anions by methanol and DMSO. However, in the presence of methanol in Figure 2c, four additional and unexpected ions are also observed. These fragment ions correspond to the species, $(M-F)^-$, $(M-2F)^-$, $F^-(HF)_2$, and $F^-(HF)_2(CH_3OH)_{1-3}$, with relative intensities of 0.96, 0.50, 0.57 and 0.15, respectively.

In Figure 3 the corresponding HPECMS spectra for SF_6 are shown. Again, only the expected M^- ion in pure methane, or the expected M^- and M^-S ions with added DMSO are observed in spectra 3a and b. Again, additional fragment ions appear with added methanol in spectrum 3c. These fragment ions are primarily attributed to the species $F^-(HF)_2(CH_3OH)_{0-1}$ ($m/z = 59$ and 91) and $F^-(HF)_1(CH_3OH)_{1-3}$ ($m/z = 71, 103, 135$).

Figure 2. Electron capture mass spectra of C_7F_{14} measured at 35 °C (a) in 3.0 torr pure methane, and (b) with 2.1 mtorr DMSO or (c) 10.9 mtorr methanol added to the 3 torr methane. The partial pressure of C_7F_{14} is 0.23 mtorr in all cases.

Figure 3. Electron capture mass spectra of SF_6 measured at 35 °C (a) in 3.0 torr pure methane, and (b) with 2.1 mtorr DMSO or (c) 65 mtorr methanol added to the 3 torr methane. The partial pressure of SF_6 is 0.15 mtorr in all cases.

As shown in Figures 4 and 5, increasing the temperature of the ion source has the effect of simplifying the HPECMS spectra of C_7F_{14} and SF_6 when methanol is present in the buffer gas. As expected [18], the relative intensities of the $\text{M}^-(\text{CH}_3\text{OH})$ cluster ions are greatly decreased in both cases by increased temperature. It is seen that the relative intensities of most of the fragment ions are also greatly decreased with increased temperature. At the highest temperature used (150 °C), the only fragment ions detected in Figures 4f and 5f, along with the dominant M^- ions, are the

Figure 4. Electron capture mass spectra of C_7F_{14} (0.23 mtorr) in 3.0 torr methane, which also contains 10.9 mtorr methanol at various temperatures between 35 °C and 150 °C.

Figure 5. Electron capture mass spectra of SF_6 (0.15 mtorr) in 3.0 torr methane, which also contains 61 mtorr methanol at various temperatures between 35 °C and 150 °C.

$(\text{M-F})^-$ fragment ions, and these are present at about 10% relative intensities in both cases. At 150 °C in pure methane buffer gas, the spectrum (not shown) of each of these compounds is changed very little relative to those shown in Figures 2a and 3a, which were recorded at 35 °C; the relative intensities of the $(\text{M-F})^-$ ions are then less than 1% for both C_7F_{14} and SF_6 . Therefore, it is clear that most of the $(\text{M-F})^-$ ions in Figures 4f and 5f for C_7F_{14} and SF_6 in the presence of methanol at 150 °C cannot be attributed to a simple EC process in which the M^- and $(\text{M-F})^-$ ions are simultaneously formed. Additional secondary reactions involving methanol are clearly operative at 150 °C, and these are producing most of the $(\text{M-F})^-$ ions observed in Figures 4f and 5f even though cluster ions are not directly observed.

Clustering Equilibria by Pulsed e-beam Measurements

In order to obtain additional information concerning the clustering and fragmentation processes that lead to the spectra discussed above, pulsed e-beam measurements were also made. These experiments were performed primarily at the lowest temperature conveniently achieved with the pulsed e-beam ion source, 35 °C, where the number and intensity of unexpected fragment ions are relatively large. An example of one of these measurements for the C_7F_{14} -DMSO system is shown in Figure 6. An e-beam pulse is applied once every 100 ms. During the initial 5 ms after a pulse, the total negative ion signal grows from a near-zero value to a maximum value. This delay in the onset of initial signal is caused primarily by a positive ion space-charge field that momentarily exists after the electron pulse [7, 17]. This field holds all negative ions within the gaseous volume of the ion source until most of

