1024 *J. Phys. Chem. A* **2007,** *111,* 1024−1029

Electron Attachment to SF_5X Compounds: $SF_5C_6H_5$, $SF_5C_2H_3$, S_2F_{10}, and SF_5Br, 300−550 K

Thomas M. Miller,*,[†,‡] A. A. Viggiano,[†] William R. Dolbier, Jr.,[§] Tatiana A. Sergeeva,[§] and Jeffrey F. Friedman[‖]

Air Force Research Laboratory, Space Vehicles Directorate, Hanscom Air Force Base, Bedford, Massachusetts 01731-3010, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, and Department of Physics, University of Puerto Rico, Mayaguez, Puerto Rico 00681-9016

Received: October 10, 2006; In Final Form: November 10, 2006

Rate constants and ion product channels have been measured for electron attachment to four SF_5 compounds, $SF_5C_6H_5$, $SF_5C_2H_3$, S_2F_{10}, and SF_5Br, and these data are compared to earlier results for SF_6, SF_5Cl, and SF_5CF_3. The present rate constants range over a factor of 600 in magnitude. Rate constants measured in this work at 300 K are $9.9 \pm 3.0 \times 10^{-8}$ ($SF_5C_6H_5$), $7.3 \pm 1.8 \times 10^{-9}$ ($SF_5C_2H_3$), $6.5 \pm 2.5 \times 10^{-10}$ (S_2F_{10}), and $3.8 \pm 2.0 \times 10^{-10}$ (SF_5Br), all in $cm^3\ s^{-1}$ units. SF_5^- was the sole ionic product observed for 300−550 K, though in the case of S_2F_{10} it cannot be ascertained whether the minor SF_4^- and SF_6^- products observed in the mass spectra are due to attachment to S_2F_{10} or to impurities. G3(MP2) electronic structure calculations (G2 for SF_5Br) have been carried out for the neutrals and anions of these species, primarily to determine electron affinities and the energetics of possible attachment reaction channels. Electron affinities were calculated to be 0.88 ($SF_5C_6H_5$), 0.70 ($SF_5C_2H_3$), 2.95 (S_2F_{10}), and 2.73 eV (SF_5Br). An anticorrelation is found for the Arrhenius *A*-factor with exothermicity for SF_5^- production for the seven molecules listed above. The Arrhenius activation energy was found to be anticorrelated with the bond strength of the parent ion.

I. Introduction

We have earlier measured electron attachment rate constants and ion product branching fractions for SF_6, SF_5Cl, and SF_5CF_3.[1−3] As is well-known, thermal electron attachment to SF_6 proceeds near the collisional rate (at least, for pressures over 10^{-4} Torr) and yields both SF_6^- and SF_5^-.[1,4] Attachment to SF_5Cl and SF_5CF_3 both yields only SF_5^- ion product, up to 550 K, with rate constants that are 15% and 25% efficient at room temperature, respectively.[2,3] Electron attachment to SF_5Cl and SF_5CF_3 has also been studied in an atmosphere of N_2 and CO_2 and as a function of electron energy in beam-gas and laser photoelectron attachment experiments.[5−9] In the present work, we extend the measurements on SF_5X compounds to $SF_5C_6H_5$ (pentafluorosulfanylbenzene), $SF_5C_2H_3$ (pentafluorosulfanylethylene), S_2F_{10} (disulfur decafluoride), and SF_5Br (pentafluorosulfanylbromide). Provisional product channels for these species are given below.

$$e^- + SF_5C_6H_5 \rightarrow SF_5C_6H_5^- \qquad \Delta H_{rxn} = -0.88\ \text{eV} \tag{1}$$

$$\rightarrow SF_5^- + C_6H_5 \qquad \Delta H_{rxn} = -0.38\ \text{eV} \tag{2}$$

$$\rightarrow SF_5 + C_6H_5^- \qquad \Delta H_{rxn} = +2.54\ \text{eV} \tag{3}$$

$$e^- + SF_5C_2H_3 \rightarrow SF_5C_2H_3^- \qquad \Delta H_{rxn} = -0.62\ \text{eV} \tag{4}$$

$$\rightarrow SF_5^- + C_2H_3 \qquad \Delta H_{rxn} = -0.44\ \text{eV} \tag{5}$$

$$\rightarrow C_2H_3^- + SF_5 \qquad \Delta H_{rxn} = +2.89\ \text{eV} \tag{6}$$

$$e^- + S_2F_{10} \rightarrow S_2F_{10}^- \qquad \Delta H_{rxn} = -2.86\ \text{eV} \tag{7}$$

$$\rightarrow SF_5^- + SF_5 \qquad \Delta H_{rxn} = -2.07\ \text{eV} \tag{8}$$

$$\rightarrow SF_6^- + SF_4 \qquad \Delta H_{rxn} = -1.94\ \text{eV} \tag{9}$$

$$\rightarrow SF_4^- + SF_6 \qquad \Delta H_{rxn} = -2.46\ \text{eV} \tag{10}$$

$$e^- + SF_5Br \rightarrow SF_5Br^- \qquad \Delta H_{rxn} = -2.76\ \text{eV} \tag{11}$$

$$\rightarrow SF_5^- + Br \qquad \Delta H_{rxn} = -1.97\ \text{eV} \tag{12}$$

$$\rightarrow Br^- + SF_5 \qquad \Delta H_{rxn} = -1.33\ \text{eV} \tag{13}$$

where the reaction enthalpies (ΔH_{rxn} at 298 K) are from G3(MP2) calculations (G2 for SF_5Br) to be described in section IV.[10−15]

The SF_5X represents an excellent series of molecules to look for trends in electron attachment. The properties of the molecules, such as electron affinity, bond length of the neutral and anion, exothermicity, and bond dissociation energy, vary widely. For most of the species, the calculated geometry of X varies little between that found in SF_5X and X itself, with C_2H_3 being an exception (section IV). The calculated SF_5 geometry

---

* To whom correspondence should be addressed. E-mail: thomas.miller@hanscom.af.mil.

