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Swarm Experiments

Product ion distributions and rate coefficients for the attachment reactions of electrons with $CHCl_2Br$, CCl_2Br_2, and $CHClBr_2$

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Abstract

Attachment rate coefficients, β, and product ion distributions, R, have been determined for the chlorobromomethanes $CHCl_2Br$, CCl_2Br_2, and $CHClBr_2$ using the flowing afterglow/Langmuir probe (FALP) method. Thus β and R have been determined at two attaching gas temperatures, T_g, of 300 K and 540 K and at electron temperatures, T_e, ranging from T_g to about 5000 K. The results show that T_g rather than T_e has the stronger influence on both β and R and that Br^- ions are the major products of these three reactions. Both β and Cl^- increase markedly with T_g, but the variations of β and R with T_e, although not so straightforward, are nevertheless well defined. Thus, it is apparent that dissociation to reaction products of the nascent negative ions is efficiently promoted by preheating the attaching molecules (increasing T_g), and to a lesser extent by increasing T_e, which is generally in accordance with a model we previously developed to describe other haloalkane attachment reactions. Electron capture by $CHCl_2Br$ and CCl_2Br_2 vary with T_e as predicted by capture rate theory, whereas autodetachment apparently seriously decreases the effective capture rate by $CHClBr_2$. By combining β and R values for these reactions under truly thermalised conditions, the partial rate coefficients for the Br^- and Cl^- reaction channels have been derived and from their variation with T_g, Arrhenius activation energies for Br^- and Cl^- production have been estimated. Small fractions of dihalogen negative ions are produced in these attachment reactions with $ClBr^-$ ions representing a significant fraction of the product ion distribution for the $CHClBr_2$ reaction. (Int J Mass Spectrom 205 (2001) 243–252) © 2001 Elsevier Science B.V.

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1. Introduction

Electron attachment can occur to any gas atom or molecule that has a stable negative ion state; atomic and molecular oxygen are well known examples of these [1]. An electrical discharge through oxygen results in the formation of O^- ions and O_2^- ions by the two processes of dissociative and nondissociative electron attachment, respectively. These negative ions are important precursors in the ion chemistry of the stratosphere and the troposphere [2]. In the dissocia-

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Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

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tive process, a short-lived parent negative ion dissociates to form a fragment negative ion together with a fragment (usually radical) neutral. In the nondissociative process (often termed direct attachment) the excited parent negative ion lives long enough to be stabilised either by radiation emission or in collision with an ambient atom or molecule, thus preventing autodetachment or dissociation [1,3]. Overviews of research into electron attachment, including the experimental and theoretical methods used for such studies and discussions of the basic principles, are given in the texts by Christophorou et al. [3], McDaniel [4], and Massey [5].

The physical conditions determining the rates of these attachment processes, and indeed the ionic product distributions of such reactions that are a focus of the present article, are the attaching gas temperature, T_g, and the electron temperature, T_e [or more correctly the electron energy distribution function, $f(E)$], and also the gas pressure when the direct process occurs. Even the electron number density, n_e, relative to the attaching gas number density, n_m, can be an important factor [6,7]. Although the significance of some of these parameters in determining the rates (and ionic products) of electron attachment reactions had been appreciated for some time, it was with the advent and exploitation of new experimental techniques that their separate and individual contributions have been forcibly demonstrated. In this respect, the flowing afterglow/Langmuir probe (FALP) technique [8] is valuable, because using this technique electron attachment coefficients, β, can be determined under truly thermalised conditions [i.e. $T_g = T_e = T$, and $f(E)$ is Maxwellian] in helium carrier gas over a range of temperatures and pressures, and the influence of T_e on β at several T_g can be studied separately under nonthermal conditions [i.e. $T_e > T_g$, but with $f(E)$ still being close to Maxwellian] using argon carrier gas [8]. This compares with the other major techniques used to study attachment: the electron drift tube [1,3] and the photonisation method [9], which are nonthermal techniques where T_g and T_e are never equal and $f(E)$ is not Maxwellian. The value of the last two techniques is that the variations with electron energy of the cross section for attachment reactions can be studied over a wider range of electron energies, and such measurements have been carried out for a large number of different molecules [1,3,9].