Figure 6. Pulsed e-beam experiment for the C_7F_{14} (0.23 mtorr)-DMSO (2.2 mtorr) reaction system in 3.0 torr methane at 35 °C. In this case M^- is the molecular $C_7F_{14}^-$ ion and M^-S is the $C_7F_{14}^-(DMSO)$ single cluster ion.

the electrons have been captured and a charge-neutral plasma of positive and negative ions has been established. From that point in time, negative ions are then free to diffuse to the walls of the ion source. A small fraction of these diffuse through the small ion exit slit and are detected. The total negative ion (TNI) signal observed by the mass spectrometer (not shown in Figure 6) will decay in time by first-order diffusion to the walls (for the example shown in Figure 6, the TNI signal has exactly the same decay rate and slope as the two ions signals shown in this figure). Since the rate of ion diffusion through a gaseous medium is inversely proportional to the square root of the ion-buffer gas reduced mass, all ions of masses > 100 u will have very similar diffusion rates in a light buffer gas such as methane [19]. If ion-molecule reactions also occur, additional changes of ion intensity with time will be experienced by the individual ions involved in these reactions.

In Figure 6, the M^- ion of C_7F_{14} is the most intense ion initially observed. This is expected due to the large EC rate coefficient of C_7F_{14} and the fact that neither DMSO or methane attach thermalized electrons. An ion due to the single DMSO cluster of $C_7F_{14}^-$, called M^-S , is also relatively intense during the initial period and then decays in time with exactly the same

log (intensity)-versus-time slope as the M^- ion. The fact that the M^- and M^-S ions have constant intensity ratios throughout the duration of the experiment indicates that these ions are linked by chemical equilibrium (reaction 3), which is fast in both directions.

In all pulsed e-beam experiments involving C_7F_{14} and SF_6 in which DMSO or methanol had been added to the methane buffer gas, the establishment of chemical equilibria between the M^- and M^-S species by reaction 3 was clearly indicated by their parallel temporal signals, such as those shown in Figure 6. Equilibrium constants, K_{MS} , for these reactions were evaluated from eq 4, in which the concentration ratios of the M^-S and M^- species in the ion source is provided by the measured ion intensity ratios, and the partial pressures of the solvating compound is expressed in units of atmospheres.

$$K_{MS} = [M^-S]/[M^-][S] \quad (4)$$

The magnitude of these equilibrium constants was found to be independent of partial pressures of S used or of the total buffer gas pressure from 2.0 to 4.0 torr. These determinations of K_{MS} are listed in Table 1 along with the corresponding values for the standard free energies at 35 °C that were calculated from $\Delta G^\circ = -RT \ln K_{MS}$. A measurement of ΔG° for the clustering of the metafluoronitrobenzene anion by one methanol molecule at 35 °C was also made in order to compare our measurements of clustering equilibria with previous ones performed on this system by Chowdhury et al. [18]. Our measurement of $\Delta G^\circ = -6.6$ kcal/mol for this system at 35 °C was identical to theirs.

The $-\Delta G^\circ$ values in Table 1 for clustering of $C_7F_{14}^-$ and SF_6^- are larger when DMSO rather than methanol is involved as the clustering agent. This result can be attributed to the relative magnitudes of the dipole moments [20] of DMSO (4.0 D) and methanol (1.7 D), and has been observed in other studies of ion cluster-

Table 1. Summary of kinetic and thermodynamic measurements at 35 °C

M	S	K_{MS}^a	$-\Delta G^\circ{}^b$	k_1^c	k_2^d
C_7F_{14}	DMSO	3.0×10^5	7.7	0	0
C_7F_{14}	CH_3OH	3.4×10^4	6.4	45*	$1.0 \times 10^{-12}{}^f$
SF_6	DMSO	1.3×10^5	7.2	0	0
SF_6	CH_3OH	1.7×10^3	4.5	0	$3.3 \times 10^{-13}{}^g$

^a Equilibrium constant (atm^{-1}) for clustering reaction, $M^- + S = M^-S$.

