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ARRHENIUS BEHAVIOR OF ELECTRON ATTACHMENT TO CH3Br FROM 303 TO 1100 K

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1. Introduction

Electron attachment to CH_3Br is known to be very inefficient at room temperature because low vibrational levels do not have enough energy to reach the crossing between the neutral and anion potential surfaces [1]. As the temperature is increased, the attachment rate coefficient (k_a) increases because the internal energy rises and the Franck–Condon overlap between the initial vibrational level and the dissociating state grows. Among notable experimental results are early evidence by Wentworth et al. [2], Bansal and Fessenden [3], and Mothes [4] that attachment to CH_3Br is very inefficient at room temperature. The data of Wentworth et al. [3] also showed that k_a increased strongly with temperature, an observation later confirmed by Alge et al. [5], Petrović and Crompton [6], Datskos et al. [7], Levy et al. [8], Braun et al. [9], and in the present work. In addition, relative attachment cross sections were observed by Spence and Schulz to increase strongly up to 1250 K [10]. An accurate measurement of k_a at room temperature was given by Petrović and Crompton, $6.78 \pm 0.27 \times 10^{-12}$ cm^3 s^{-1} [6]. The experiment of Datskos et al. of k_a versus temperature (300–700 K) additionally provided k_a values versus average electron energy (~0.046–0.87 eV) [7]. The high-resolution beam measurements of Braun et al. [9] showed a vibrational Feshbach resonance associated with the $\nu_3 = 4$ vibrational level of the C–Br stretch mode in the neutral molecule, which had been predicted by the R-matrix calculations of Wilde et al. [1]. The R-matrix calculations by Wilde et al. [1], Gallup and Fabrikant [11], and Braun et al. [9] take into account the supercritical dipole moment of CH_3Br, 1.8203 ± 0.0004 D [12] and the polarizability 5.97 ± 0.61 Å^3 [13].

In the present work, we provide new values of k_a from 303 to 1100 K and examine the existing data using kinetic modeling theory that has been presented in several recent papers [14–19]. The reaction studied is:

$$e^- + CH_3Br \rightarrow CH_3 + Br^- \quad (1)$$

The exothermicity of the reaction is 0.32 eV from the difference between the electron affinity of Br (3.3635882 ± 0.0000019 eV at 0 K) [20] and the CH_3Br bond enthapy (3.048 ± 0.022 eV at 298 K) [12]. Taking into account the thermal energy at 298 K makes a difference in the exothermicity of ~0.005 eV.

2. Experimental

Two flowing-afterglow Langmuir-probe (FALP) apparatuses were used in this work. The first operates between 300 and 600 K and has been described in detail in the literature [21,22]. The second

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was designed for high temperature applications, up to 1200 K, and has also been detailed in the literature [23,24]. Briefly, a microwave discharge was used to create a weak plasma ($\sim 10^9$ cm^{-3} density) in a fast flow of He gas (typically 56 m s^{-1}). A few percent of Ar was added downstream to yield a mostly e^-/Ar^+ plasma. Still further downstream a small flow of CH_3Br was added. A movable Langmuir probe allowed measurement of $[e^-]$ along the flow tube axis. In absence of CH_3Br, those measurements yielded the plasma diffusion rate, υ_D. We tend to keep the buffer gas concentration constant (3.2×10^{16} cm^{-3}, equal to 1 Torr pressure at 300 K) with temperature, but above 600 K the increase in the diffusion rate requires that greater pumping speeds be used (higher gas velocity) in order to keep $[e^-]$ high enough to satisfy the Langmuir probe detection limit of $\sim 3 \times 10^7$ cm^{-3}, e.g., a buffer gas concentration of 1.6×10^{16} cm^{-3} at 1000 K.