[†] Air Force Research Laboratory.

[‡] Also, Institute for Scientific Research, Boston College.

[§] University of Florida.

[‖] University of Puerto Rico-Mayaguez.

10.1021/jp066656h CCC: $37.00

is also similar in most of the compounds. Correlations to these various properties will be discussed in section V.

II. Experimental Section

The present measurements were made in a flowing-afterglow Langmuir-probe (FALP) apparatus. The method has been detailed in the literature[16] as has the Air Force Research Laboratory FALP.[1,17] The attachment reactions take place in a fast-flowing electron-He^+, Ar^+ plasma at 133 Pa of He gas. The $SF_5C_6H_5$, $SF_5C_2H_3$, S_2F_{10}, and SF_5Br were synthesized for the present experiments and were used as provided, aside from freeze−pump−thaw degassing cycles with liquid samples, as needed. The syntheses of the various compounds have been published.[18−21] Mixtures of the reactant gases in He were prepared at room temperature to ensure accurate measurement of the flow rate of reactant into the FALP, with stronger mixtures for the slowest attaching gases. Mixtures of 0.32% of $SF_5C_6H_5$, 0.30% of $SF_5C_2H_3$, 6.4% of S_2F_{10}, and 3.1% of SF_5Br were used. Of these vapors, only $SF_5C_6H_5$ proved to be "sticky". Stickiness manifests itself by observing a decrease in pressure after the vapor is first introduced into a clean, empty stainless steel mixture vessel: the pressure in the vessel decreases as the walls passivate. The vessel is pumped and refilled until stable at the desired pressure. Care is then taken not to use up more than 10% of the mixture, to avoid possibly compromising the composition. Measurements with $SF_5C_6H_5$ required patience because of the need to passivate the mixture vessel, the flowmeter, and gas feedlines by flowing neat $SF_5C_6H_5$ prior to each measurement. Failure to do this would lead to an apparent k_a that was as much as 10 times too small and which increased with each subsequent measurement. Because of the limited amount of $SF_5C_6H_5$ that was synthesized and the amount needed for passivation, data were only obtained at four temperatures for this compound. A mass spectrometer at the downstream end of the flow tube allowed determination of ionic products of the attachment reactions.

An example of the data obtained in the present work is shown in Figure 1 for $SF_5C_2H_3$. The measurement of the diffusion frequency was made in absence of reactant gas. The attachment rate constant k_a was determined from a fit to the data of the solution to the rate equations describing ambipolar diffusion and electron attachment.[16,17] The measured k_a's are estimated accurate to ±25% for a case where no complications arise, as with $SF_5C_2H_3$.[17] In the present work, the passivation problem with $SF_5C_6H_5$ leads us to assign an uncertainty of ±30% to the measured k_a for this molecule. With S_2F_{10}, the possible presence of SF_6 (and perhaps SF_4) impurity forces us to place an uncertainty of ±38% on the measured k_a, as described in section III. With SF_5Br, the presence of SF_6 impurity is obvious, as explained in section III. Because SF_5Br attaches electron inefficiently, the magnitude of the correction is large, which compels us to place an uncertainty of ±50% on the measured k_a for this molecule.

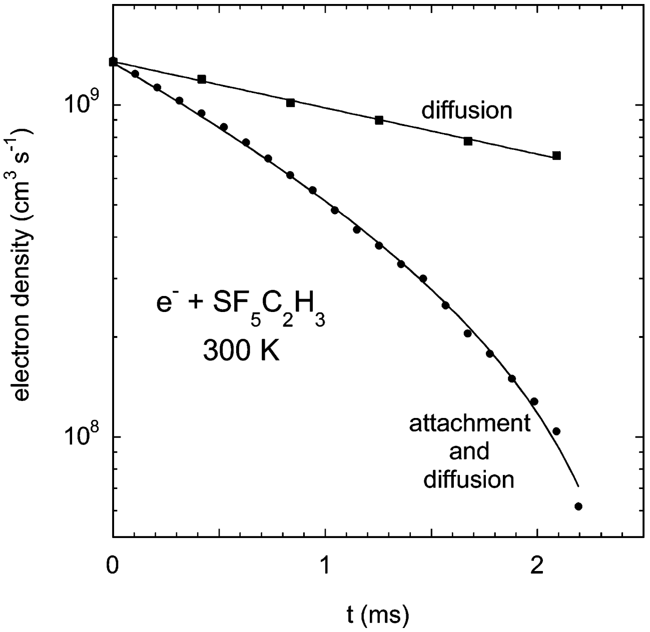

Figure 1. FALP data for electron attachment to $SF_5C_2H_3$ at 300 K. The $SF_5C_2H_3$ and He concentrations were 7.37×10^{10} and 3.22×10^{16} cm^{-3}, respectively. The diffusion frequency was measured in absence of reactant, at 323 s^{-1}. The electron attachment rate constant was measured to be $k_a = 7.3 \times 10^{-9}$ cm^3 s^{-1} from these data.

