Electronic attachment to halomethanes at high temperature: 

Electron attachment to CH2Cl2, CF2Cl2, CH3Cl, and CF3Cl attachment rate constants up to 1100K

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We have used a high-temperature flowing-afterglow Langmuir-probe apparatus to measure rate constants for electron attachment to halomethanes which attach electrons very inefficiently at room temperature, yielding Cl⁻ ion product. We studied CH2Cl2 (495-973 K), CF2Cl2 (291-1105 K), and CF3Cl (524-1004 K) and include our recent measurement for CH3Cl (700-1100 K) in the discussion of the electron attachment results. The measured attachment rate constants show Arrhenius behavior in the temperature ranges examined, from which estimates of rate constants at 300 K may be made: CH2Cl2 (1.8 x 10⁻¹⁰ cm³ s⁻¹), CH3Cl (1.1 x 10⁻¹⁷ cm³ s⁻¹), and CF3Cl (4.2 x 10⁻¹⁴ cm³ s⁻¹), all of which are difficult to measure directly. In the case of CF2Cl2, the room temperature rate constant was sufficiently large to be measured (1.6 x 10⁻⁹ cm³ s⁻¹). The Arrhenius plots yield activation energies for the attachment reactions: 390 ± 50 meV (CH2Cl2), 124 ± 20 meV (CF2Cl2), 670 ± 70 meV (CH3Cl), and 406 ± 50 meV (CF3Cl). Comparisons are made with existing data where available. G3 calculations were carried out to obtain reaction energetics. They show that the parent anions of CH2Cl2, CF2Cl2, CH3Cl, and CF3Cl are stable, though CH3Cl exists only as an electrostatically bound complex. © 2009 American Institute of Physics.
Electron attachment to halomethanes at high temperature: CH₂Cl₂, CF₂Cl₂, CH₃Cl, and CF₃Cl attachment rate constants up to 1100 K

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We have used a high-temperature flowing-afterglow Langmuir-probe apparatus to measure rate constants for electron attachment to halomethanes which attach electrons very inefficiently at room temperature, yielding Cl⁻ ion product. We studied CH₂Cl₂ (495–973 K), CF₂Cl₂ (291–1105 K), and CF₃Cl (524–1004 K) and include our recent measurement for CH₃Cl (700–1100 K) in the discussion of the electron attachment results. The measured attachment rate constants show Arrhenius behavior in the temperature ranges examined, from which estimates of rate constants at 300 K may be made: CH₂Cl₂ (1.8×10⁻¹³ cm³ s⁻¹), CH₃Cl (1.1×10⁻¹⁷ cm³ s⁻¹), and CF₂Cl₂ (4.2×10⁻¹⁴ cm³ s⁻¹), all of which are difficult to measure directly. In the case of CF₂Cl₂, the room temperature rate constant was sufficiently large to be measured (1.6×10⁻⁹ cm³ s⁻¹). The Arrhenius plots yield activation energies for the attachment reactions: 390±50 meV (CH₂Cl₂), 124±20 meV (CF₂Cl₂), 670±70 meV (CH₃Cl), and 406±50 meV (CF₃Cl). Comparisons are made with existing data where available. G3 calculations were carried out to obtain reaction energetics. They show that the parent anions of CH₂Cl₂, CF₂Cl₂, CH₃Cl, and CF₃Cl are stable, though CH₃Cl⁻ exists only as an electrostatically bound complex. © 2009 American Institute of Physics. [DOI: 10.1063/1.3212598]

I. INTRODUCTION

In a recent publication we described a high-temperature flowing-afterglow Langmuir-probe apparatus for use in measuring electron attachment rate constants at temperatures up to 1100 K.1 We presented data for NF₃ (300–900 K) and CH₃Cl (600–1100 K).1 The CH₃Cl data were found to follow Arrhenius behavior in this temperature range. Extrapolation to room temperature gave a rate constant of ~10⁻¹⁷ cm³ s⁻¹. No current apparatus is capable of measuring such a low value, and even if so, the result would be surely dominated by impurities. In the present work, we have made measurements up to 1100 K for other halomethanes which also have very low attachment rate constants at room temperature: CH₂Cl₂, CF₂Cl₂, and CF₃Cl. Two of these cases, as with CH₃Cl, are exothermic toward electron attachment,

\[ e^- + CH₂Cl₂ \rightarrow CH₂Cl + Cl^- + 237 \text{ meV}, \]  
(1)

\[ e^- + CF₂Cl₂ \rightarrow CF₂Cl + Cl^- + 67 \text{ meV}, \]  
(2)

\[ e^- + CH₃Cl \rightarrow CH₃Cl + Cl^- + 105 \text{ meV}. \]  
(3)