The bulk of the data obtained by FALP and other techniques reveals some interesting general features of electron attachment. First, all the available experimental data (with the notable exception of those for C_{60} and C_{70} [10,11]) confirm that the attachment coefficient is always less than the s-wave electron capture rate coefficient. This is described by $\beta_{\max} = \langle \pi(\lambda/2\pi)^2 v \rangle$, where λ is the de Broglie wavelength of the incoming electron and v is the electron velocity [12]. Thus $\beta_{\max}$ is predicted to vary with T_e as

$$\beta_{\max} = 5 \times 10^{-7} (300\ \mathrm{K}/T_e)^{1/2} \mathrm{cm}^3\ \mathrm{s}^{-1} \qquad (1)$$

When β for a dissociative attachment reaction is close to $\beta_{\max}$ under thermal conditions at a temperature of 300 K or below, the available data show that β remains close to $\beta_{\max}$ at elevated T_g and T_e also. Under these special circumstances there is usually no conflict between the results obtained (and derived) for β using different techniques (a good example is attachment to CCl_4 [13]). However, there are startling differences between the results of dissociative electron attachment studies from the thermal and nonthermal experiments when β for such reactions are appreciably smaller than $\beta_{\max}$ [13]. Then, the thermal FALP experiments indicated that β usually increases, sometimes very rapidly, with increasing $T_g (= T_e)$, whereas the nonthermal experiments for the same reactions indicate that an increasing T_e (or E) sometimes results in a decreasing β [13]. Clearly, these differences result from the (thermal) vibrational excitation of the attaching molecules. From FALP data, “activation energies,” E_a, for several dissociative attachment reactions have been obtained [8] by applying the Arrhenius formulation to the variation of β with temperature, T:

$$\beta = A \exp - E_a/kT \qquad (2)$$

Here, A is a preexponential factor that can sometimes be equated to $\beta_{\max}$ [8,14,15]. A summary of these and the other FALP attachment data is given in our review article [8].

Now some interesting question arise, especially when attempting to analyse the kinetics of electron attachment reactions occurring in electric discharges where T_e and T_g are invariably different. Two important questions are: (1) How do β for the reactions of specific molecules vary with T_e and T_g? (2) When branching into two ionic products can occur as, for example, in the dissociative attachment reactions of mixed halocarbons, how do the branching ratios vary with T_g and T_e?

We have investigated question (1) using the FALP apparatus by studying how β varies with T_g and T_e for the dissociative attachment reaction of $CHCl_3$ in which only Cl^- is an ionic product. This reaction proceeds via relatively inefficient dissociative attachment [14] and β increases rapidly with T $(= T_g)$. An activation energy, E_a, of 120 meV has been derived from these experiments [assuming Arrhenius behaviour according to Eq. (2)]. The increase of β with T_e for this reaction is seen to be much slower. The difference between the T and T_e variations occurs because as T increases the internal temperature of the attaching molecules increases, which promotes the dissociation of the nascent negative ion. However, when only T_e increases, the attaching molecule remains at a fixed (low) vibrational temperature prior to the electron molecule interaction. We have constructed a model to describe this attachment reaction that reconciles the T_e and the T data [14]. This model is based on the following premises: (a) The initial electron capture step proceeds with a rate coefficient $\beta_{\max}$ forming a nascent parent negative ion in a temporarily excited state. (b) This nascent parent ion lives long enough (at least several vibrational periods) for the additional kinetic energy of the captured electron, E_e $(= kT_e$ in the plasma in which electron attachment is occurring) to be randomised amongst the accessible vibrational energy states of the parent ion, thus increasing the vibrational temperature of the molecular ion, T_v. (c) The dissociation probability for the molecular ion is promoted by this increase in T_v. Hence, in accordance with the Arrhenius law, β for the reaction can be expressed as:

$$\beta = 5 \times 10^{-7}(300\ \mathrm{K}/T_e)^{1/2}\exp - E_b/kT_v\ \mathrm{cm}^3\ \mathrm{s}^{-1} \quad (3)$$