^b Free energy (kcal/mol) of clustering reaction at 35 °C.

^c First-order rate constant (s^{-1}) for unimolecular decomposition of M^-S .

^d Second-order rate constant ($cm^3 s^{-1}$) for decomposition of M^-S by reaction with another S molecule.

^e The product of this reaction is 100% $(M - F)^-$.

^f The products of this reaction are 41% $(M - F)^-$, 18% $(M - 2F)^-$, and 41% $F^-(HF)_2S_{0-1}$.

^g The products of this reaction are 72% $F^-(HF)_2S_{0-1}$ and 28% $F^-(HF)_3S_{1-3}$.

ing in which the negative ions possessed either highly localized charge density, as in Cl⁻ [21-23], or delocalized charge density, such as in the molecular anions of substituted nitrobenzenes [18]. It is also noted in Table 1 that the $-\Delta G^\circ$ for DMSO clustering of C₇F₁₄ and SF₆ are relatively similar, differing by only 0.5 kcal/mol in favor of C₇F₁₄. Since the electron affinities of C₇F₁₄ and SF₆ are almost identical [8], this result is also consistent with previous observations in which similar $-\Delta G^\circ$ values were observed for various substituted nitrobenzenes of similar EA [18]. It is interesting to note, however, that the $-\Delta G^\circ$ values for clustering by methanol differ by a significantly larger margin, 1.9 kcal/mol, again in favor of C₇F₁₄. This observation of preferential methanol attachment to C₇F₁₄ over SF₆ relative to the corresponding difference for DMSO attachment can be considered in terms of the structures of the ions and the two solvating molecules, in accordance with arguments previously put forth by Kebarle and co-workers [18, 22]. While the dipole moment of methanol is smaller than that of DMSO, its positive end is highly localized on its hydroxy hydrogen atom and can closely approach the region of negative charge density on a negative ion. If the charge density of the negative ion is also highly localized, the effective ion-dipole interaction radius of the complex can be made quite small and, in this case, a particularly strong interaction with methanol can be expected. While the dipole moment of DMSO is larger, its positive end is less localized than that of methanol and is sterically hindered in its interaction with a negative ion by its two methyl groups [22]. For these reasons, DMSO is less able than methanol to closely approach a negative ion of highly localized charge. Therefore, the preferential solvation of C₇F₁₄ by methanol observed here suggests that negative charge density in C₇F₁₄ is actually more localized than that in the smaller SF₆ ion.

Fragmentation Dynamics by Pulsed e-beam Experiments

Another pulsed e-beam experiment for C₇F₁₄ is shown in Figure 7 where methanol, rather than DMSO as in Figure 6, has been added to the methane buffer gas. Some of the same features as discussed above for Figure 6 are also evident here. A state of equilibrium for the solvation reaction symbolized by reaction 3 is again evident where the M⁻ and M⁻(CH₃OH) ions are held in constant relative abundance throughout the period of the experiment. A significant difference in this case, however, is that with methanol the decay of the M⁻ and M⁻(CH₃OH) ions in time is significantly faster than the decay of the TNI signal (not shown). Also, the four fragment ions, (M-F)⁻, (M-2F)⁻, and F⁻(HF)₂(CH₃OH)₀₋₁, which were noted previously in spectra 2c, are shown in Figure 7 along with the M⁻ and M⁻(CH₃OH) ions. As these fragment ions have very low relative intensities during the earliest moments of negative ion appearance, it is clear that they

Figure 7. Pulsed e-beam experiment for the C₇F₁₄ (0.23 mtorr)-methanol (10.9 mtorr) reaction system in 3.0 torr methane at 35 °C. In this case lines determined by averaging the accumulated ion signals are shown.