The remaining case, of electron attachment to CF₃Cl, is endothermic

\[ e^- + CF₃Cl \rightarrow CF₃ + Cl^- - 143 \text{ meV}. \]  
(4)

The energies given in Eqs. (1)–(4) are those calculated using the G3 compound method 2 at 0 K, carried out using the GAUSSIAN-03W program.3 The G3 prescription, which includes empirical corrections based on accurate experimental energies, approximates a quantum configuration interaction calculation with a large basis set. Neutral and anion geometries are optimized at the MP2/6-31G(d) level of theory, and zero-point energies are calculated from scaled Hartree–Fock harmonic frequencies.2 The G3 method is good, on average, within ±91 meV for enthalpies of formation of non-hydrogen-containing molecules and ±49 meV for hydrogen-containing molecules.4 Thus, on the basis of G3 calculations, Eq. (2) cannot be said to be definitely exothermic. However, the quoted exothermicities agree quite well with those derived from tabulated bond dissociation energies (DBEs) and the electron affinity (EA) of Cl, as will be seen later.

G3 calculations (Table I) show that the parent anions exist, and, in fact, CF₃Cl⁻ and CF₂Cl₂⁻ have been observed in electron attachment experiments to CF₂Cl and CF₂Cl₂ clusters.5,6 The parent anions are not observed for electron attachment to the monomers, in beam or thermal experiments, implying that transient parent anions are too short lived even where the gas pressure is high enough that collisional stabilization might occur. Table I includes a comparison of computational and experimental adiabatic EAs where available.5–8

II. EXPERIMENTAL

The HT-FALP apparatus1,10 has been described previously. The HT-FALP utilizes an electron-He⁺, Ar⁺ plasma...
moving at high speed in a flow tube reactor entrained in a He buffer gas which contains a few percent Ar. The gas pressure ranged from 1 to 2 Torr. The plasma density decays along the flow tube axis with a movable Langmuir probe. The ion products of the attachment reaction are sampled at the terminus of the flow tube and mass analyzed. The neutral products are not detected but are usually apparent from the reaction energetics. The plasma velocity is measured in order to provide the time scale for the reaction. Complete data runs for each halomethane were carried out over the available temperature range sequentially, starting with the slowest-attaching gas, to minimize contamination of the feedlines.

The electron attachment frequency $v_a$ is obtained from the equation describing the coupled effects of diffusion and attachment on the electron density, $n_e(t)$, as a function of time $t$ down the flow tube axis: \[ n_e(t) = n_e(0) \left( v_a \exp(-v_d t) - v_d \exp(-v_d t) \right) / (v_d - v_a). \]

TABLE I. Calculated G3 total energies, adiabatic EAs, and C-Cl BDEs at 0 K for CH$_3$Cl, CF$_3$Cl, CH$_2$Cl, CF$_2$Cl, and dissociation fragments relevant to the energetics of attachment reactions. CHF$_3$ is included as relevant to comments in the text on endothermic electron attachment to CHF$_3$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Total energy (hartree)</th>
<th>EA neutral (eV)</th>
<th>BDE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Neutral</td>
<td>Anion</td>
<td>Neutral</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>-959.371 21$^b$</td>
<td>-959.394 40</td>
<td>0.631</td>
</tr>
<tr>
<td>CF$_3$Cl</td>
<td>-1157.787 91</td>
<td>-1157.808 56</td>
<td>0.562</td>
</tr>
<tr>
<td>CH$_2$Cl</td>
<td>-499.913 02$^b$</td>
<td>-499.917 68</td>
<td>0.127</td>
</tr>
<tr>
<td>CF$_2$Cl</td>
<td>-797.546 21</td>
<td>-797.558 14</td>
<td>0.325</td>
</tr>
<tr>
<td>CHF$_3$</td>
<td>-338.086 56$^b$</td>
<td>-337.993 00</td>
<td>-2.546</td>
</tr>
</tbody>
</table>