A rough analysis of the purities of the S_2F_{10} and SF_5Br samples was attempted via charge transfer to Ar^+ and Kr^+. While not successful from the standpoint of purity analysis, the results are worth noting. We first saw that Ar^+ reacting with neat SF_6 forms mostly SF_5^+ ion product, with a small amount of SF_3^+ (∼8%). (The plasma also contains a few percent He^+, which can contribute to the SF_3^+ signal.) It is endothermic for Kr^+ to produce SF_6^+ from SF_6 (by 1.3 eV), and it is slightly endothermic to produce SF_5^+ from SF_6 (by 0.18 eV). Thus, from the outset, it is seen that Ar^+ and Kr^+ are not useful for detecting SF_6 in the reactant samples, as the SF_5 compounds we studied ($SF_5C_6H_5$, etc.) could be expected to yield mainly SF_5^+ ion product. It is exothermic for Ar^+ to fractionate SF_6 and SF_4 into $SF_5^+ + F$ and $SF_3^+ + F$, respectively. Likewise, Kr^+ can fractionate SF_4 into $SF_3^+ + F$, but it is endothermic for Kr^+ to fractionate or ionize SF_6. However, SF_5^+ was the major product ion observed in the $Kr^+ + S_2F_{10}$ mass spectra (no $S_2F_{10}^+$ was found), implying that all of the SF_5^+ observed comes directly from S_2F_{10}. Evidence will be presented in section III that S_2F_{10} was decomposing at high temperatures. Because of the fractionations, the Ar^+ and Kr^+ reactions could not prove or disprove this idea. Kr^+ reacting with SF_5Br at 299 K gave 75% SF_5^+, 18% SF_4Br^+, and 7% SF_3^+. The first two ionic products are reasonable for the SF_5Br target. The final one may indicate that an impurity such as SOF_4 is in the SF_5Br sample, which might also yield the SOF_3^- observed in the electron attachment mass spectra.

III. Electron Attachment Results

Electron attachment results for $SF_5C_6H_5$, $SF_5C_2H_3$, S_2F_{10}, and SF_5Br are given in Table 1 and are plotted in Figure 2 in an Arrhenius manner along with earlier results for SF_6, SF_5Cl, and SF_5CF_3.[1−3] At 300 K, k_a ($SF_5C_6H_5$) = $9.9 \pm 3.0 \times 10^{-8}$ cm^3 s^{-1}, which amounts to one attachment event for every three collisions, on the basis of the electron−molecule *s*-wave collision rate expression developed by Klots.[22,23] The k_a increased with temperature in a way that may be described by an activation energy of 32 meV (with 50% uncertainty because of the passivation problem).

Measurements with $SF_5C_2H_3$ presented no such difficulty. The value k_a ($SF_5C_2H_3$) = $7.3 \pm 1.8 \times 10^{-9}$ cm^3 s^{-1} was determined at 300 K (implying attachment on 1 out of every 40 collisions[22,23]). The Arrhenius analysis (Figure 2) for $SF_5C_2H_3$ yields an activation energy of 80 meV (±15%), the largest for any of the compounds discussed here.

S_2F_{10} and SF_5Br did not present any handling problems, but the very slow attachment rates did cause difficulty in interpreting

TABLE 1: Rate Constants for Electron Attachment (k_a) Measured in the Present Work at 133 Pa

T (K)	k_a ($SF_5C_6H_5$)[a]	k_a ($SF_5C_2H_3$)[a]	k_a (S_2F_{10})[a]	k_a (SF_5Br)[a]
300	9.9(−8)	7.3(−9)	6.5(−10)	3.8(−10)
334		9.5(−9)		
363			6.7(−10)	3.5(−10)
370	1.4(−7)	1.3(−8)		
409		1.5(−8)		
425			6.7(−10)	4.3(−10)
448	1.4(−7)	2.0(−8)		
487				4.7(−10)
499		2.5(−8)		
550	1.9(−7)	3.1(−8)		5.4(−10)

[a] The notation 9.9(−8) in the table means 9.9 × 10^{-8} $cm^3\ s^{-1}$. Each entry is the average of 2−10 data. The experimental uncertainties are ±30% ($SF_5C_6H_5$), ±25% ($SF_5C_2H_3$), ±38% (S_2F_{10}), and ±50% (SF_5Br). SF_5^- was the ionic product of attachment, except for S_2F_{10}, where a less precise result stands: SF_5^- ≥0.70, SF_6^- ≤0.25, SF_4^- ≤0.05.

