Ion cyclotron resonance studies of radiative and dissociative electron attachment processes at low pressures\textsuperscript{a)}

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Ion cyclotron resonance spectroscopy is used to measure nondissociative electron attachment rate constants for C\textsubscript{6}F\textsubscript{6} (perfluorobenzene), C\textsubscript{6}F\textsubscript{8} (perfluorotoluene), C\textsubscript{6}F\textsubscript{6} (perfluorocyclobutane), and C\textsubscript{6}F\textsubscript{14} (perfluoromethylcyclohexane) at low pressure (< 10\textsuperscript{-4} Torr). Infrared emission is assumed to stabilize excited species leading to long-lived molecular negative ions. Combining the present data with negative ion lifetimes measured at low pressures by time-of-flight methods and electron attachment rates measured at high pressures in swarm experiments allows estimates of radiative lifetimes to be made. These all fall in the range from 0.4 to 1.5 msec, which are typical of infrared radiative lifetimes. Data are also presented for dissociative electron attachment to CCl\textsubscript{4}, where the rate limiting step is shown to be thermalization of the electron energy distribution. A number of different buffer gases are examined and the ion cyclotron resonance results extrapolate to yield the attachment rate measured in high pressure swarm experiments.

1. INTRODUCTION

Studies of electron attachment processes using ion cyclotron resonance (ICR) techniques at first glance might appear to have generated more confusion than understanding relating to this important phenomenon.\textsuperscript{1,3} ICR experiments yield negative ion lifetimes which are orders of magnitude longer than those measured using time-of-flight techniques.\textsuperscript{2,3} In addition, rate constants for electron attachment measured at the low pressures typical of ICR experiments (10\textsuperscript{-8}-10\textsuperscript{-5} Torr) are orders of magnitude less than those measured in high pressure (carrier gas pressure usually in excess of 500 Torr) swarm experiments.\textsuperscript{2-4} It is well known that lifetimes and attachment rates are sensitive functions of the electron energy distribution.\textsuperscript{3,5,6} However, this alone does not adequately account for the apparent discrepancies among the reported studies of negative ion lifetimes and attachment rates.

The scheme depicted in Eq. (1) can be employed to describe electron attachment.\textsuperscript{1} Reaction of molecule A with an electron of kinetic energy \(E_{\text{kin}}\) results in formation of the excited negative ion \([\text{A}^-]^*\) which contains internal excitation at least equal to the electron affinity of A. The species \([\text{A}^-]^*\) may then autodetach an electron (with autodetachment lifetime \(\tau_s\)), decompose (\(k_d\)), radiate (with radiative lifetime \(\tau_r\)) or be collisionally stabilized (\(k_s(M)\)). The species \([\text{A}^-]^*\) may still possess internal excitation, but it is insufficient for autodetachment to be energetically possible. Further radiative or collisional events lead to thermal equilibrium. Processes involving \([\text{A}^-]^*\) are expected to be sensitive to the internal energy content of \([\text{A}^-]^*\) and hence to the initial electron energy. In general, cross sections for nondissociative electron attachment show sharp maxima for low energy (< 0 eV) electrons.\textsuperscript{3,4,7}

Earlier we presented an ICR study of SF\textsubscript{6} in which a radiative mechanism for formation of stable SF\textsubscript{6} at low pressure was inferred.\textsuperscript{1} In the present study we present results for nondissociative electron attachment to a wide variety of molecules, including C\textsubscript{6}F\textsubscript{6} (perfluorobenzene), C\textsubscript{6}F\textsubscript{8} (perfluorotoluene), C\textsubscript{6}F\textsubscript{6} (perfluorocyclobutane), and C\textsubscript{6}F\textsubscript{14} (perfluoromethylcyclohexane). In addition, results for dissociative attachment to CCl\textsubscript{4} are presented. Data are now available from a variety of other experiments such that comparison of high and low pressure data is possible. The combined results are interpreted in terms of the mechanism of Eq. (1).

II. EXPERIMENTAL

Trapped ion ICR techniques have been described in detail in the literature.\textsuperscript{8} An initial electron beam pulse fills the source region of the ICR cell with electrons which may react with neutral species to form negative ions. After a suitable trapping time, mass spectrometric analysis provides relative ion abundances. The instrument used in these studies was built in the Caltech shops and utilizes a 23.4 kG electromagnet, flat ICR cell, and standard marginal oscillator detector. All experiments are carried out at ambient temperature (298 °K).