The attachment rate constant $k_a$ is obtained by $k_a = v_a / n_r$, where $n_r$ is the reactant concentration in the flow tube. In practice, Eq. (5) is used during data acquisition, and a numerical model that includes possible correction for electron-ion recombination is later fit to the data. A discussion of the rate equations including electron-ion recombination has been given earlier.$^1$ A recombination correction is only significant when a large concentration of molecular cations is formed from He$^+$ and Ar$^+$ reacting with the attaching gas since molecular cations possess large recombination rate constants, typically $\sim 3 \times 10^{-7}$ cm$^3$ s$^{-1}$ at 300 K, in contrast to the negligible ones for atomic cations. Few molecular cations are usually present in the attachment experiments. Correction becomes noticeable only when $k_a$ is very small ($< 5 \times 10^{-10}$ cm$^3$ s$^{-1}$) because large $n_r$ is required to achieve a decade of decay of $n_e(t)$ in the reaction zone. The use of low $n_r(0)$ mitigates the problem. In the present work, corrections for electron-ion recombination contribution to $n_e(t)$ decay were as high as 15% at the lowest temperatures for the CF$_3$Cl and CH$_2$Cl data, but were only 2% at 900 K because the attachment rate constants were larger and the estimated ion molecule and recombination rates were lower.$^1$ We will assign a larger uncertainty to results for which appreciable recombination correction was required. The numerical model also accounts for ion-ion mutual neutralization, though an indiscernible effect for the $n_e(0)$ used in the present work. Rate constants for Ar$^+$+CH$_3$Cl, CF$_3$Cl, CH$_2$Cl, and CF$_2$Cl were measured at 300 K by Smith et al.$^{11}$ and assumed in the
Electron attachment to halomethanes at high T

The solid curves are solutions of rate equations using $k = 6.6 \times 10^{-11}$ cm$^{-3}$ s$^{-1}$. The diffusion data ($f_1$) were obtained in the absence of the Langmuir probe. Which are more difficult to measure accurately with the value, 14%, through the use of a low value of $n(0) = 5.7 \times 10^{8}$ cm$^{-3}$. The rapid increase in production of molecular cations (M$^+$) is needed. Note enough that a large concentration of CH$_2$Cl$_2$ is produced in reaction with Ar$^+(a)$ and some He$^+$. The Ar$^+ +$CH$_2$Cl$_2$ reaction rate was taken to be $1.5 \times 10^{-9}$ cm$^{-3}$ s$^{-1}$, and the electron recombination rate constant was estimated at $2.3 \times 10^{-9}$ cm$^{-3}$ s$^{-1}$ at 495 K.

The present work to decrease with temperature according to the trajectory calculations of Su and Chesnavich. The electron recombination rate constant was estimated at $3 \times 10^{-7}$ cm$^{-3}$ s$^{-1}$ (300 K) in all cases.

Figure 1 gives an example of data obtained with the HT-FALP apparatus for CH$_2$Cl$_2$ at 495 K, where $k_2$ is small enough that a large concentration of CH$_2$Cl$_2$ is needed. Note the rapid increase in production of molecular cations (M$^+$ in Fig. 1) due to the reaction between Ar$^+$ and CH$_2$Cl$_2$. The electron-ion correction in that case was held to an acceptable value, 14%, through the use of a low value of $n_e(0) = 5.7 \times 10^{10}$ cm$^{-3}$. The disadvantage of low $n_e(0)$ is that long reaction times correspond to low electron concentrations, which are more difficult to measure accurately with the Langmuir probe.

The estimated uncertainty in the data is ±25% except for cases where significant correction is required for electron-ion recombination. If $k_e < 5 \times 10^{-10}$ cm$^3$ s$^{-1}$, then the estimated uncertainty is ±35%.