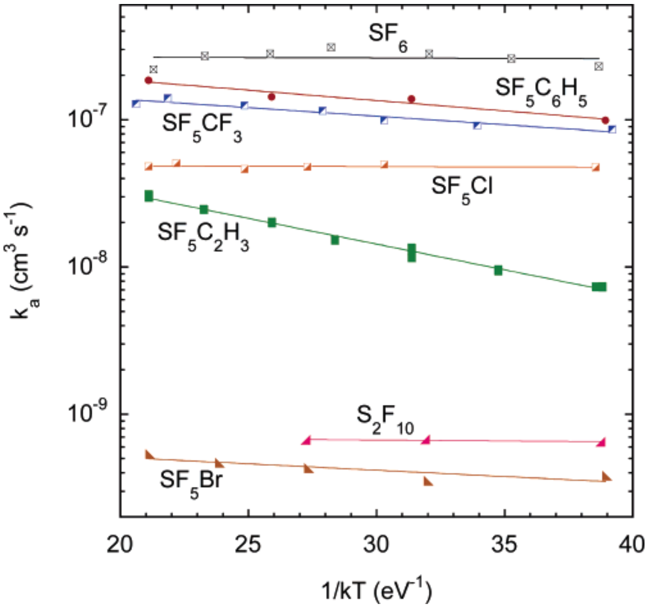

Figure 2. Electron attachment rate constants for SF_5X, plotted in Arrhenius fashion. Those for $SF_5C_6H_5$, $SF_5C_2H_3$, S_2F_{10}, and SF_5Br are from the present work. The other data were taken from refs 1 (SF_6), 2 (SF_5Cl), and 3 (SF_5CF_3).

data. The attachment mass spectra showed SF_6^-, and some SF_4^- in the S_2F_{10} case and some SOF_3^- in the SF_5Br case. If because of low-level impurities, these ion peaks would be barely noticeable with a rapidly attaching gas. However, S_2F_{10} and SF_5Br attach electrons so inefficiently that the SF_6^- especially stands out clearly in the mass spectra.

Modeling of the S_2F_{10} attachment data indicates that an impurity level of only 800 parts per million by volume of SF_6 or SF_4 in the S_2F_{10} sample could explain the observed SF_6^- and SF_4^- mass peaks. (Modeling is possible because k_a's for SF_6 and SF_4 are known.) Modeling showed that even this small level of impurity causes the apparent k_a to be 32% greater than the true k_a for S_2F_{10}, if there is indeed impurity present. The main problem comes in identifying the products of attachment to S_2F_{10}. Intuition says that SF_5^- product is expected. However, eqs 9 and 10 show that SF_6^- and SF_4^- are exothermic channels for thermal electron attachment. We are thus left with uncertainty in both k_a and the identification of the ion products of attachment, aside from SF_5^-; it is unlikely that a sample with purity greater than 99.9% can be obtained to completely solve the problem. The rate constants in Table 1 for S_2F_{10} are therefore averages of the measured (apparent) k_a and the k_a deduced from modeling of the attachment mass spectra. The range between the apparent and deduced k_a can be covered by adding 13 percentage points to the "normal" uncertainty of 25%. Thus, a 38% uncertainty is assigned to k_a for S_2F_{10} in Table 1. The attachment rate constant measured at 300 K is 6.5 ± 2.5 × 10^{-10} $cm^3\ s^{-1}$, an attachment efficiency of only 1 in every 500 collisions.[22,23] For the reasons detailed above, we are forced to say that the branching fractions of the ion products are uncertain: at 300 K, that for SF_5^- is ≥0.70, that for SF_6^- is ≤0.25, and that for SF_4^- is ≤0.05.

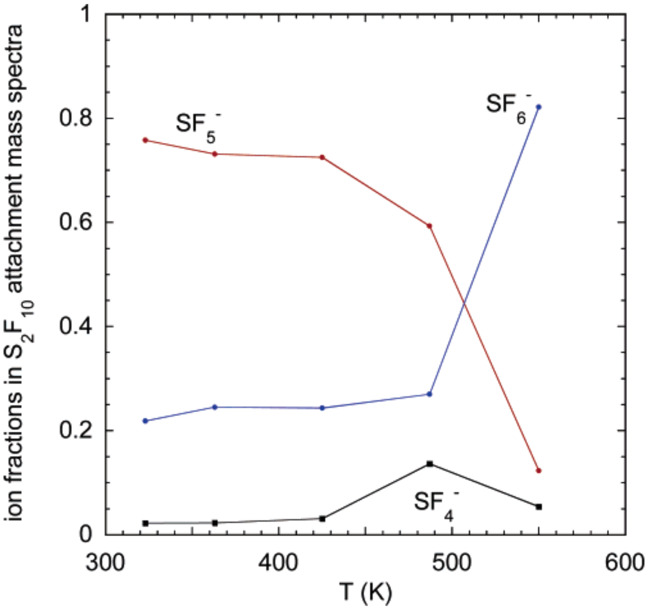

Figure 3. Branching fractions of ions observed in attachment to the S_2F_{10} sample, implying decomposition of the gas.

A second problem arose with S_2F_{10}. The branching fractions for SF_5^-, SF_6^-, and SF_4^- underwent a dramatic change as the temperature was increased past 425 K, as if the S_2F_{10} was decomposing before electron attachment occurred. No other system we know of undergoes such rapid change.[16,24,25] Figure 3 shows these branching fractions. The apparent k_a increased 100-fold between 425 and 550 K, as if the S_2F_{10} was decomposing into SF_6 + SF_4. Because of this evidence, we are not reporting k_a beyond 425 K. We stress that such decomposition can be homogeneous in the He buffer or can occur on the walls of the hot glass feedline that runs half the length of the flow tube (50 cm). Calculations described in section IV show that it is exothermic for S_2F_{10} to dissociate into SF_4 + SF_6 by 0.89 eV at 298 K. The same calculations show that it is endothermic for S_2F_{10} to separate into $2SF_5$ by 1.98 eV at 298 K. The fact that S_2F_{10} is stable must therefore be due to a barrier against dissociation.