are not formed during the initial e-beam pulse of electrons. Instead, they are formed later in time and must be produced from either the M⁻ or M⁻(CH₃OH) ions. Because multiple cluster ions of the type M⁻(CH₃OH)₂ are not observed and because C₇F₁₄ shows no tendency to thermally decompose in pure methane buffer gas, it is reasonable to assume that the single cluster ion M⁻(CH₃OH) is involved in the formation of the fragment ions. Perhaps the simplest mechanism suggested by these initial observations is mechanism 5,

in which the single cluster ion is envisioned to be unstable and undergoes unimolecular decomposition to form the various fragment ions in a single, branched reaction. If this mechanism were operative, the slope, V_{obs} , of the $\ln(\text{intensity})$ -versus-time plot for the M⁻ and M⁻(CH₃OH) ions in Figure 7 would be given by

$$V_{\text{obs}} = k_1 Q + V_d \quad (6)$$

where $Q = [M^-S]/([M^-] + [M^-S]) = K_{MS}[S]/(1 + K_{MS}[S])$, and V_d is the first-order rate constant for the loss of all ions by diffusion to the walls (V_d is determined from parallel measurements of the TNI signal decay rate under identical pulsed e-beam conditions). In Figure 8, a plot of $V_{\text{obs}} - V_d$ versus Q for all C₇F₁₄-methanol measurements is shown in which a variety of methanol partial pressures were used in 3.0 torr methane pressure and 35 °C. The resulting curved line indicates that this reaction system is poorly described by mechanism 5. In addition, it was found that the intensity of the (M-F)⁻ ion increases somewhat relative to those of the other fragment ions as progressively smaller partial pressures of methanol were used. This observation suggests that the fragment ions in Figures 2c and 7 come from at least two competitive processes of differing orders with respect to methanol concentration. The following generalized scheme, in which the fragment ions are produced by competitive first- and

Figure 8. The observed reaction velocity corrected for diffusional loss is plotted against $Q = [M^-S]/([M^-] + [M^-S])$ for the C_7F_{14} -methanol reaction system at 35 °C. This plot is a test of the applicability of eq 6 and mechanism 5 for this reaction system. Q has been varied by changing the partial pressure of methanol from about 0.5 to 15 mtorr. The total pressure of methane buffer gas was 3.0 torr, except for the two square data points for which the methane pressure was 2.0 and 4.0 torr.

second-order reactions from the single cluster ion, was then tested for the C_7F_{14} -methanol system

It is noted that one of the product ions, $F^-(HF)_2$, becomes stoichiometrically more reasonable with mechanism 7 because its two hydrogen atoms can be supplied by the two hydroxy protons of the two methanol molecules involved in the second order process. It is also noted that this ion appears as two ions, the other being $F^-(HF)_2S$, due to its fast clustering/declustering reactions with methanol. If mechanism 7 is operative, the slope, V_{obs} , of the $\ln(\text{intensity})$ -versus-time data for the M^- or M^-S ions in Figure 7 will be given by:

$$V_{obs} = (k_1 + k_2[S])Q + V_d \quad (8)$$

where Q and V_d have the same definitions as given for eq 6. The results of the C_7F_{14} -methanol experiments have been plotted again in Figure 9 in the form $(V_{obs} - V_d)/Q$ versus $[S]$. A straight line, consistent with eq 8 and mechanism 7, is then obtained. The slope and intercept of this line provide $k_2 = 1.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $k_1 = 45 \text{ s}^{-1}$.

It is useful to consider what the most likely neutral products might be in the C_7F_{14} -methanol reactions shown in mechanism 7. Three of the four decomposition reactions in mechanism 7 involve the loss of one or two fluorine atoms. Each of these departing fluorine atoms undoubtedly reacts with one of the methanol molecules present in the reaction complex as follows: $F + CH_3OH \rightarrow HF + CH_3O$. This hydro-

Figure 9. The same measurements described in Figure 8 are plotted here in a form that tests for applicability of eq 8 and mechanism 7 to the C_7F_{14} -methanol reaction system at 35 °C.

gen atom transfer step provides about -32 kcal/mol^* of enthalpy change to the overall reaction [23] and, therefore, will be a driving force in these reactions. These reactions probably also provide the source of HF in the fourth terminal ion, $F^-(HF)_2^-$, included in mechanism 7. More specifically, $F^-(HF)_2$ might be produced from the same reaction complex that leads to $(M-2F)^-$ and 2HF in the following way: immediately following a significant fraction of these reactions, the two HF product molecules remain attached to the $(M-2F)^-$ product ion and induce it to decompose further to $F^-(HF)_2$. Supporting evidence for the formation of F^- ions by the assistance of solvation will be related in a later section dealing with APIMS measurements.