III. RESULTS AND DISCUSSION

Table II lists the present attachment data for CH$_2$Cl$_2$, CF$_2$Cl$_2$, and CF$_3$Cl. Figure 2 shows these data plotted in Arrhenius form in comparison with literature data from Birmingham University,$^1$ Oak Ridge National Laboratory (ORNL),$^{14,15}$ and Boston College.$^{16}$ Outside the temperature scale of Fig. 2 are data for CF$_2$Cl$_2$ obtained at temperatures of 75–170 K at the University of Rennes using a low temperature nozzle jet, which show the breakdown of Arrhenius behavior at low temperatures.$^{17}$ The Birmingham University FALP data$^{11}$ for CF$_2$Cl$_2$ (295–590 K) lie above those of Boston College$^{16}$ (293–777 K) and the present data (291–1105 K), but the Arrhenius activation energies are in rough agreement (150, 127, and 124 meV, respectively). A complete review and critical examination of data for attachment to CF$_2$Cl$_2$, including beam experiments, has been given by Skalny et al.$^{18}$ and Christophorou and Olthoff.$^{19}$

Figure 2 and Table II include results for CH$_2$Cl$_2$ that we deduced from drift tube data of the ORNL group.$^{17}$ The deduced thermal $k_e$ merge well with the present results at higher temperature, and the Arrhenius slopes agree well (378 meV, ORNL data, and 390 meV, present data) for CH$_2$Cl$_2$. The Boston College data show a lower Arrhenius slope of 248 meV.$^{16}$ The CF$_2$Cl$_2$ data in Fig. 2 likewise give a lower slope for Boston College data$^{16}$ (316 meV) than found in the present work (406 meV).

Figure 3 shows temperature dependences for the fluorine- and chlorine-containing halomethanes along with our earlier CH$_2$Cl data$^1$ and some data from other sources.$^{13,14,20}$ It was not possible to fit all literature data clearly on this one figure. Shown are the present data for CH$_2$Cl$_2$, CF$_2$Cl$_2$, and CF$_3$Cl, our recently published data for CH$_3$Cl$^1$, ORNL data for CH$_2$Cl$_2$,$^{14}$ temperature-dependent data for CCl$_4$, CFCl$_3$, and CHCl$_3$ from Birmingham.

![Figure 1](image)

**TABLE II.** Electron attachment rate constants $k_e$ for CH$_2$Cl$_2$, CF$_2$Cl$_2$, and CF$_3$Cl obtained at temperatures $T$. Data for CH$_2$Cl$_2$ were given in Ref. 1. The present experimental uncertainty is ±25% except for cases where significant correction for electron-ion recombination was made: If $k_e < 5 \times 10^{-10}$ cm$^3$ s$^{-1}$, then the estimated uncertainty is ±35%.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>CH$_2$Cl$_2$ $k_e$ (cm$^3$ s$^{-1}$)</th>
<th>$T$ (K)</th>
<th>CF$_2$Cl$_2$ $k_e$ (cm$^3$ s$^{-1}$)</th>
<th>$T$ (K)</th>
<th>CF$_3$Cl $k_e$ (cm$^3$ s$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>300</td>
<td>$2.6 \times 10^{-13}$</td>
<td>291</td>
<td>$1.6 \times 10^{-9}$</td>
<td>524</td>
<td>$3.1 \times 10^{-11}$</td>
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<td>400</td>
<td>$7.0 \times 10^{-13}$</td>
<td>352</td>
<td>$3.4 \times 10^{-9}$</td>
<td>654</td>
<td>$2.6 \times 10^{-10}$</td>
</tr>
<tr>
<td>500</td>
<td>$9.5 \times 10^{-11}$</td>
<td>400</td>
<td>$6.0 \times 10^{-9}$</td>
<td>800</td>
<td>$8.2 \times 10^{-10}$</td>
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<td>$7.0 \times 10^{-11}$</td>
<td>500</td>
<td>$1.1 \times 10^{-8}$</td>
<td>898</td>
<td>$1.3 \times 10^{-9}$</td>
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<tr>
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<td>652</td>
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<td>900</td>
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<td>973</td>
<td>$5.5 \times 10^{-8}$</td>
<td>1004</td>
<td>$6.3 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1105</td>
<td>$6.1 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$The present data extrapolated to 300 K imply $k_e = 1.8 \times 10^{-13}$ cm$^3$ s$^{-1}$.