SF_5Br presents a similar problem related to its very small attachment efficiency. A large SOF_3^- peak appears in the mass spectrum. The SOF_3^- could either be the result of an impurity in the SF_5Br sample container or be the result of a heterogeneous reaction with water molecules on the surfaces of feedlines. In modeling the attachment reactions, we assumed that the impurity attached electrons rapidly. Modeling of the mass spectra implied the impurity level to be 2.3%. The effect on k_a is large: the true k_a is 8 times smaller than the observed k_a, at 300 K, yielding a value of 3.8 ± 2.0 × 10^{-10} $cm^3\ s^{-1}$ (an attachment efficiency

TABLE 2: Results of G3(MP2)[a] and G2[a] Calculations for Neutral and Anionic SF_5X

quantity	$SF_5C_6H_5$	$SF_5C_2H_3$[b]	S_2F_{10}	SF_5Br
		Neutral		
point group (state)	C_{2v} ($^1A_1$)	C_s (^1A)	D_{4d} ($^1A_1$)	C_{4v} ($^1A_1$)
total energy, 0 K	−1127.72021	−974.32247	−1792.93163	−3468.99604
enthalpy, 298 K	−1127.70931	−974.31389	−1792.92024	−3468.98852
ZPE	0.10510	0.05921	0.03675	0.01829
EA (eV)	0.88	0.70	2.95	2.73
$D_{298}°$ ($X-SF_5$) (eV)[c]	3.74	3.68	1.98[d]	2.21
C−S (Å)[e]	1.798	1.783		
S−S (Å)			2.252	
S−Br (Å)				2.238
$S-F_p$ (Å)[f]	1.614	1.611	1.592	1.596
$S-F_e$ (Å)[f]	1.623	1.622	1.608	1.608
angle (deg)[g]	92.3	122.7	45.0	90.7
		Anion		
point group (state)	C_{2v} ($^2A_1$)	C_1 (^2A)	D_{4d} ($^2B_2$)	C_{4v} ($^2A_1$)
total energy, 0 K	−1127.75259	−974.34830	−1793.03998	−3469.09651
enthalpy, 298 K	−1127.73929	−974.33641	−1793.0255	−3469.08760
ZPE	0.09845	0.04914	0.02878	0.01469
$D_{298}°$ ($X-SF_5^-$) (eV)[c]	0.50	0.24	0.79	0.79
C−S (Å)[e]	1.833	4.000		
S−S (Å)			2.634	
S−Br (Å)				2.671
$S-F_p$ (Å)[f]	1.876	1.635	1.620	1.629
$S-F_e$ (Å)[f]	1.731	1.734[h]	1.673	1.676
angle (deg)[g]	89.3	99.6	45.0	93.6

[a] Compound method G3(MP2) of ref 11 used for these results, except for SF_5Br, where the G2 method of ref 10 was used. Total energy, enthalpy, and zero-point energy (ZPE) are in hartrees, and EA and bond energy are in eV. [b] There is a conformer of $SF_5C_2H_3$ with SF_5 bound to the CH_2 end of the C_2H_3 fragment. It lies 3.19 eV above the ground $SF_5C_2H_3$. The corresponding anion lies 18 meV above the ground $SF_5C_2H_3^-$ given in the table. Both anions are weakly bound ion-induced-dipole clusters. [c] X = C_6H_5, C_2H_3, SF_5, or Br, respectively. [d] Also, $D_{298}°$ (SF_4-SF_6) = −0.89 eV. [e] The shortest C−S bond. [f] F_p represents the polar F atom, and F_e represents the four equatorial F atoms in SF_5. [g] $-C-S-F_e$ for $SF_5C_6H_5$; −S−C−C for $SF_5C_2H_3$; dihedral F_e-S-S-F_e for S_2F_{10} (see Figure 4); $-Br-S-F_e$ for SF_5Br. [h] Average of four different equatorial $S-F_e$ bond lengths (1.715, 1.720,1.741, and 1.761 Å).

of 1 in every 800 collisions[22,23]). Unlike the case of S_2F_{10}, there is no ambiguity: the SOF_3^- in the mass spectrum cannot come directly from attachment to S_2F_{10}, so the lower k_a obtained from the modeling is accepted as the true one, though with large uncertainty (±50%). A possible secondary ion−molecule explanation for the SOF_3^- signal is ruled out by the small amount of background ions in the mass spectrum when SF_5Br is absent and by the low concentration of SF_5Br (1.8×10^{11} cm^{-3} at 300 K) in the flow tube.

IV. Computational Method and Results

Calculations of electron affinities (EAs) and bond strengths for the SF_5 compounds and fragments were carried out using the G3(MP2) compound method, primarily to obtain electron attachment reaction enthalpies.[13−15] We used the GAUSSIAN-03W set of programs.[26] The G3(MP2) method has been shown accurate on average to ±56 meV for ionization potentials and electron affinities of a test set of molecules.[13−15] Because the GAUSSIAN-03W program has not yet implemented the G3-(MP2) method for atoms beyond Ar, we applied the G2 method to SF_5Br.[10−12] The G2 method is slightly less accurate than G3-(MP2), and any nonrelativistic method applied to Br-containing molecules will contain still greater uncertainty. Results of the calculations are given in Table 2 and in the reaction enthalpies of eqs 1−13.