The identical pulsed e-beam experiments as described above were also performed for SF_6 in the presence of DMSO and methanol. These experiments revealed that SF_6^- undergoes reactions that are similar to those described above for $C_7F_{14}^-$ in the presence of these two clustering agents. In the presence of DMSO, only the M^- and $M^-(DMSO)$ ions, and no fragment ions, are observed. In the presence of methanol, the fragment ions shown previously in Figure 3c are observed, along with the M^- and $M^-(CH_3OH)$ ions. As shown in Figure 10, the measured decay rate of the $SF_6^-(CH_3OH)$ ion at 35 °C is again best described by mechanism 7. In this case, however, the intercept in Figure 10 indicates that k_1 is too small to be accurately determined under these conditions, while $k_2 = 3.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. All rate constants, equilibrium constants, and product ion distributions produced through mechanism 7 in the solvation of SF_6^- and $C_7F_{14}^-$ by DMSO and methanol are summarized in Table 1.

The dominant mechanism for the methanol-assisted decomposition of $C_7F_{14}^-$ and SF_6^- appears to change as the ion source temperature is made higher. In the previous discussion of Figures 4f and 5f, it was shown that most of the $(M-F)^-$ ions that are observed at 150 °C are produced by virtue of methanol's presence. In additional measurements at 150 °C, it was found that the

* Calculated from $H_f(F) = 19$, $H_f(HOCH_3) = -48$, $H_f(HF) = -65$, and $H_f(CH_3O) = 4 \text{ kcal/mol}$, taken from ref [23].

Figure 10. This plot tests the applicability of eq 8 and mechanism 7 to the SF₆-methanol reaction system at 35 °C in 3.0 torr methane. The partial pressure of SF₆ is 0.15 mtorr and the partial pressure of methanol has been varied from about 15 to 70 mtorr.

relative intensity of the (M-F)⁻ ions in the HPECMS spectra of C₇F₁₄ and SF₆, such as those shown in Figures 4f and 5f, were directly proportional to the concentration of methanol added to the buffer gas. This observation is most consistent with unimolecular mechanism 5 in which K_{MS} is small at 150 °C, but k₁ is very large, so that the M⁻S cluster ion is involved as a short-lived intermediate that is not directly observed.

Effects of Methanol and Water on the EC-APIMS Spectra of C₇F₁₄ and SF₆

Due to the much higher partial pressures of solvating compound that can be added to a buffer gas at 1.0 atmosphere total pressure, the effects of the methanol-assisted decomposition reactions discussed above might be expected to be greatly amplified in the EC-APIMS spectra of C₇F₁₄ and SF₆. These expectations are clearly demonstrated for C₇F₁₄ in Figure 11. In Figure 11a, the EC spectrum of C₇F₁₄ at 150 °C is very simple in pure nitrogen carrier gas; it consists of a dominant M⁻ ion and a low-intensity (M-F)⁻ ion. As the temperature of the ion source is lowered from 150 °C (not shown in the figure), the relative intensity of the (M-F)⁻ in pure nitrogen buffer gas becomes even lower than indicated in Figure 11a. The EC-APIMS spectrum of C₇F₁₄ in the presence of 13 torr methanol at 150 °C is shown in Figure 11b. This spectrum is dominated by the (M-F)⁻ fragment ion, and the molecular M⁻ ion is no longer observable. Recall (Figure 4f) that the intensity of the (M-F)⁻ ion for C₇F₁₄ at 150 °C was modest relative to that of the dominant M⁻ ion under conditions of much lower methanol partial pressure. The approximately thousandfold increase in methanol concentration in the APIMS experiment appears to account for the reversal of the M⁻ and (M-F)⁻ ion intensities in spectrum 11b.