$^2$The present data extrapolated to 300 K imply $k_e = 4.2 \times 10^{-14}$ cm$^3$ s$^{-1}$.

$^3$ORNL data (Ref. 14) extrapolated to thermal energies.
Published data from Boston College and Oak Ridge National Laboratory (ORNL, Ref. 14, extrapolated to thermal energy in the present work). Off scale are Rennes data (Ref. 16) at temperatures of <170 K.

There are four main points to be made from Fig. 3.

(a) The halomethane data in Fig. 3 cover seven orders of magnitude in attachment rate constant.

(b) The temperature dependences all seem to be pointing toward a collisional rate constant (at infinite temperature) in the neighborhood of $4 \times 10^{-7}$ cm$^3$ s$^{-1}$. Even if the extrapolations were accurate, the collisional rate constant will not be the same for all of these molecules because of their differing polarizabilities and dipole moments.

(c) The ORNL 300 K data and the general Arrhenius picture formed from temperature-dependent data in Fig. 3 allow one to make an educated guess as to the temperature dependence for attachment to these other compounds. Generally speaking, the lower the rate constant lies at 300 K, the greater will be the temperature dependence, as if pointing toward a collisional rate constant at infinite temperature. However, we assume that the ORNL result and the one of Fessenden and Bansal for the slowest-attaching halomethane shown, CHF$_3$, is in error because dissociative electron attachment is 2 eV endothermic, and there is no evidence for a stable parent anion. CHF$_3$ has a negative EA, $-2.55$ eV (G3 calculation, Table I), consistent with the fact that no parent anion has been observed. Wang et al. found a $k_a$ value of $1.3 \times 10^{-13}$ cm$^3$ s$^{-1}$ but noted that the reaction was probably endothermic and concluded that attachment to CHF$_3$ is very weak or absent at thermal energy. Jarvis et al. reported no measurable electron attachment to CHF$_3$ within the sensitivity of their instrument (about $2 \times 10^{-13}$ cm$^3$ s$^{-1}$). The CHF$_3$ data reinforce a point made earlier that extremely small $k_a$ is difficult to measure because the slightest impurity may dominate. With three of the halomethanes we have studied, CH$_2$Cl$_2$, CH$_3$Cl, and CF$_3$Cl, we did not measure the rate constants below 500 or 600 K because of the difficulty of measuring small $k_a$.

(d) Replacing Cl atoms by either H or F atom reduces $k_a$, but replacement with an F atom is much less dramatic. Starting with CCl$_4$, replacement with a single F barely changes $k_a$, but replacement with a single H changes $k_a$ by two orders of magnitude. A second Cl replacement
with an F atom changes \( k_a \) by a larger amount and makes the reaction nearly thermoneutral. Replacement of Cl with a second H atom has a much greater effect in reducing \( k_a \). The importance of the Cl atoms has, of course, been noted before (see Refs. 20 and 27).

These statements are illustrated in Fig. 4. The reaction energies at 298 K used in Fig. 4 were obtained (a) from G3 calculations and (b) from 298 K BDEs listed in the Hand- book of Chemistry and Physics, subtracted from the EA of Cl (unchanged between 0 and 298 K). The two methods agree well except for a 0.12 eV discrepancy for the CF\(_2\)Cl\(_2\) case. However, the BDE in that case is tabulated as uncertain to \( \pm 0.09 \) eV, and the G3 calculations have a similar uncertainty.