Not shown in Table 2 are the total energies calculated for the various fragments (C_2H_3, etc.) needed for specifying bond strengths and reaction enthalpies. Those for SF_6, SF_5, and SF_4 were published in ref 27. One fragment (C_6H_5) defied optimization with the methods described above. The closed-shell $C_6H_5^-$ presented no problem, however, and neither the neutral nor anion was a problem for density functional theory (DFT; the hybrid functional B3LYP with the Gaussian basis set 6-311++G(3df,-2p) was used), which gave EA(C_6H_5) = 1.061 eV, in good agreement with the experimental value of 1.096 ± 0.006 eV.[28] For this reason, the G3(MP2) total energy (at 0 K) of C_6H_5 was estimated from that for the anion, minus 1.096 eV. The 298 K enthalpy correction was then estimated by scaling the DFT value using the ratio of G3(MP2) and DFT enthalpy corrections for the anion. Total energies at 298 K for the various fragments are listed in ref 29.

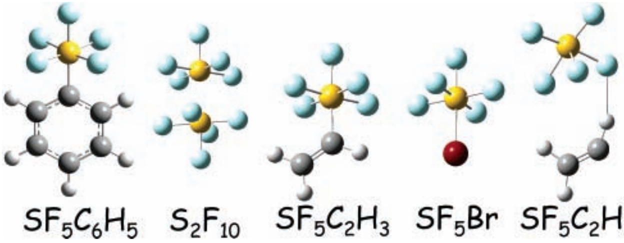

Figure 4. Structures optimized at the MP2(Full)/6-31G(d) level of theory, for which the G3(MP2) total energies are given in Table 2 (G2 for SF_5Br). Only the $SF_5C_2H_3^-$ anion is shown, because the other anions closely resemble the respective neutrals except for the S−C, S−S, or S−Br bond lengths listed in Table 2.

Structures for the neutral SF_5-compounds are shown in Figure 4, optimized at the MP2(Full)/6-31G(d) level of theory for which the G3(MP2) and G2 total energies are calculated. Only the $SF_5C_2H_3^-$ anion is shown, because $SF_5C_6H_5^-$, $S_2F_{10}^-$, and SF_5Br^- structures are so similar to the neutrals, differing mainly in the S−C or S−S or S−Br bond lengths, which are listed in Table 2 along with a few other structural parameters. The twisted structure (Figure 4), the Mulliken charges (−0.95 unit charge on the SF_5 portion of the molecule), and the weak bond strength (0.24 eV) for $SF_5C_2H_3^-$ imply that the anion is bound mainly

TABLE 3: Calculated[a] Properties of the Molecules and Anions for SF_5X Relevant for Electron Attachment, Together with Measured Rate Constants and Arrhenius Fits

X	$D_{298}{}^0$ (SF_5-X) (eV)	$D_{298}{}^0$ ($SF_5{}^{-}-X$) (eV)	(SF_5-X)[b] (Å)	($SF_5{}^{-}-X$)[b] (Å)	EA (SF_5X) (eV)	$-\Delta H$[c] (eV)	k_a (300 K)($cm^3\ s^{-1}$)	A-factor[d] ($cm^3\ s^{-1}$)	E_a[d] (meV)
C_6H_5	3.74	0.50	1.798	1.833	0.88	0.88	9.9×10^{-8}	3.6×10^{-7}	32
C_2H_3	3.68	0.24	1.783	4.000	0.70	0.62	7.3×10^{-9}	1.6×10^{-7}	80
SF_5	1.98	0.79	2.252	2.634	2.95	2.86	6.5×10^{-10}	7.3×10^{-10}	2.9
Br	2.21	0.79	2.238	2.671	2.73	2.76	3.8×10^{-10}	7.6×10^{-10}	20
Cl	2.70	1.03	2.059	2.589	2.47	1.46	4.0×10^{-8}	5.0×10^{-8}	1.0
F[e]	4.58	1.69	1.592	1.720	1.05[f]	−0.12	3.0×10^{-7}	2.7×10^{-7}	1.1
CF_3	3.12	0.26	1.915	3.695	1.24	0.95	8.6×10^{-8}	2.4×10^{-7}	27

[a] Calculated using method G3(MP2) for $SF_5C_6H_5$, $SF_5C_2H_3$, and S_2F_{10} and G2 for SF_5Br (present work), G3 for SF_5Cl (ref 2) and SF_6 (ref 27), and G3(MP2) for SF_5CF_3 (ref 3). [b] Bond length. [c] For electron attachment to form $SF_5{}^- + X$. [d] Temperature dependence of k_a fit to the Arrhenius expression $A \exp(-E_a/kT)$. [e] $SF_6{}^-$ is the main product ion for attachment to SF_6. [f] Experimental value from ref 30.

by an ion-induced-dipole electrostatic potential. It is interesting that the carbon bond lengths in the benzene ring are hardly affected by the replacement of one H atom by SF_5 or $SF_5{}^-$, shortening by only 1−2 mÅ, according to the calculations. The C=C bond length in ethane is shortened by 6 mÅ as a result of replacing one H atom by SF_5 and by 46 mÅ if by $SF_5{}^-$. Cartesian coordinates for the subject neutrals and anions have been archived with the journal as Supporting Information. Included in the Supporting Information are higher-energy isomers of $SF_5C_2H_3$ and $SF_5C_2H_3{}^-$ in which the SF_5 portion of the molecules is closest to the C atom which has 2 H atoms bound to it.