With CH_3Br present, $[e^-]$ decays faster along the flow tube due to the coupled effects of diffusion and electron attachment as described by the equation [25]

$$[e^-]_t = \frac{[e^-]_0(\upsilon_a \exp(-\upsilon_a t) - \upsilon_D \exp(-\upsilon_D t))}{(\upsilon_a - \upsilon_D)}, \quad (2)$$

where $[e^-]_0$ is measured at the CH_3Br inlet, $[e^-]_t$ is measured downstream at time t, and υ_a is the attachment frequency. The attachment rate coefficient is $k_a = \upsilon_a/[CH_3Br]$. The timescale is determined from a velocity (typically 100 m s^{-1}) measurement of the flowing plasma [21,22]. An orifice at the downstream end of the flow tube allows sampling of ions in the plasma for mass analysis in a high vacuum region using an rf electric quadrupole. The ion products of electron attachment were determined from the anion mass spectra, and the ion products of the reaction $Ar^+ + CH_3Br$ were determined from the cation mass spectra. The latter are often irrelevant in electron attachment experiments because $[e^-]$ and the cation concentrations are small enough that e^-/cation recombination is negligible; the Ar^+ and any remaining He^+ do not recombine with e^- to a measurable extent. However, the CH_3Br attachment rate coefficient in the range 300–400 K is so small (<10^{-10} cm^3 s^{-1}) that a large $[CH_3Br]$ ($\sim 10^{13}$ cm^{-3} at 303 K) was needed to affect significant decay in $[e^-]$ along the flow tube. The result is that within a very short time the plasma consists of e^- and molecular cations, which may undergo e^-/cation recombination, causing decay in $[e^-]$ beyond that expected solely from diffusion and attachment. Those cations are initially the CH_3^+ and CH_2Br^+ product of reaction with Ar^+, and CH_3^+ quickly reacts with CH_3Br to form higher-mass cations in secondary and possibly tertiary reactions.

In order to account for the recombination, a numerical solution of the rate equations describing diffusion, attachment, and recombination is required instead of Eq. (2). The rate coefficient for the $Ar^+ + CH_3Br$ reaction was measured at 302 K as described in Section 4, and was taken to drop slightly with temperature according to theory [26]. The effective recombination rate coefficient k_r was allowed to vary along with k_a in order to fit the data. To aid in the determination of k_r and k_a, sets of data were obtained at three different $[e^-]_0$, 7×10^8, 4×10^9, and 1×10^{10} cm^{-3}, at each of 303, 350 and 400 K. Because k_r depends on the plasma density squared (and k_a directly on the plasma density), the importance of k_r increases with $[e^-]_0$. The actual value of k_r has no usefulness outside of analyzing the present data because the plasma contains several cation types, including clusters which commonly undergo rapid evaporative recombination with electrons.

The uncertainty in the k_a are usually estimated at ±25%. The major uncertainty of ±10% is in knowing $[CH_3Br]$, which is determined from the flow tube pressure and temperature and the relative flow rates of buffer and CH_3Br gases (measured with MKS Instruments mass flow meters). The plasma velocity is measured to better than 1%. The relative reaction distances (the Langmuir probe positions) are good within 0.2 mm or 2% of the average reaction distance. However, there is an end effect associated with reactant gas filling a cross section of the flow tube rapidly at the 6-radial-needle gas inlet. Various tests indicate an end-effect uncertainty of as much as ±5% depending on the magnitude of k_a. Data at each temperature were obtained using more than one reactant flow rate to verify k_a independence on $[CH_3Br]$. The $[e^-]$ measurements are nominally very accurate, but will become poor at extremes due to plasma sheath expansion around the Langmuir probe at low $[e^-]$ or a sheath radius approaching that of the probe at high $[e^-]$. Both extremes are avoided. In any case, only relative values of $[e^-]$ are involved in determining k_a, provided that $[e^-]_0$ is low enough that electron-ion recombination is negligible. In the present case of CH_3Br, at low temperatures additional uncertainty is introduced in calculating a recombination correction, leading to an overall ±50% uncertainty at 303 K and ±35% at 350–400 K.