As shown in Figure 11c, the EC-APIMS spectrum of C₇F₁₄ is further altered by the combined effects of

methanol's presence and low temperature, and bears little resemblance to either of the spectra shown in Figure 11a and b. The intensity of the (M-F)⁻ ion is very low in spectrum 11c, which is dominated by fragment ions of the type F⁻(CH₃OH)₂₋₁₀. In additional experiments at 40 °C, it was found that the relative intensity of (M-F)⁻ was continuously decreased and F⁻(CH₃OH)_n increased as the partial pressure of methanol was increased. This trend is consistent with the following reaction sequence in which the final location of the excess negative charge is influenced by the solvation of the reaction intermediate shown in reaction 9.

As the partial pressure of methanol is made very high, a larger number, *n*, of methanol molecules will be available for clustering to the intermediate species as its bond to a fluorine atom is being lengthened. As *n* is made larger, the magnitude of this stabilizing force will be much greater if the excess negative charge is retained on the smaller F atom rather than on the larger molecular portion of the intermediate species. Therefore, as the partial pressure of methanol is increased, the preferred location of negative charge changes from the (M-F) to the F portions of the reaction intermediate.

In Figure 12 the corresponding EC-APIMS spectra of SF₆ are shown. Again, in the absence of added methanol, spectrum 12a indicates that the normal

Figure 11. The EC-APIMS spectra of C₇F₁₄ in pure nitrogen buffer gas (a) at atmospheric pressure and 150 °C, and (b) with 13 torr methanol added to the nitrogen buffer gas at 150 °C, (c) and at 40 °C.

Figure 12. The EC-APIMS spectra of SF_6 in pure nitrogen buffer gas (a) at atmospheric pressure and 150°C , and (b) with 13 torr methanol added to the nitrogen buffer gas at 150°C , and (c) at 40°C .

products of EC by SF_6 at atmospheric pressure are a dominant M^- ion and an $(\text{M-F})^-$ ion of very low relative intensity. However, with 13 torr methanol added to the buffer gas, only ions of the type $\text{F}^-(\text{CH}_3\text{OH})_n$ are observed at both high and low ion source temperatures; the $n = 2$ and 3 species are observed at 150°C , and the $n = 2$ -10 species at 40°C . The fragment ion of the type $(\text{M-F})^-$, which was dominant at high ion source temperature for C_7F_{14} , is not observable even at high temperature for SF_6 . In terms of mechanism 9, this may be due to the fact that the SF_5 fragment is smaller and has a lower EA [24] than the C_7F_{13} fragment and, therefore, is less able to compete with a highly solvated F species for retention of the negative charge in reaction 9.

In Figure 13 the EC-APIMS spectra of C_7F_{14} measured in the presence of 16 torr water using both high and low ion source temperatures are shown. These spectra bear close resemblance to the corresponding spectra obtained in the presence of methanol (spectra 11b and c). At 150°C , spectrum 13a is again dominated by the $(\text{M-F})^-$ fragment ion, and at 40°C spectrum 13b consists entirely of ions of the type $\text{F}^-(\text{H}_2\text{O})_n$ where $n = 2$ -23 in this case. The distribution of ions in spectrum 13b (as well as those shown previously in spectra 11c and 12c) is not thought to represent the actual distribution of cluster ions in the ion source. Calculations [25] of the actual F^- water cluster distribution expected under the conditions resulting in spectrum 13b indicate that the most abundant ions within the ion source will be cluster ions having $n = 5$ -7 water molecules. The

much larger cluster ions shown in spectrum 13b are being produced only in the region of the ion-sampling aperture of the APIMS ion source, where adiabatic expansion of the atmospheric pressure gas leads to gas cooling and additional cluster growth just prior to their mass analysis and detection [15].