V. Discussion

The present data along with previously published data on SF_5Cl, SF_6, and SF_5CF_3 represent an excellent data set in which to look for correlations with properties of the molecules. Rate constants for these similar molecules vary over almost 3 orders of magnitude. Temperature dependences also vary, though to a lesser extent. Detailed calculations of the complete potential curves for molecules this size are quite difficult, so correlations are made to bond energies, bond lengths, and exothermicities. Table 3 lists the dissociation energies for the neutral and parent ion, the bond lengths of both species, the electron affinity of the parent anion, and the exothermicity to form $SF_5{}^-$, along with Arrhenius parameters [$k_a = A \exp(-E_a/kT)$, where E_a is the activation energy] for fits to the temperature dependences. The quantities in Table 3 are calculated ones, except for EA(SF_6)[30] and measured values of k_a and Arrhenius fit parameters. The Arrhenius A-factors range over a span of 500 from largest to smallest, and the E_a's vary from near zero to 80 meV. The largest activation energy is associated with attachment to $SF_5C_2H_3$, a case in which there is a large geometry change of the leaving group (C_2H_3) after attachment. Thus, it may not be surprising that that system has the largest activation energy.

Correlations of the Arrhenius parameters and 300 K rate constants versus the various molecular parameters were investigated. The 300 K rate constant is anticorrelated with the exothermicity for $SF_5{}^-$ production with the exception of X = C_2H_3. The deviation for $SF_5C_2H_3$ is probably related to the geometry change mentioned in the previous paragraph. The Arrhenius A-factors have a similar anticorrelation for all molecules, as shown in Figure 5, and bring the $SF_5C_2H_3$ case into agreement with the average behavior of the trend observed for the seven SF_5X. It is quite interesting that the more exothermic the reaction, the slower it becomes. A-factor correlations with other properties of the neutral are also relatively good, that is, with bond length and bond strength of the S−X bond. Without detailed calculations of the entire surface, it is hard to speculate on the cause of the correlation.

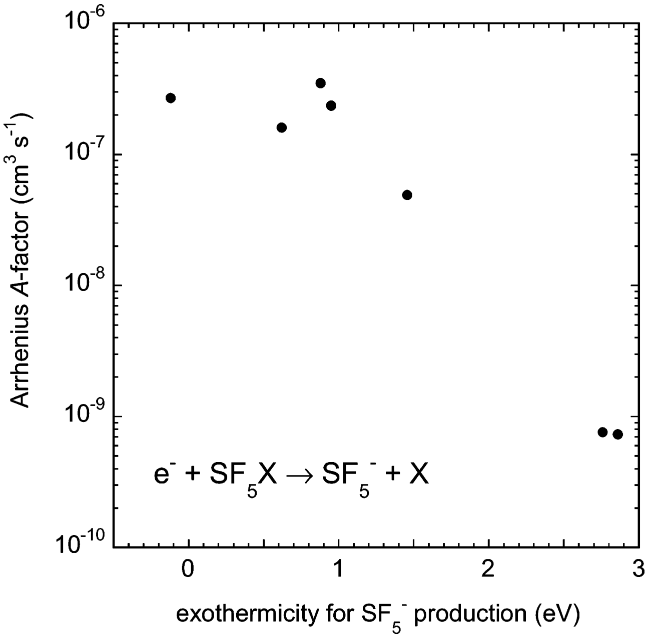

Figure 5. Arrhenius A-factors from fits to the electron attachment rates for SF_5X vs exothermicity for $SF_5{}^-$ production.

The E_a's for many of the SF_5X are quite small even if the overall rate constants are small. We have found similar results for species that attach to form the parent ion, in many cases, but often dissociative attachment gives larger activation energies when the attachment is slow. The E_a shows a gross correlation with bond strength of the anion. The E_a decreases as the bond strength increases, again opposite to the trend one might expect. The difference between the neutral and anion bond length does not seem to be correlated with E_a.

VI. Conclusions

Rate constants for electron attachment to $SF_5C_6H_5$, $SF_5C_2H_3$, S_2F_{10}, and SF_5Br were measured with an FALP apparatus from 300 to 550 K in a He buffer at a pressure of 133 Pa. The rate constants are listed in Table 1 and are compared to our earlier measurements for SF_6, SF_5Cl, and SF_5CF_3 in Figure 2. $SF_5C_6H_5$, $SF_5C_2H_3$, and SF_5Br yielded only $SF_5{}^-$ ion product upon attachment in the 300−500 K temperature range. The S_2F_{10} attachment mass spectrum contains considerable $SF_6{}^-$ and $SF_4{}^-$ intensity. Because the energetics (eqs 9, 10) of the reaction permit these pathways in addition to the $SF_5{}^-$ one, and because the attachment rate constant is so small, it cannot be ascertained whether the $SF_6{}^-$ and $SF_4{}^-$ are due to attachment to S_2F_{10} or to impurities.

G3(MP2) calculations (G2 in the case of SF_5Br) were carried out to determine the energetics of the attachment reactions (eqs 1−13). Electron affinities were calculated to be 0.88 ($SF_5C_6H_5$), 0.70 ($SF_5C_2H_3$), 2.95 (S_2F_{10}), and 2.73 eV (SF_5Br). Other results are given in Table 2, and structures are sketched in Figure 4.

The overall rates and *A*-factors seem to be inversely correlated with exothermicity, a trend that appears curious. Similarly puzzling is that the activation energies seem to decrease with increasing bond strength in the ion. More details of potential surface are needed to understand these correlations.