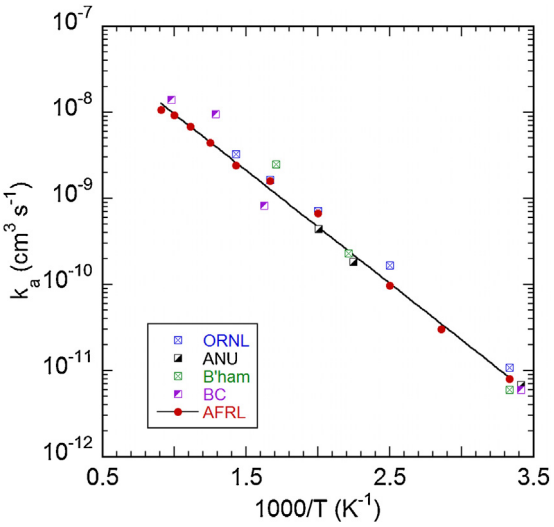

Fig. 1. Present k_a data (labeled AFRL, see Table 1) for electron attachment to CH_3Br along with data from earlier experiments for which the temperature dependence was studied. References: Oak Ridge National Laboratory (ORNL), Ref. [7]; Australian National University (ANU), Fig. 1 of Ref. [6]; Birmingham University (B'ham), Ref. [5]; and Boston College (BC), Ref. [8]. Not shown are relative measurements of Braun et al. (300–600 K, Ref. [9]).

3. Electron attachment results

The present k_a values for 303–1100 K are given in Table 1 and are shown in Fig. 1 along with data from earlier experiments for which the temperature dependence was studied. Br^- was the sole anion product of attachment over the entire temperature range, in agreement with earlier work. The most accurate measurement in the neighborhood of room temperature is that of Petrović and Crompton, $6.78 \pm 0.27 \times 10^{-12}$ cm^3 s^{-1} at 293 K [6]. It is interesting that in the case of CH_3Br, the definition of "room temperature" is rather important: the present data show that at 303 K, k_a has already risen to 8.0×10^{-12} cm^3 s^{-1}.

Other measurements (in cm^3 s^{-1} units) at room temperature are: $5.3 \pm 0.1 \times 10^{-12}$ (Szamrej et al.) [27], $6 \pm 3 \times 10^{-12}$ (300 K, Alge et al.) [5], 1.08×10^{-11} (300 K, Datskos et al.) [7], 6.0×10^{-12} (293 K, Levy et al.) [8], 7.0×10^{-12} (298 K, Bansal and Fessenden) [3], 3.6×10^{-12} (300 K, Mothes et al.) [4], and 1.0×10^{-11} (Schindler, quoted by Mothes et al.) [4]. Many older reports do not specify an uncertainty. The electron capture rate coefficient may be calculated [28] as $k_a = 4.00 \times 10^{-7}$ cm^3 s^{-1} based on the polarizability [13] of 5.97 Å^3 and dipole moment [12] of 1.82 D. The reaction is so inefficient at room temperature that, roughly speaking, there are only 20 attachment events per million collisions.

Table 1
Electron attachment rate coefficients (k_a) measured in the present work for CH_3Br as a function of temperature (T). Each datum is the average of 3–5 measurements of different CH_3Br concentration. Br^- was the sole anion product of attachment at all temperatures. The k_a are judged accurate to ±25% except for 303 K (±50%) and 350–400 K (±35%).

T (K)	k_a ($cm^3\ s^{-1}$)	T (K)	k_a ($cm^3\ s^{-1}$)	T (K)	k_a ($cm^3\ s^{-1}$)	T (K)	k_a ($cm^3\ s^{-1}$)
303	8.0×10^{-12}	500	6.7×10^{-10}	800	4.5×10^{-9}	1000	9.2×10^{-9}
350	3.0×10^{-11}	600	1.6×10^{-9}	900	6.9×10^{-9}	1100	1.1×10^{-8}
400	6.6×10^{-11}	700	2.4×10^{-9}				

The Arrhenius activation energy derived from the present data is 260 ± 20 meV. As visually obvious from Fig. 1, this result compares reasonably with earlier determinations (in meV units): 260 ± 15 (Petrović and Crompton) [6], 300 ± 60 (Alge et al.) [5], 279 (Levy et al.) [8], and 257 (Datskos et al.) [7], and with two others not shown in Fig. 1: 247 ± 17 (Wentworth et al.) [2], and 311 meV (Braun et al.) [9]. R-matrix theory finds similar activation energies, 249 (Wilde et al.) [1] and 298 meV (Braun et al.) [9]. Potential energy curves were shown in the last two references for the neutral and anion systems, including the adiabatic curve through the curve-crossing region. The absolute values of k_a calculated with R-matrix theory by Braun et al. [9] are slightly smaller than the consensus of experiment shown in Fig. 1.

