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Competition between nondissociative and dissociative electron attachment to halogenated cyclic alkenes in the gas phase

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Abstract

A flowing-afterglow Langmuir probe apparatus with mass spectral analysis was used to measure rate constants, identify reaction products, and measure branching fractions for electron attachment to 1,2-dichlorohexafluorocyclopentene (c-$C_5F_6Cl_2$) and 1,2-dichlorooctafluorocyclohexene (c-$C_6F_8Cl_2$) over the temperature range 295–555 K and buffer gas density range of $1.3–2.1 \times 10^{16}$ cm^{-3}. Electron attachment to both of these compounds is efficient over this temperature range and the rate coefficient for attachment is relatively independent of temperature. At 295 K the electron attachment rate coefficient for c-$C_5F_6Cl_2$ is $2.5 \pm 0.6 \times 10^{-7}$ cm^3 s^{-1} and for c-$C_6F_8Cl_2$ is $3.5 \pm 0.9 \times 10^{-7}$ cm^3 s^{-1}. At 300 K, electron attachment to both neutral reactants is predominantly nondissociative. At higher temperatures, a dissociative reaction channel forming Cl^- is observed for both reaction systems. Significant branching fractions for Cl^- (≥ 0.05) are observed at temperatures greater than 425 K for c-$C_5F_6Cl_2$ and at temperatures greater than 375 K for c-$C_6F_8Cl_2$. Over the temperature range of 300–550 K the branching fractions for formation of the nondissociative and dissociative products were not dependent on buffer gas density in the range of $1.3–2.1 \times 10^{16}$ cm^{-3}. (Int J Mass Spectrom 195/196 (2000) 517–523) © 2000 Elsevier Science B.V.

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1. Introduction

Investigation of the reactions of halogenated hydrocarbons with electrons in the gas phase has been an active field of research. The observation that these types of molecules often attach electrons efficiently while many other types of molecules do not led to the recognition that electron attachment reactions could be used to sensitively and selectively detect trace quantities of these species in the environment.

Recently we began studying electron attachment reactions in which multiple reaction channels are observed. Our goal is to better understand the parameters that determine the reaction paths observed and their relative efficiency. Our recent study of electron attachment to chlorine nitrate [1], where three disso-

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Dedicated to Bob Squires for his many seminal contributions to mass spectrometry and ion chemistry.

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ciative reaction channels are active at room temperature, demonstrated that in this case the relative exothermicity of the reaction channel is not the major factor in determining the branching ratio (percent product) observed. Others have made similar observations [2–6]. It has also been observed that no simple correlation can be made between the magnitude of the electron affinity of the parent neutral and branching fraction for nondissociative attachment [1,6]. For example, $ClONO_2$ has an electron affinity [7] of 2.9 ± 0.3 eV but no significant nondissociative product is observed [1]. In the chemical series C_6F_5X, the nondissociative pathway dominates for $X = Cl$, Br, but is $<3\%$ of products observed for $X = I$ [6]. In the present study, we investigate electron attachment reactions where the nondissociative reaction channel and a dissociative reaction channel are both operative. Such a situation was observed for the well-studied electron attachment reaction of SF_6. For this system, at low temperature the nondissociative pathway is dominant, but at higher temperatures dissociative pathways are significant [8].

Several groups have investigated electron attachment to halogenated alkenes. Olthoff et al. [9] and Burrow et al. [10] found that electron attachment to chloroethylene molecules proceeds via dissociative attachment, primarily forming the halogen anion and the resulting hydrocarbon/halocarbon radical. In contrast, Wiley et al. [11] and Stemmler [3] observed both nondissociative and chloride ion dissociative products from electron attachment to chloroethylene molecules containing more than one chlorine. In the present study of the reactions of electrons with the cyclic haloalkenes 1,2-dichlorohexafluorocyclopentene (c-$C_5F_6Cl_2$) and 1,2-dichlorooctafluorocyclohexene (c-$C_6F_8Cl_2$) in the temperature range of 300–550 K, we also observe both nondissociative and dissociative products, finding that the observed branching ratio is strongly dependent on temperature. The observation that the parent ion is formed in these reactions indicates that these molecules have positive electron affinities. Our experiments, results, and conclusions are presented below.