The Arrhenius plots of the present data may be used to predict 300 K values of \( k_a \) for these compounds: CH\(_2\)Cl\(_2\) \( (1.8 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}) \), CHCl\(_3\) \( (1.1 \times 10^{-17} \text{ cm}^2 \text{s}^{-1}) \), and CF\(_2\)Cl\(_2\) \( (4.2 \times 10^{-14} \text{ cm}^2 \text{s}^{-1}) \). The extrapolated value for CHCl\(_3\) may be compared to the 300 K estimate of 2.6 \( \times 10^{-13} \text{ cm}^2 \text{s}^{-1} \) from our analysis of ORNL drift tube data. Considering uncertainties in both sets of data and extrapolations, the agreement is reasonable if not surprisingly so. However, three older measurements for CH\(_2\)Cl\(_2\) are tabulated by Christophorou et al.\(^{20}\) which tend to cluster around a value 20 times larger, at \( 4.7 \times 10^{-12} \text{ cm}^2 \text{s}^{-1} \) at 300 K. For CHCl\(_3\), only upper limits are tabulated by Christophorou et al.\(^{20}\) which extend to a measurement at room temperature, obtaining \( k_a = 1.6 \times 10^{-9} \text{ cm}^2 \text{s}^{-1} \). Christophorou and Olthoff\(^{19}\) tabulated measured values of \( k_a \) for CF\(_2\)Cl\(_2\) with a mean value of 1.57 \( \times 10^{-9} \text{ cm}^2 \text{s}^{-1} \) at 293–300 K. The Birmingham group measured 3.2 \( \times 10^{-9} \text{ cm}^2 \text{s}^{-1} \) for CF\(_2\)Cl\(_2\) at 300 K.\(^{11}\) Their results for 205–590 K are shown in Fig. 3.

The negative of the slopes\(^{29}\) of the Arrhenius plots (multiplied by Boltzmann’s constant) are used as the activation energy needed to overcome endothermicity or to surmount a barrier if the reaction is exothermic. Fabrikant and Hotop\(^{10}\) gave an analysis of Arrhenius plots for dissociative electron attachment. For our sole endothermic case, that of CF\(_2\)Cl, their analysis indicates that the Arrhenius activation energy should be close to the threshold energy. The Arrhenius plot shown in Fig. 2 yields an activation energy of 406 \( \pm 50 \) meV. The calculated endothermicity of the reaction is only 143 meV at 298 K (118 meV at 298 K), so there is apparently a barrier to attachment beyond simply the endothermicity. The barrier is likely related to the crossing point of the anion potential surface, requiring vibrational energy input to CF\(_2\)Cl in order to access the anion surface efficiently.\(^{30}\)

Relevant to the exothermic CH\(_2\)Cl\(_2\), CHCl\(_3\), and CF\(_2\)Cl\(_2\) reactions, the Fabrikant–Hotop analysis says that the Arrhenius activation energy is lower than the barrier height, but comes closer to the barrier height if the vibrational frequency of the molecule most active in dissociation is a low frequency.\(^{30}\) The Arrhenius activation energies are 390 \( \pm 50 \) meV (CH\(_2\)Cl\(_2\)), 670 \( \pm 70 \) meV (CHCl\(_3\)), and 126 \( \pm 20 \) meV (CF\(_2\)Cl\(_2\)). The C–Cl stretching frequencies are in the neighborhood of 700 cm\(^{-1}\) (87 meV), a value which is not “small” in the Fabrikant–Hotop analysis.\(^{30}\) Thus, the anion potential surface for the three exothermic cases studied here would seem to be crossing the neutral surface at a point well above the energies given by the Arrhenius slopes. Calculation of the neutral and anion potential curves along a C–Cl bond for these molecules would be useful in understanding the measured activation energies.