A few notes on earlier experiments are warranted. The Oak Ridge National Laboratory data were obtained in a drift tube apparatus with N_2 buffer gas at pressures in the neighborhood of 1 atm [7]. The apparatus did not have a mass spectrometer. The Boston College experiment was performed in a flow tube apparatus with relative electron density detection via an electron paramagnetic resonance spectrometer [8]. All $k_a(CH_3Br)$ measurements were normalized to $k_a(SF_6)$ by flowing SF_6 at the same rate as CH_3Br, with the assumption that $k_a(SF_6) = 2.2 \times 10^{-7}\ cm^3\ s^{-1}$ at all temperatures. The temperatures were said to be uncertain by perhaps ±50 K at 777 K, and more than ±100 K at 1022 K. The apparatus included mass analysis of product anions. The Birmingham University data were obtained with a FALP apparatus in much the same way as in the present experiment [5]. The Australian National University (ANU) apparatus was a Cavalleri diffusion cell in which a pulse of x-rays was used to produce a small number of electrons in 4–15 Torr of various buffer gases with a small admixture of CH_3Br [6]. The electrons then thermalized, diffused, and attached to CH_3Br over known times. In Fig. 1, we show data taken from Fig. 1 of the ANU paper, on the assumption that the middle-temperature datum is misprinted in the text [6,29].

4. Ion–molecule reaction

In the process of making a correction for electron-cation recombination loss of electron density in the attachment data, we measured the rate coefficient k_{im} for the $Ar^+ + CH_3Br$ reaction, which has not been studied previously. The experiment is straightforward: as the CH_3Br concentration is increased stepwise, the Ar^+ intensity measured by the mass spectrometer is recorded. The exponential decrease in the Ar^+ intensity, divided by the reaction time, gives k_{im}. The mass spectra also provided the cation products of reaction, including those of secondary and tertiary reactions. Account must be taken of mass discrimination in the experiment, which may be due to differential ion diffusion in the flow tube, the sampling aperture and lenses, the rf electric quadrupole mass spectrometer, and the ion detection device (which utilizes a conversion dynode near a channel electron multiplier). To map out the discrimination versus ion mass, Ar^+ was reacted with molecules CH_4, NH_3, SO_2, and SF_6, and checking for ion signal balance between Ar^+ and ion products. (With NH_3 a secondary reaction is important.) For the present case of $Ar^+ + CH_3Br$, self-consistency may be found for the secondary reaction yielding $(CH_3Br)CH_3^+$, in that the sum of the CH_3^+ and $(CH_3Br)CH_3^+$ signals should show up as a flat line on a branching fraction plot (relative to CH_2Br^+) if properly corrected for mass discrimination.