The APIMS measurements reported above indicate that the molecular negative ions of PFCs may not be generally observable under electron capture or negative chemical ionization conditions when protic compounds such as methanol and water are present at partial pressures of several torr. Because ambient air typically contains this much water vapor, for example, only cluster-assisted fragment ions might be expected in the analysis of PFCs in real air by the direct introduction of the whole air sample into a negative ion APIMS ion source. These processes might also be expected to be important in the analysis of PFCs by liquid chromatography/mass spectrometry (LC/MS) if a protic compound is used in the mobile phase. A recent report by Huang et al. [26] provides support for this latter expectation. In their determinations of a variety of PFCs (including C_7F_{14}) by LC/MS, they observed ions primarily of the type $(\text{M-F})^-$ when using the "filament on" mode of "thermospray" effluent vaporization with water added to the mobile phase at high ion source temperature. Our results, shown in spectra 13a, indicated preferential formation of the $(\text{M-F})^-$ from C_7F_{14} under conditions that were very similar to these. It seems very likely, therefore, that the $(\text{M-F})^-$ fragment ions observed by Huang et al. [26] also originated through the cluster-assisted decomposition reactions described here.

Conclusions

We have shown that the molecular negative ions of C_7F_{14} and SF_6 are made unstable when clustered by the protic molecule methanol and that they then read-

Figure 13. The EC-APIMS spectra of C_7F_{14} in nitrogen buffer gas, which also contains 15 torr water at (a) 150°C and (b) 40°C .

ily decompose into various smaller fragment ions. It was demonstrated that water also causes fragmentation of these molecular anions while the dipolar aprotic molecule DMSO does not. These previously unknown reactions have direct implications for the analysis of PFCs by negative ionization methods under conditions in which protic compounds (including water) are present in the buffer gas. We have demonstrated that these cluster-assisted decomposition reactions can dominate the APIMS negative ion spectra of PFCs if the partial pressure of methanol or water in the buffer gas exceeds a few torr.

While it is acknowledged that the preferred geometries of the $\text{C}_7\text{F}_{14}^-$ and SF_6^- ions are possibly distorted through clustering by a methanol molecule, it is nevertheless interesting to consider whether the fragment ions produced by the decomposition of the clustered ions provide additional insight concerning the structures of the core SF_6^- and $\text{C}_7\text{F}_{14}^-$ ions. In particular, it is interesting to consider the possibility, mentioned earlier, that SF_6^- and $\text{C}_7\text{F}_{14}^-$ might be better represented as nondiscrete ion-complexes of the type $(\text{SF}_5)\text{F}^-$ and $(\text{C}_7\text{F}_{13})\text{F}^-$. The pulsed e-beam experiments reported here indicate that the dominant fragment ion formed from the methanol cluster ion of $\text{C}_7\text{F}_{14}^-$ is the $(\text{M-F})^-$ ion for all ion source temperatures. This could be viewed to be consistent with the possibility that $\text{C}_7\text{F}_{14}^-$ is an ion of the type $(\text{C}_7\text{F}_{13})\text{F}^-$, because the loss of the unique F atom and retention of the negative charge on C_7F_{13} could then be easily envisioned in an encounter of this species with methanol molecules. In that case, the neutral products might reasonably be assumed to be HF and the CH_3O radical. However, this line of reasoning does not provide similar support for the $(\text{SF}_5)\text{F}^-$ representation of SF_6^- . The major fragment ions formed by the decomposition of the methanol cluster of SF_6^- at 35 °C were not ions of the type $(\text{M-F})^-$, but rather were ions of the type $\text{F}^-(\text{HF})_{1-2}$ in which two or three fluorine atoms were separated from the parent cluster ion. In this discussion, it is also interesting to recall that the $-\Delta G^\circ$ values for clustering reported here suggested that negative charge density in $\text{C}_7\text{F}_{14}^-$ is more localized than in the smaller SF_6^- ion. This observation also argues against the $(\text{SF}_5)\text{F}^-$ representation of SF_6^- and might be interpreted to be supportive of the $(\text{C}_7\text{F}_{13})\text{F}^-$ representation of $\text{C}_7\text{F}_{14}^-$.

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