2. Experiment

A variable-temperature flowing-afterglow Langmuir probe (FALP) apparatus at the Air Force Research Laboratory was utilized for the electron attachment study. The FALP apparatus and methodology is well established and has been described in detail elsewhere [12,13]. A diffusion-dominated electron/positive-ion plasma was produced in fast-flowing helium gas in a 1-m-long flow tube (7.8 cm diameter) with a microwave discharge. The helium buffer gas density was varied from 1.3 to 2.1×10^{16} cm^{-3} for these experiments. Argon was added (at a partial pressure of ~0.02 Torr) 30 cm upstream of the neutral reactant inlet port to remove metastable-excited He by Penning ionization and He_2^+ by charge transfer, resulting in a plasma consisting of electrons He^+ and Ar^+. A dilute mixture of the neutral reactant vapor in helium gas (~0.2%) was prepared in a 1-L passivated stainless steel bulb, and the dilute vapor was introduced into the flow tube through an inlet port consisting of three hollow needles protruding into the flow tube radially at a point halfway down the flow tube. Calibrated flow controllers allowed accurate delivery and measurement of the neutral reactant flow [14]. The concentration of neutral reactant used was at least an order of magnitude larger than the electron density for rate coefficient determinations to maintain pseudo-first-order kinetics with respect to the neutral reactant. Downstream of the entry port, decay of the electron density is due to the coupled effects of ambipolar diffusion and electron attachment to the neutral reactant. The axial electron density was determined along the interaction region with a movable, cylindrical Langmuir probe (0.0025 cm diameter and 0.4 cm long) [12,13]. Briefly, the probe potential was swept from 2 V below the plasma potential to 2 V above the plasma potential and the current to the probe was measured. The slope of the line formed by plotting the square of the current versus voltage (for voltages collecting electrons rather than positive ions) is proportional to the electron density. The electron attachment rate coefficient was determined from a fit of the electron density data to the solution of the differential equation describing decay due to diffusion and attachment [12,13]. The electron density and neutral reactant concentrations were kept sufficiently small (2×10^8–2×10^9 cm^{-3}, and 10^{10}–10^{11} cm^{-3}, respectively) so that electron-ion recombination was negligible [15]. Only relative values of the electron density are needed in this fit to the data since the decay of electrons by diffusion and reaction are first order and pseudo-first-order, respectively. The plasma velocity ($\sim 10^4$ cm s^{-1}) in the flow tube was constant throughout each experiment and was measured by pulsing the plasma density and observing propagation of the disturbance using the Langmuir probe. As a result, distances along the reaction zone could be converted into a time scale for rate coefficient determinations. The ambipolar diffusion rate coefficient was measured in the absence of neutral reactant vapor. Errors due to diffusion are small in the present work because the electron attachment decay rate exceeded the ambipolar diffusion rate by a factor of 3–4. Rate coefficients were measured at a fixed buffer gas density of 1.9×10^{16} cm^{-3}. The reported values have an estimated uncertainty of ±25%.

Ions reaching the end of the flow tube in the FALP apparatus were sampled through a 0.3-mm diameter aperture, mass analyzed, and detected with a particle multiplier. Both negative ion and positive ion mass spectra were collected over the full temperature range of investigation. Branching ratios for electron attachment were determined from the relative value of the product anion signals at a small extent of reaction (low neutral reactant flow). Mass discrimination was minimized by collecting the spectra at low mass resolution. While we recognize that adjusting the resolution does not reduce detector discrimination, our experience indicates that detector discrimination is generally minimal when the ion attraction potential to the detector is kept large (4 kV in our case). Branching ratios reported were determined with a precision of <4 percentage points and have an estimated accuracy of ±15 percentage points, based on our past experience.

Samples of 1,2-dichlorohexafluorocyclopentene (c-$C_5F_6Cl_2$) and 1,2-dichlorooctafluorocyclohexene (c-$C_6F_8Cl_2$) were purchased from PCR (now part of Lancaster Synthesis Inc., Windham, NH) and used without further purification except for degassing through several freeze-pump-thaw cycles. The sample purity quoted by the manufacturer for both compounds is >97%. Possible influence of impurities on the observed data is discussed below.