For ion–molecule studies with the FALP apparatus, the plasma density is kept small, e.g., $5 \times 10^8\ cm^{-3}$, and a small concentration of CCl_4 ($3.5 \times 10^{10}\ cm^{-3}$) is added at the reactant inlet to quickly eliminate free electrons, giving a plasma dominated by Ar^+ and Cl^- prior to addition of CH_3Br. The reason for doing this is that the Ar^+/Cl^- plasma has a smaller diffusion rate than does the Ar^+/e^- plasma. The diffusion rate itself is not of consequence, but a *change* in the diffusion rate as CH_3Br is added, depleting electrons, would affect the ion intensities at the mass spectrometer, causing curvature in the expected exponential decay in the Ar^+ signal. With a reaction distance of 44 cm and a plasma velocity of 97 m s^{-1}, we determined $k_{im} = 1.8 \pm 0.4 \times 10^{-9}\ cm^3\ s^{-1}$ at 302 K and 1 Torr buffer gas pressure. As typical for Ar^+ reactions, this result is close to the calculated collision rate coefficient, $2.0 \times 10^{-9}\ cm^3\ s^{-1}$ [26]. The mass spectra showed primary reaction products CH_3^+ (80%) and CH_2Br^+ (20%), and showed a secondary reaction in which CH_3^+ clustered with CH_3Br. Modeling the secondary reaction gave a rate coefficient of $2.8 \pm 1.0 \times 10^{-9}\ cm^3\ s^{-1}$ at 302 K. At the larger concentrations of CH_3Br used in attachment experiments at low temperatures, tertiary reactions may be taking place. Henis et al. used an ion cyclotron resonance apparatus to study $CH_3^+ + CH_3Br$, which produced CH_2Br^+ cation product at pressures too low for the clustering reaction to occur [30]. The rate coefficient they measured for this process ($5 \pm 1 \times 10^{-11}\ cm^3\ s^{-1}$) is too small to show up in the present experiment in the face of the rapid $Ar^+ + CH_3Br$ reaction yielding the same product cation (Fig. 2).

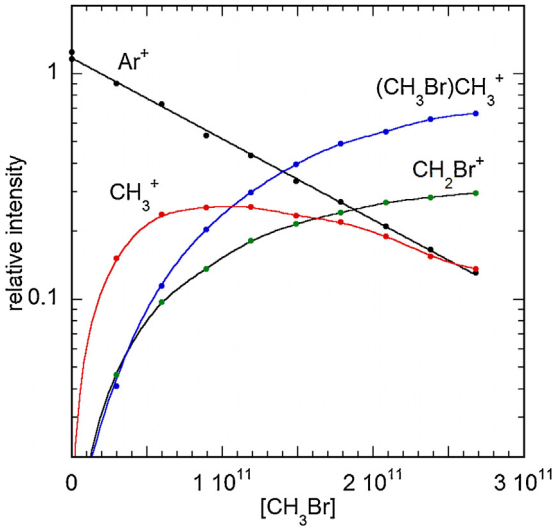

Fig. 2. Data for the reaction $Ar^+ + CH_3Br$ for a reaction time of 4.65 ms. The primary ion products are CH_3^+ (82%) and CH_2Br^+ (18%). The CH_3^+ then undergoes a secondary clustering reaction yielding $(CH_3Br)CH_3^+$.

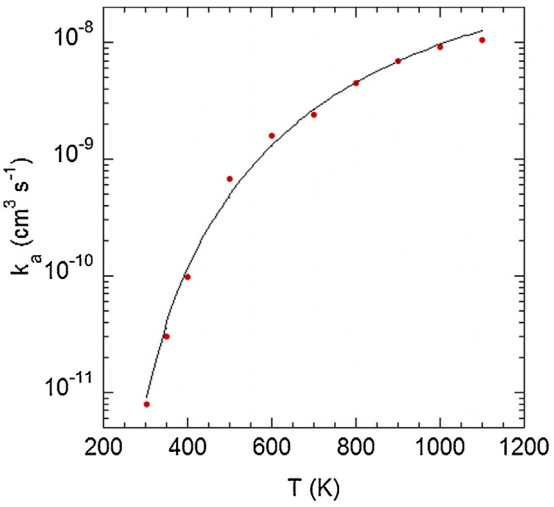

Fig. 3. A kinetic modeling fit (solid curve) to the present $k_a(CH_3Br)$ data based on a nuclear barrier height of 280 meV. Note that the barrier is slightly larger than the Arrhenius value, as predicted for dissociative electron attachment [34].