We note that many other measurements have been made of the activation energy in the CF\(_2\)Cl\(_2\) attachment reaction. In electron beam experiments, the activation energy has been obtained from the growth with temperature of the zero-energy resonance. Hahndorf and Illenberger\(^{11}\) studied the temperature dependence of attachment to several halomethanes, including CF\(_2\)Cl (no observable zero-energy resonance) and CF\(_2\)Cl\(_2\), between 350 and 700 K. Skalny et al.\(^{18}\) analyzed many different results for CF\(_2\)Cl obtained in beam, electron swarm, and true thermal experiments to reconcile the results from the very different experiments. They compiled \( k_a \) values ranging from 75 to 777 K. The lowest-temperature data (75–171 K) are from the Rennes group,\(^{17}\) and the highest-temperature data included (293–777 K) are from the Boston College group.\(^{16}\) The Arrhenius plot containing all of these data shows Arrhenius behavior for temperatures greater than 150 K. Values of \( k_a \) below this temperature (from Rennes)\(^{17}\) show much less variation with temperature, which may be a result of population of only the lowest vibrational levels. Skalny et al. pointed out that while there is considerable difference in the activation energies determined from all of the experiments (73–195 meV), it is clear that activation energy from electron beam experiments (\( \approx 85 \) meV) are lower than those from swarm and thermal experiments (\( \approx 150 \) meV).\(^{18}\)
the efficiency of the measured reactions. Using tabulated polarizabilities and dipole moments, the formula of Dashevskaya et al. gives \( k_a = 3.81 \) (\( \text{CH}_2\text{Cl}_2 \)), 3.02 (\( \text{CF}_2\text{Cl}_2 \)), 4.06 (\( \text{CH}_3\text{Cl} \)), and 2.78 (\( \text{CF}_3\text{Cl} \)) at 300 K, in units of \( 10^{-7} \text{ cm}^3 \text{s}^{-1} \). Attachment to all of these molecules is inefficient at 300 K, with \( \text{CH}_2\text{Cl} \) attaching electrons in only one of every \( 3.7 \times 10^{10} \) collisions at 300 K.

IV. CONCLUSIONS

We have measured electron attachment rate constants for \( \text{CH}_2\text{Cl}_2 \) (495–973 K), \( \text{CF}_2\text{Cl}_2 \) (291–1105 K), \( \text{CH}_3\text{Cl} \) (700–1100 K), and \( \text{CF}_3\text{Cl} \) (524–1004 K) using a HT-FALP apparatus. The results display Arrhenius behavior in the studied temperature ranges and allow estimates of extremely small rate constants at 300 K to be made. The activation energies range from 124 meV (\( \text{CF}_2\text{Cl}_2 \)) to 670 meV (\( \text{CH}_3\text{Cl} \)). The \( \text{CH}_2\text{Cl}_2 \) results merge well with rate constants measured at lower temperatures by the ORNL group, extrapolated to thermal energies. Arrhenius plots of the present data, taken together with attachment rate constants measured at 300 K by others (which cover seven orders of magnitude), allow one to estimate the high-temperature behavior for several other halomethanes. The attachment rate constants show a strong dependence on reaction exothermicity. G3 calculations were carried out, showing that the parent anions of \( \text{CH}_2\text{Cl}_2 \), \( \text{CF}_2\text{Cl}_2 \), \( \text{CH}_3\text{Cl} \), and \( \text{CF}_3\text{Cl} \) are stable, though \( \text{CH}_2\text{Cl}^− \) exists only as an electrostatically bound complex. However, the parent anions are not observed in attachment experiments to the monomer neutrals. G3 calculations imply that \( \text{CF}_2 \) should not undergo an electron attachment reaction at all, whether dissociatively or nondissociatively.

Literature studies for \( \text{CH}_2\text{F}_2 \) underscore a point that extremely small attachment rate constants are difficult to measure because of interference from even trace impurities.

Note added in proof: Recent experiments with high electron energy resolution have been carried out by K. Graupner, S. A. Haughey, T. A. Field, C. A. Mayhew, T. H. Hoffmann, O. May, J. Fedor, M. Allan, I. I. Fabrikant, E. Illenberger, M. Braun, M.-W. Ruf, and H. Hotop (to be published) which show cusps in the electron attachment cross section for \( \text{CF}_2\text{Cl}_2 \) at thresholds for vibrational excitation of the \( \nu_3 (a_1) \) mode due to interaction between attachment and vibrational excitation channels, among other results.

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The dipole polarizabilities are $7.2 \, \text{Å}^3$ (CH$_3$Cl), $7.93 \, \text{Å}^3$ (CF$_2$Cl$_2$), $5.35 \, \text{Å}^3$ (CH$_2$Cl), and $5.72 \, \text{Å}^3$ (CF$_3$Cl). The dipole moments are $1.60 \pm 0.03 \, \text{D}$ (CH$_3$Cl), $0.51 \pm 0.05 \, \text{D}$ (CF$_2$Cl$_2$), $1.8963 \pm 0.0002 \, \text{D}$ (CH$_2$Cl), and $0.50 \pm 0.01 \, \text{D}$ (CF$_3$Cl).