Table 1
Rate coefficient for electron attachment to c-$C_5F_6Cl_2$ and c-$C_6F_8Cl_2$ as a function of temperature

c-$C_5F_6Cl_2$		c-$C_6F_8Cl_2$	
T (K)	k (10^{-7} cm^3 s^{-1})	T (K)	k (10^{-7} cm^3 s^{-1})
295	2.5	295	3.5
350	2.5	348	3.1
405	2.2	367	3.1
449	2.3	405	2.8
478	2.4	451	2.8
555	2.3	466	2.8
		522	3.0
		553	3.1

3. Results and discussion

3.1. Electron attachment rate constant

Since these reactions were not studied previously, care was taken to look for evidence of electron detachment from the product negative ions, which complicates analysis of the electron attachment rate coefficient. If electron detachment is taking place, the electron is replenished by thermal detachment, resulting in a different shape to the decay curve [16]. No such evidence was observed. The rate coefficients for electron attachment to c-$C_5F_6Cl_2$ and c-$C_6F_8Cl_2$ over the temperature range 295–555 K were determined as described in the section above and are presented in Table 1. These data indicate that these reactions are efficient and that the electron attachment rate coefficient for both reactions is, at most, weakly dependent on temperature. The maximum cross section for s-wave electron attachment to a point molecule is $\lambda^2/(4\pi)$, where λ is the electron wavelength [6]. The corresponding maximum attachment rate coefficient at 300 K is 5×10^{-7} cm^3 s^{-1} [6]. This model predicts that the maximum attachment rate coefficient should decrease slightly with temperature, having a

$T^{-1/2}$ dependence. Klots [17] gave an expression for the maximum cross section, which takes into account the polarization attraction between the electron and molecule. The maximum cross section estimated by the Klots model is smaller than that predicted by the *s*-wave model [17]. Assuming the maximum rate coefficient derived from the Klots model [17] (estimating the polarizability of the reactant neutrals [18] as 14 ± 2 Å^3) is the collision rate coefficient, we can estimate the efficiency of attachment from the ratio of the observed rate coefficient to the collision rate coefficient. The calculated efficiencies (ranging from 0.7 to 0.8 for *c*-$C_5F_6Cl_2$ and 0.9 to 1.0 for $C_6F_8Cl_2$) indicate that for both these systems, reaction takes place in nearly every collision over the full temperature range investigated.

3.2. Electron attachment products

At room temperature and buffer gas densities in the range of 1.3–2.1 × 10^{16} cm^{-3} the major product of electron attachment to *c*-$C_5F_6Cl_2$ and *c*-$C_6F_8Cl_2$ is the nondissociative parent ion. As the temperature is increased, formation of Cl^- is observed. Based on mass balance, the neutral product of this dissociative attachment process is the halocarbon radical. The parent anion and Cl^- were the only major anionic products observed for these reactions over the temperature range investigated, 300–550 K. Very small signals from Cl_2^- and $C_6F_8^-$ (≤2% and ≤1%, respectively, over the entire temperature range) were observed in the negative ion spectra obtained for the *c*-$C_6F_8Cl_2$ reaction with electrons, and a tiny signal from $C_5F_6^-$ (≪1%) was observed in a few spectra for the reaction of *c*-$C_5F_6Cl_2$ with electrons. These trace ions may arise from reactions with minor impurities in the sample and therefore are not included in the reported branching ratios. The observation of the parent anion over the temperature range 300–550 K, together with the lack of a thermal electron detachment signature in the rate coefficient data for both these systems, indicates that the electron affinities of *c*-$C_5F_6Cl_2$ and *c*-$C_6F_8Cl_2$ are greater than ~0.6 eV [16]. These conclusions are consistent with recent density functional theory calculations, which estimate the electron affinities of *c*-$C_5F_6Cl_2$ and *c*-$C_6F_8Cl_2$ to be 1.2 ± 0.3 eV and 1.5 ± 0.3 eV, respectively [19]. The temperature dependences of the branching ratios for the nondissociative product channel and the Cl^- dissociative product channel for both reaction systems are shown in Fig. 1. The branching ratios were determined at each temperature for two buffer gas densities (1.3 × 10^{16} cm^{-3} and 2.1 × 10^{16} cm^{-3}) and were found to be essentially independent of buffer gas density within this range.