Pressure measurements are made with a Schultz-Phelps type ionization gauge calibrated against a MKS Baratron Model 90H1-E capacitance manometer. Error in pressure measurement is estimated to be ±20%, and is the major source of inaccuracy in rate constant measurements.

All chemicals used in this study were obtained from commercial sources and used without further purification. Condensable gases were removed by several
freeze–pump–thaw cycles; impurities were negligible as determined by mass spectrometry.

III. RESULTS AND DISCUSSION

Electron attachment rate constants are measured in the same manner as for SF₈. It has been shown in previous studies that C₄F₆, C₅F₈, c-C₅F₈, and C₅F₁₄ attach low-energy electrons. 5,7,8 In ICR experiments only electrons scattered from the beam and trapped in the source region of the ICR cell attach to SF₈, 10 and the same is assumed for the processes studied here. Consistent with this, negative ion signal intensity increases with increasing electron energy as more inelastically scattered electrons are produced. For C₄F₆, C₅F₈, c-C₅F₈, and C₅F₁₄, non-dissociative attachment is observed. In addition, a dissociative attachment process, reaction (2), is observed for C₅F₁₄. The ratio of C₅F₁₄ to C₅F₁₄ is approximately 25:1.

\[
\text{C₅F₁₄} + e^- \rightarrow \text{C₅F₁₄} + \text{CF}_₃^-. \tag{2}
\]

Since attachment cross sections peak at very low electron energies (~0 eV), observation of reaction (2) implies that ~4% of the C₅F₁₄ molecules possess sufficient internal energy prior to electron attachment such that dissociation of C₅F₁₄ is then rapid compared to radiative stabilization.

Figure 1 shows typical trapped-ion data for formation of C₅F₈. Similar results obtain for C₄F₆, C₅F₈, and C₅F₁₄. After the initial 10–20 msec, the curve in Fig. 1 is accurately described by a simple exponential function, Eq. (3), where \([M^-]_0\) is the anion abundance

\[
[M^-] = [M^-]_0 \left[ 1 - \exp \left( -k_{app}(M) t \right) \right] \tag{3}
\]

at long time and \(k_{app}\) is the apparent bi-molecular rate constant. Figure 2 shows the measured electron attachment rate constant, \(k_{app}\), for C₄F₆, C₅F₈, c-C₅F₈, and C₅F₁₄ plotted as a function of pressure of the pure gas. Within experimental error the electron attachment rate constants for these molecules are pressure independent at pressures less than \(3 \times 10^4\) Torr. Measurements of the attachment rate constant for C₅F₁₄ was not possible at pressures above \(2 \times 10^5\) Torr because the time scale for formation of C₅F₁₄ becomes comparable to the sampling time of the experiment. Average values of the electron attachment rate constants from Fig. 2 are listed in Table I along with literature values of thermal attachment rate constants determined in swarm experiments. Also included are data for SF₈ at low pressures. Data from swarm experiments are obtained at high buffer gas pressures such that every ion formed is collisionally stabilized. 3 In accord with the scheme shown in Eq. (1), we equate the high pressure attachment rate constants with \(k_p\).

As described in our previous ICR study of SF₈, 1 scattered electrons in the source region of an ICR cell can have kinetic energy from approximately thermal to 0.9 eV.

![FIG. 1. Typical trapped ion data for electron attachment to C₅F₈. The trap is filled with electrons by a 10 msec electron beam pulse. C₅F₈ pressure is 2×10⁻⁷ Torr.](image)

![FIG. 2. Electron attachment rate constants as a function of pressure for C₄F₆ (perfluorobenzene), C₅F₈ (perfluorotoluene), c-C₅F₈ (perfluorocyclooctane) and C₅F₁₄ (perfluoromethylcyclohexane).](image)