5. Kinetic modeling

We have used a kinetic modeling approach to electron attachment data to understand the various factors which govern the efficiency of reaction – why some molecules (e.g., SF_6) attach electrons rapidly, while seemingly similar molecules (e.g., SF_4) do not [14–19]. Further, the modeling allows us to predict k_a outside of the conditions of particular experiments, for example, to higher pressures, higher gas temperatures, and higher electron temperatures. The modeling has been generally quite successful in reproducing experimental results, and recently predictions made using the modeling have been validated by extending the initial range of experimental conditions.

The kinetic modeling fit to the present thermal data is shown in Fig. 3. Kinetic modeling provides little information about the attachment process for CH_3Br because the high barrier so dominates the dynamics over this temperature range that there is little deviation from Arrhenius behavior. More importantly, unlike previous systems studied [31] the kinetic modeling fails to reproduce non-thermal attachment data for CH_3Br [7]. At gas temperatures below 400 K, the attachment rate coefficient was observed to increase with electron temperature [7]. Kinetic modeling assumes a full separation of the molecular internal energy and the electron energy. Internal energy is assumed to contribute to overcoming the energetic barrier between the neutral and anion surfaces, leading to a strictly positive electron temperature dependence. Increased electron energy is assumed to decrease the timescale on which the incident electron and neutral species interact, decreasing the likelihood of crossing to the anion surface prior to separation, and leading to a strictly negative temperature dependence. These assumptions appear to be valid for many dissociative electron attachment systems, and it is interesting that they fail in the present case. Smith et al. [32] and Španěl et al. [33] noted 3 cases for molecules with small k_a (at 300 K) which showed positive electron temperature dependences, which they attributed to electron-impact vibrational excitation of the neutral molecule. For the $CHCl_3$ case, Španěl et al. [33] were able to account for the behavior versus both gas and electron temperature with a model that increased the vibrational temperature of the neutral due to the incoming electron energy.

Like with other methyl halides, electron attachment to CH_3Br displays vibrational Feshbach resonances [1,9]. That is, a temporary bound state may be formed between the incident electron and a vibrationally excited level of the ground electronic state of the neutral molecule. It is likely the existence of these resonances along with the large electronic barrier to crossing between the neutral and anion surfaces is what results in a failure of the kinetic modeling. The large barrier is responsible for the very low probability of attachment at lower temperatures. Even a small channel to attachment mediated by the vibrational Feshbach resonance, a feature not accounted for by the modeling, may then lead to a measurable increase in the total attachment rate. The advantages of the kinetic modeling approach lie in its simplicity, and systems such as CH_3Br where subtle aspects of the potential appear quite important are more appropriately investigated using more difficult approaches such as R-matrix theory [1].

It is useful to identify some criteria to judge whether or not the kinetic modeling approach is likely to fail for a given system. Any system with a large permanent dipole moment may show a vibrational Feshbach resonance. If a system also has a very small attachment rate coefficient, for instance due to a large energetic barrier, the kinetic modeling approach should be used with caution.

6. Conclusions

Measurements of k_a are reported for electron attachment to CH_3Br over the temperature range 303–1100 K. At 303 K, $k_a(CH_3Br) = 8.0 \pm 2.0 \times 10^{-12}$ cm^3 s^{-1}, and k_a increases strongly with temperature, as described by an activation energy of 260 ± 20 meV. The attachment reaction produces Br^- anions. These results are in substantial agreement with earlier work. Kinetic modeling of the present data and the data of Datskos et al. [7] shows that the behavior of k_a is dominated by a high nuclear barrier, but at low temperatures (~300 K) some measure of vibrational excitation is needed in order to surmount the barrier as the electron temperature is increased.

In the course of this work, we measured the rate coefficient for the $Ar^+ + CH_3Br$ reaction and determined $k_{im} = 1.8 \pm 0.4 \times 10^{-9}$ cm^3 s^{-1} at 302 K and 1 Torr buffer gas pressure. The primary reaction products are CH_3^+ (82%) and CH_2Br^+ (18%). A secondary reaction was observed in which CH_3^+ clusters with CH_3Br. Modeling the secondary reaction gave a rate coefficient of $2.8 \pm 1.0 \times 10^{-9}$ cm^3 s^{-1} at 302 K.

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