Acknowledgment. We thank Michael R. Berman for suggesting this project. We are grateful for the support of the Air Force Office of Scientific Research for this work. T.M.M. is under contract to the Institute for Scientific Research of Boston College (contract no. FA8718-04-C0006). W.R.D. thanks Prof. Gary Gard of Portland State University for providing samples of SF_5SF_5 and SF_5Br.

Supporting Information Available: Cartestian coordinates have been archived as Supporting Information for the neutral molecules and anions studied in the present work, calculated at the MP2/6-31G(d) level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Miller, T. M.; Miller, A. E. S.; Paulson, J. F.; Liu, X. *J. Chem. Phys.* **1994**, *100*, 8841−8848.

(2) Van Doren, J. M.; Miller, T. M.; Viggiano, A. A.; Španěl, P.; Smith, D. *J. Chem. Phys.* **2006**, submitted. Van Doren, J. M.; Miller, T. M.; Viggiano, A. A. *J. Chem. Phys.* **2006**, submitted.

(3) Miller, T. M.; Arnold, S. T.; Viggiano, A. A.; Knighton, W. B. *J. Chem. Phys.* **2002**, *116*, 6021−6027.

(4) Chistrophouou, L. C.; Olthoff, J. K. *Fundamental Electron Interactions with Plasma Processing Gases*; Kluwer Academic/Plenum Publishers: New York, 2004.

(5) Kennedy, R. A.; Mayhew, C. A. *Int. J. Mass Spectrom.* **2001**, *206*, i−iv.

(6) Mayhew, C. A.; Critchley, A.; Jarvis, G. K. *Int. J. Mass Spectrom.* **2004**, *233*, 259−265.

(7) Mayhew, C. A.; Critchley, A. D. J.; Howse, D. C.; Mikhailov, V.; Parkes, M. A. *Eur. Phys. J. D* **2005**, *35*, 307−312.

(8) Braun, M.; Ruf, M.-W.; Hotop, H.; Cicman, P.; Scheier, P.; Märk, T. D.; Illenberger, E.; Tuckett, R. P.; Mayhew, C. A. *Int. J. Mass Spectrom.* **2006**, *252*, 234−241.

(9) Sailer, W.; Drexel, H.; Pelc, A.; Grill, V.; Mason, N. J.; Illenberger, E.; Skalny, J. D.; Mikoviny, T.; Scheier, P.; Märk, T. D. *Chem. Phys. Lett.* **2002**, *351*, 71−78.

(10) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1991**, *94*, 7221−7230.

(11) Blaudeau, J.-P.; McGrath, M. P.; Curtiss, L. A.; Radom, L. *J. Chem. Phys.* **1995**, *107*, 5016−5021.

(12) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning, R. *J. Chem. Phys.* **1995**, *103*, 6104−6113.

(13) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2005**, *123*, 124107.

(14) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703−4709.

(15) Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 9287−9295.

(16) Smith, D.; Španěl, P. *Adv. At., Mol., Opt. Phys.* **1994**, *32*, 307−343.

(17) Miller, T. M. *Adv. At., Mol., Opt. Phys.* **2005**, *51*, 299−342.

(18) Kostov, G.; Ameduri, B.; Sergeeva, T. A.; Dolbier, W. R., Jr.; Winter, R.; Gard, G. L. *Macromolecules* **2005**, *38*, 8316−8326.

(19) Sergeeva, T. A.; Dolbier, W. R., Jr. *Org. Lett.* **2004**, *6*, 2417−2419.

(20) Winter, R.; Terjeson, R. J.; Gard, G. L. *J. Fluorine Chem.* **1998**, *89*, 105−106.

(21) Winter, R.; Nixon, P. G.; Gard, G. L. *J. Fluorine Chem.* **1998**, *87*, 85−86.

(22) Klots, C. E. *Chem. Phys. Lett.* **1976**, *38*, 61.

(23) The polarizability of the SF_5-compounds were taken from density functional calculations with a large basis set [B3LYP/6−311++G(3df,2p)]: 7.88 Å^3 for $SF_5C_6H_5$, 7.88 Å^3 for $SF_5C_2H_3$, 9.04 Å^3 for S_2F_{10}, and 7.68 Å^3 for SF_5Br yielding electron capture (maximum) rate constants of 3.1, 3.1, 3.2, and 3.1 × 10^{-7} cm^3 s^{-1}, respectively.

(24) Hotop, H.; Ruf, M. W.; Allan, M.; Fabricant, I. I. *Adv. At., Mol., Opt. Phys.* **2003**, *49*, 85−216.

(25) Christophorou, L. G. Electron Attachment Processes. In *Electron-Molecule Interactions and Their Applications*; Christophorou, L. G. Ed.; Academic: New York, 1984; pp 477−617.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03W*, Revision C.02; Gaussian, Inc.: Pittsburgh PA, 2003.

(27) Miller, T. M.; Arnold, S. T.; Viggiano, A. A. *Int. J. Mass Spectrom.* **2003**, *227*, 413−420.

(28) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601−620.

(29) Enthalpies at 298 K obtained from G3(MP2) calculations, in hartrees: −231.14832 (C_6H_5, estimated, see text), −231.18849 ($C_6H_5^-$), −77.75509 (C_2H_3), −77.78171 ($C_2H_3^-$), and from G2 calculations, −2572.52822 (Br) and −2572.65605 (Br^-).

(30) Grimsrud, E. P.; Chowdhury, S.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 1059−1068.