![TABLE I. Attachment rate constants, autodetachment lifetimes, and radiative lifetimes for electron attachment to SF₈, C₄F₆, C₅F₈, c-C₅F₈, and C₅F₁₄. Also included are known electron affinities.](table)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(k_{app})</th>
<th>(k_p)</th>
<th>(\tau_e)</th>
<th>(\tau_r)</th>
<th>EA*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₈</td>
<td>1.6 ± 0.2(^t)</td>
<td>2.72</td>
<td>25</td>
<td>0.4</td>
<td>&gt;0.6(^{t})</td>
</tr>
<tr>
<td>C₄F₆</td>
<td>0.16 ± 0.03(^d)</td>
<td>1.02</td>
<td>12</td>
<td>0.8</td>
<td>≥1.8(^d)</td>
</tr>
<tr>
<td>C₅F₈</td>
<td>0.66 ± 0.15(^b)</td>
<td>2.44</td>
<td>12.2</td>
<td>0.5</td>
<td>≥1.7(^b)</td>
</tr>
<tr>
<td>c-C₅F₈</td>
<td>0.04 ± 0.01(^a)</td>
<td>0.11</td>
<td>14.8</td>
<td>0.5</td>
<td>0.4(^a)</td>
</tr>
<tr>
<td>C₅F₁₄</td>
<td>2.7 ± 0.5(^a)</td>
<td>0.52</td>
<td>595</td>
<td>1.5</td>
<td>NA(^a)</td>
</tr>
</tbody>
</table>

\(^a\) Units are \(10^3\) cm³ molecule⁻¹ sec⁻¹. Errors quoted are for one standard deviation.

\(^b\) High pressure thermal attachment rate constants, equated with \(k_p\) in accordance with Eq. (1). Units are \(10^3\) cm³ molecule⁻¹ sec⁻¹. Data from Ref. 2.

\(^c\) Units are \(\mu\)sec. Data from Ref. 2.

\(^d\) Units are m/sec. Calculated according to Eq. (4).

\(^e\) Units are eV.

\(^f\) Reference 1.

\(^g\) Reference 2.

\(^h\) Measured in this work.

\(^i\) Reference 13.

\(^j\) Data not available.

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leading to formation of long-lived stable molecular negative ions at low pressure \cite{Eq. (1)}. This conclusion is supported by the bimolecular behavior of the rate constants shown in Fig. 2. Assuming steady-state conditions for $[\text{A}]^n$ in Eq. (1), Eq. (4) results for $k_{\text{app}}$ providing $1/\tau_a \gg 1/\tau_r \gg k_a[M]$. 

$$k_{\text{app}} = \frac{k_f \tau_f}{\tau_r}.$$  

The data in Table I in conjunction with Eq. (4) can be used to estimate radiative lifetimes. Calculated values of $\tau_r$ are shown in Table I. The calculated radiative lifetimes, 0.4–1.5 msec, are not unreasonable for infrared emission.\cite{Infrared} Infrared radiative lifetimes (calculated from integrated absorption intensities) for C–F modes in C\textsubscript{6}F\textsubscript{6}, C\textsubscript{4}F\textsubscript{6}, and C\textsubscript{4}F\textsubscript{6} are 3, 1.1, 0.4, and 0.2 msec, respectively.\cite{Infrared}

It is of interest to examine the data in Table I for c–C\textsubscript{4}F\textsubscript{6} and c–C\textsubscript{4}F\textsubscript{6}. Even though C\textsubscript{4}F\textsubscript{6} rapidly attaches electrons at low pressures, the radiative lifetime is somewhat larger than for other species. In contrast with C\textsubscript{4}F\textsubscript{6}, c–C\textsubscript{4}F\textsubscript{6} is the slowest to attach electrons yet has an autodetachment lifetime and radiative rate comparable to the other ions. In the case of C\textsubscript{4}F\textsubscript{6}, the long (783 msec) autodetachment lifetime is responsible for the rapid attachment process. For a large molecule, internal energy is shared by a large number of modes resulting in a slow unimolecular decomposition (autodetachment) rate. For comparable internal energy content, a larger molecule will also have a lower internal temperature since the energy is distributed over more internal modes. The lower internal temperature results in a longer radiative lifetime, and may explain the long radiative lifetime calculated for C\textsubscript{4}F\textsubscript{6}. On the other hand, c–C\textsubscript{4}F\textsubscript{6} has a short radiative lifetime (Table I). The small attachment rate constant measured at low pressure thus reflects the smaller thermal attachment rate ($k_f$) measured at high pressure (Table I). While the electron affinity (included in Table I) of C\textsubscript{4}F\textsubscript{6} is not known, it is expected to be comparable to or at most slightly higher than the electron affinity of c–C\textsubscript{4}F\textsubscript{6}.\cite{Paige}