Here, E_b is again an activation energy, but in this case it is appropriate to a varying T_v (not T), k is the Boltzmann constant, and the s-wave capture rate coefficient [given by Eq. (1)] is used as the preexponential factor A [as indicated in Eq. (2)]. The FALP experimental data for $CHCl_3$ attachment agree well with the prediction of this model [14], thus indicating that the above assumptions made in constructing the model are valid for this attachment reaction. The procedure for calculating T_v is given in the original article [14]. Thus, using Eq. (3), the variations of β with T_e or E for different T_g can be predicted as is required in the modelling of gaseous discharges containing attaching molecules such as halocarbons.

Perhaps the most important success of the ideas involved in this model is the clarification of the apparent discrepancies in the SF_5^-/SF_6^- branching ratio for the SF_6 electron attachment reaction as determined in different experiments [3,6,16–18]. Thus, our study showed that the lifetime against unimolecular dissociation of the nascent excited negative ion $(SF_6^-)^*$ and its quenching rate in collisions with background atoms were of first order importance in determining the SF_5^-/SF_6^- branching ratio in relatively high pressure systems like the FALP experiment [19]. We return to the concept of dissociation lifetime to assist the interpretation of the results of the present experiments on the chlorobromomethanes.

We have begun to consider the more complex question (2) above by studying electron attachment to CCl_3Br [20]. It is important to summarise the findings of this study prior to presenting the results of the present experiments involving some other chlorobromomethanes. The CCl_3Br reaction is interesting because both Cl^- and Br^- are ionic products

$$CCl_3Br + e \rightarrow Br^- + CCl_3 + 0.4\ \mathrm{eV} \quad (4a)$$

$$\rightarrow Cl^- + CCl_2Br + 0.2\ \mathrm{eV} \quad (4b)$$

The overall attachment rate coefficients, β, and the branching ratios into the Cl^- and the Br^- product channels, $R = Cl^-/(Cl^- + Br^-)$, have been measured using our FALP apparatus as a function of T_g in the range 300–540 K, and at T_e, from T_g to 4000 K. These studies show that the overall β increases with

T_g for reaction (4) and thus an activation energy E_b of 55 meV for this reaction was derived using the model described above. The simultaneous increase of the overall β and R combine to produce a rapid increase with T_g of the partial rate coefficient for reaction (4b), indicating that there is a barrier to Cl^- production in this reaction. Similarly, the effective partial rate coefficient for Br^- production [reaction (4a)] reduces somewhat, roughly in accordance with the s-wave capture rate prediction [i.e. as $T_e^{-1/2}$; Eq. (1)] [20]. At both T_g values the overall β decreases with T_e somewhat slower than does $\beta_{\max}$, due to some vibrational heating by the incoming electron [20].

These studies also show that R approaches the simple statistical value of 3/4 at $T_g = 540$ K and that both Cl_2^- and $ClBr^-$ molecular ions were also observed at about the 2% level [20]. Clearly, at this attaching molecule temperature, the potential barrier to Cl^- production has been overcome. These FALP results are supported by crossed beam studies of the relative attachment cross sections for the production of Cl^- and Br^- in reaction (4) as a function of electron energy E in the range from near zero up to ~2 eV and at several T_g within the range 311–423 K [20].

The variation of R with T_e at the lower T_g of 300 K shows that an increase in T_e changes R from the strongly nonstatistical toward statistical, but even at the highest accessible T_e, R is only about 2/4 instead of the statistical value of 3/4. This again indicates that the heating of the $(CCl_3Br^-)^*$ temporary negative ion by the incoming (attaching) electron is not efficient enough at $T_e = 4000$ K and $T_g = 300$ K to effectively overcome the barrier for Cl^- production. This is most probably due to the short lifetime of the $(CCl_3Br^-)^*$ nascent negative ion that does not allow sufficient time for the additional (electron) energy to be dispersed around the ion before fast unimolecular dissociation to Br^- and CCl_3 occurs. Interestingly, the measured branching ratio, R, obtained as a function of T_g, could be used as an indicator of the true vibrational temperature, T_v (as governed by T_g and T_e) for this reaction [20]. This offers a possible diagnostic indicator of the conditions in gaseous discharges containing this molecule.