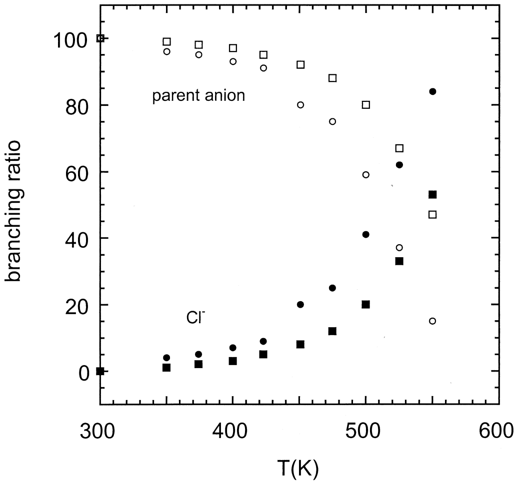

Fig. 1. Product branching ratio for reaction of electrons with *c*-$C_5F_6Cl_2$ (squares) and the reaction of electrons with *c*-$C_6F_8Cl_2$ (circles) as a function of temperature. Solid symbols represent the branching ratios for the dissociative product channel (formation Cl^-) and open symbols represent the nondissociative product channel.

Before further analysis of these branching fraction data presented in Fig. 1 can be made we must address the question of whether impurities or thermal decomposition of the reactant neutral or stabilized nondissociative product ion are responsible for the Cl^- ions observed. The maximum impurity level in each of the samples, as quoted by the manufacturer, is 3%. This value is too small to account for the efficient formation of Cl^- at high temperatures; at the highest temperatures the rate coefficient for formation of Cl^- is ~40% of the maximum collision rate coefficient for *c*-$C_5F_6Cl_2$ and ~90% of the maximum collision rate coefficient for *c*-$C_6F_8Cl_2$. Furthermore, the total rate coefficient for electron attachment does not change significantly with temperature. If the Cl^- were arising from electron attachment to an impurity at higher temperatures, one would expect an increase in the overall attachment rate coefficient, assuming that the rate coefficient for attachment to the neutral reactant of interest is approximately constant with temperature. The positive ion spectra, arising from reaction of the neutral reactant with He^+ and Ar^+, while complicated, does not change significantly over the full temperature range studied. These data suggest that thermal decomposition of the neutral reactant is also not significant. If formation of Cl^- arises from attachment to the products of thermal decomposition of the neutral reactant, one would expect to observe changes in the positive ion spectra of the neutral reactant(s) at higher temperatures. Finally, density functional theory calculations indicate that the carbon-chloride ion bond energy in both nondissociative product anions is sufficiently large to preclude thermal decomposition of the stabilized (thermal) nondissociative product anion to form Cl^- [19]. For these reasons we do not believe impurities, thermal decomposition of the reactant neutral, or thermal decomposition of the stabilized nondissociative product anion play important roles in the formation of Cl^- in our experiment.

The branching ratio for the reaction of c-$C_6F_8Cl_2$ with electrons is nearly 100% for the nondissociative channel at 300 K but changes to ~85% for the dissociative channel by 550 K. The fact that the reaction proceeds via one reaction channel at low temperature and a different reaction channel at high temperature, while the total attachment rate coefficient remains approximately constant, indicates that both channels are accessible from all or nearly all of the state or states of the temporary negative ion initially formed upon association of the electron and the neutral reactant. The change in the branching ratio for the reaction of c-$C_5F_6Cl_2$ over the temperature range studied (~100% nondissociative product at 300 K to ~45% nondissociative product and ~55% dissociative product at 550 K), although not as large, also occurs while the total rate coefficient stays relatively constant and large. This implies as well that some or all of the temporary negative ions can access both reaction channels.

What is not clear is whether the branching ratio temperature dependence is a reflection of the changing time scales for dissociation as compared with stabilization [8], a RRKM (Rice, Ramsperger, Kassel, Marcus theory) shift, or a potential energy barrier to dissociation. In an analysis of the competition between nondissociative and dissociative channels for electron attachment to SF_6, Spanel et al. [8] suggested that kinetic competition (a RRKM shift) played a significant role in the observed branching ratios measured in moderate pressure flow tube experiments. To test this hypothesis, we measured the branching ratios at a fixed temperature but varying buffer gas density. The observation that the branching ratios observed are independent of buffer gas density, or collision frequency, even at temperatures where the branching ratios for the two reaction channels are similar in value suggests that such kinetic competition is not the controlling factor. While the density range accessible in our instrument is small, a change in the branching ratio should be observed (i.e. measurable) if stabilization proceeds primarily through collisions and most of the temporary negative ions formed can access both reaction channels.