For electron attachment to the molecules in Table I the rate limiting step at low pressure appears to be stabilization of the excited molecular ion. For molecules which undergo dissociative attachment no stabilization is needed and attachment rates at low pressures should not differ from high pressure results. Carbon tetrahalide undergoes dissociative electron attachment of low energy electrons to give Cl\textsuperscript{+} and CCl\textsubscript{4}, Eq. (5).\cite{Klotz} In pure CCl\textsubscript{4}, relaxation of the electron energy distribution

$$\text{CCl}_4 + e^-(E_{\text{kin}}) = \text{Cl}^+ + \text{CCl}_3$$  

is relatively slow and is the rate limiting step at low pressure.\cite{Klotz} This contrasts the behavior observed for the molecules listed in Table I, for which the apparent attachment rates are found to be pressure independent over the accessible range of study (Fig. 2). Addition of a gas efficient at relaxing the electron energy distribution (such as CO\textsubscript{2}) should allow low pressure dissociative attachment rates in CCl\textsubscript{4} to approach high pressure attachment rates. Figure 4 shows CCl\textsubscript{4} low pressure dissociative attachment rates plotted as a function of CO\textsubscript{2} pressure added to 5.7 x 10\textsuperscript{-6} Torr of CCl\textsubscript{4}. The dashed line indi-
cates the attachment rate as calculated from the high pressure attachment rate constant of $2.7 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. Over the range of CO$_2$ pressures used in the present experiments, attachment rates are proportional to CO$_2$ concentration. From the slope of the linear portion of the curve in Fig. 4 a rate constant of $2.2 \times 10^{-8}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ is calculated for thermalization of electrons by CO$_2$. Higher CO$_2$ pressures cannot be used because the total rate of Cl$^-$ formation becomes comparable to the experimental sampling time. Compared to CO$_2$, CH$_4$, and N$_2$ were found to be inefficient at relaxing the electron energy distribution. Benzene-d$_4$ thermalizes electrons at a rate only slightly slower than CO$_2$. These results are attributed to low-lying temporary electron attachment processes involving CO$_2$ and C$_2$H$_6$, not available to CH$_4$ or N$_2$ (except at higher energies), which permit energetic electrons to attach and subsequently autodetach with lower energy.

Warman and Sauer have reported related studies of electron thermalization in irradiated gases using CCl$_4$ as an electron energy probe. They derive a thermalization rate constant of $5.8 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for CO$_2$, which is significantly higher than the present result. Phelps has calculated relaxation rates of thermal electron energy distributions from mobility and diffusion data. In good agreement with the present experiments, his results yield a mean thermalization rate of $2.5 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for electrons in CO$_2$. The rate is not strongly dependent on electron energy between thermal energies and 1 eV. As reported by Warman and Sauer, the relative thermalization rates for CO$_2$, benzene, CH$_4$, and N$_2$ are 1.0, 0.76, 0.15, and 0.004, respectively. Christophorou and co-workers have reported data for electron thermalization times as a function of mean electron energy in a number of gases. Their results indicate that above $\sim 0.1$ eV, electron thermalization times are relatively constant, and decrease significantly at lower mean electron energies. Using the higher energy limits gives approximate relative efficiencies of 1.0, 0.053, and 0.0040 for CO$_2$, CH$_4$, and N$_2$, respectively. These results are in agreement with the present work in which CH$_4$ and N$_2$ are found to be inefficient compared to CO$_2$ and benzene.

**IV. CONCLUSIONS**

With data on electron attachment now becoming available from a variety of experiments under various conditions of pressure, temperature and initial electron energy distribution, the various processes involved [Eq. (1)] are becoming increasingly well characterized. Whereas high pressure experiments yield information on initial attachment rates and autodetachment lifetimes, low pressure ICR techniques are especially well suited for studying processes such as radiative and collisional stabilization. It is seen in this work that formation of stable molecular negative ions at very low pressure is not unique to SF$_6$, but is observed for a large variety of molecules where autodetachment and dissociation lifetimes are long enough to allow radiative stabilization. Combination of ICR data with high pressure data allows estimates of radiative lifetimes to be made, with results that are consistent with an infrared emission process. Dissociative electron attachment, such as observed in CCl$_4$, occurs at low pressure with nearly the same facility as at high pressure because no stabilization process is required. In low pressure ICR experiments, the rate limiting step in dissociative electron attachment appears to be relaxation of the electron energy distribution.

**ACKNOWLEDGMENTS**

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18A. V. Phelps, in Defense Nuclear Agency Reaction Rate Handbook (DNA 1948H), edited by M. H. Bortner and T. Bauer; Chap. 21. See also the discussion of this work in Ref. 17.