While the free energy for each of the dissociative electron attachment reactions cannot be determined from experimental data in the literature, information on related systems and recent calculations on the systems of interest indicate that the enthalpy for the dissociative reaction channel is small and likely positive [18–20], supporting the idea that a potential energy barrier is the cause of the observed branching ratio temperature dependence. Carbon-chlorine (C–Cl) bond strengths are known for a few unsaturated halocarbon systems (e.g. vinyl chloride and chlorobenzene) [20] and are similar in value to the electron affinity of Cl [18]; the difference between these values is approximately the reaction enthalpy. Density functional theory calculations, studying the reactants and products of the dissociative electron attachment reaction channel, estimate reaction enthalpies as 0.5 ± 0.3 eV and 0.3 ± 0.3 eV for reaction of c-$C_5F_6Cl_2$ and c-$C_6F_8Cl_2$, respectively [19]. A large difference between the reaction enthalpy/activation energy for these two reactions is not expected, since little differ-

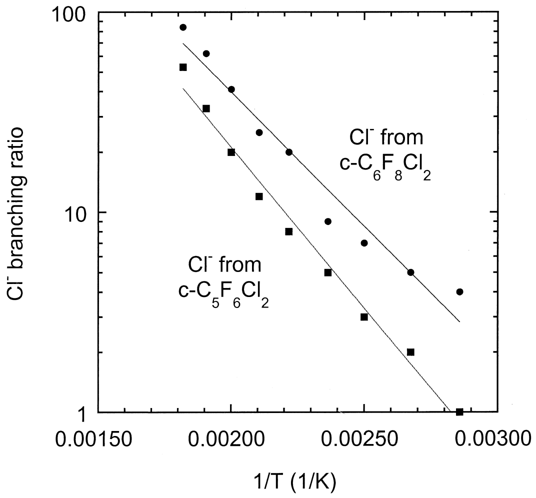

Fig. 2. Cl^- dissociative product branching ratio as a function of $1/T$ for reaction of *c*-$C_5F_6Cl_2$ (squares) and *c*-$C_6F_8Cl_2$ (circles) with electrons.

ence is expected between the C–Cl bond energy in *c*-$C_5F_6Cl_2$ as compared with *c*-$C_6F_8Cl_2$, because there is relatively little ring strain in these systems. Assuming that an energy barrier to dissociation is present and that every temporary negative ion formed that has sufficient energy to overcome the barrier will result in Cl^- formation, we can use the experimental Cl^- branching ratio data to estimate the size of the barrier by applying a simple Arrhenius-type analysis (Fig. 2). (Because the overall rate coefficient is essentially independent of temperature, the product branching ratio is proportional to the rate coefficient for the reaction channel at all temperatures.) Arrhenius analysis gives activation energies of 0.32 ± 0.05 eV for *c*-$C_5F_6Cl_2$ and 0.26 ± 0.05 eV for *c*-$C_6F_8Cl_2$, values similar in value to the calculated reaction enthalpies. We recognize that the data do not fit the Arrhenius equation well (in fact, the data of Fig. 1 seem to be nearly identical except for a simple shift in temperature scale), but the activation energies derived do provide an experimental measure of the energy required to promote the dissociative attachment reaction channel.

Based on our data and the arguments put forth above, we believe the primary origin of the branching ratio temperature dependence observed in these reactions is an energetic barrier to dissociation. A further test of our hypothesis could be provided by investigations of these reactions at very low pressures (not possible in our experiment) where the parent anion could not be stabilized and therefore would not be observed.

4. Conclusions

Electron attachment to *c*-$C_5F_6Cl_2$ and *c*-$C_6F_8Cl_2$ is efficient over the temperature range 295–555 K with average rate coefficients of 2.4×10^{-7} cm^3 s^{-1} for *c*-$C_5F_6Cl_2$ and 3.1×10^{-7} cm^3 s^{-1} for *c*-$C_6F_8Cl_2$, respectively. The total electron attachment rate coefficient is relatively independent of temperature. In contrast, the products of electron attachment in both of these reactions appears to depend strongly on the temperature. At 300 K, the dominant reaction channel is nondissociative attachment for both reactions, whereas at higher temperatures a dissociative product channel forming Cl^- is observed. The efficiency of the dissociative reaction channel in both reactions increases with temperature, whereas that for nondissociative attachment decreases. The onset for dissociative electron attachment is different for the two reaction systems, with a lower temperature onset for the *c*-$C_5F_6Cl_2$ system as compared with the *c*-$C_6F_8Cl_2$ system. Based on the absence of a dependence of the branching ratio on buffer gas density, we believe that the branching ratio temperature dependence observed primarily arises from an energetic (rather than kinetic) barrier to dissociation.

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