To compliment these data, we have carried out similar FALP studies of the dissociative attachment reactions of CCl_2Br_2, $CHCl_2Br$, and $CHClBr_2$ with electrons. The results of these studies are presented in this article after we have outlined the essential features of the FALP technique as used in this work.

2. The FALP technique

The FALP technique is used to study gas phase plasma reaction processes at and near thermal energies. It has been used extensively to study electron attachment [6,8] as well as positive ion–electron recombination [21] and positive ion–negative ion recombination [22]. Originally developed by Smith and colleagues [23], it is now also used in several other laboratories around the world [24,25]. In brief, a flowing afterglow plasma is created along the length of a metre-long flow tube by establishing a continuous microwave cavity discharge in the upstream region of a fast flowing carrier gas at a pressure of approximately 1 Torr. When the carrier gas is helium, the T_e in the afterglow quickly relaxes to the carrier gas temperature T_g due to the very large momentum transfer cross section for electron–helium atom collisions [26]. Under these conditions, the plasma is truly thermalised and $T_e = T_g$. A cylindrical Langmuir probe that can be located at any position along the axis of the plasma is used to measure the axial gradients of the electron number density, n_e, and T_e. Thus, by varying the temperature of the whole flow tube/carrier gas, plasma reaction processes can be studied over a range of true temperature T ($= T_e = T_g$) [8]. A downstream mass spectrometer sampling system identifies the positive and negative ions present in the afterglow plasma. Thus the ion products of reactions can be determined if care is taken to minimise the occurrence of secondary reactions [6].

By using argon carrier gas, plasma reaction processes can be studied at elevated (suprathermal) T_e as high as 5000 K [27]. This is possible because the deep Ramsauer minimum in the electron/argon atom momentum transfer cross section near an electron energy of about 0.3 eV [26] effectively limits the cooling rate

Table 1
Attachment rate coefficients measured in truly thermalised plasma ($T_e = T_g$) at two different T_g. β are the overall attachment rate coefficients. β_{Br} and β_{Cl} are the partial attachment rate coefficients for the reaction channels leading to Br^- and Cl^- product ions. The relative error of measurement is ±15%. Note that small fractions of dihalogen negative ions are also produced in these reactions, notably $ClBr^-$ in the $CHClBr_2$ reaction at 540 K. β_{max} is 5×10^{-7} cm^3 s^{-1} at 300 K and 3.7×10^{-7} cm^3 s^{-1} at 540 K [see Eq. (1) in the text]

	300 K			540 K		
$T_g = T_e$	β [cm^3 s^{-1}]	β_{Br} [cm^3 s^{-1}]	β_{Cl} [cm^3 s^{-1}]	β [cm^3 s^{-1}]	β_{Br} [cm^3 s^{-1}]	β_{Cl} [cm^3 s^{-1}]
$CHCl_2Br$	4.0×10^{-8}	3.7×10^{-8}	2.6×10^{-9}	1.2×10^{-7}	1.0×10^{-7}	1.8×10^{-8}
CCl_2Br_2	9.0×10^{-9}	8.0×10^{-9}	9.2×10^{-10}	4.5×10^{-8}	3.2×10^{-8}	1.1×10^{-8}
$CHClBr_2$	3.0×10^{-8}	2.8×10^{-8}	1.4×10^{-9}	4.9×10^{-8}	2.8×10^{-8}	1.3×10^{-8}

of the electron gas in the afterglow. However, T_e can be lowered by the addition of suitable amounts of helium to the afterglow plasma [27]. Thus, electron attachment reactions can be studied at various T_g and at elevated T_e within the range from T_g to 5000 K. Addition of controlled amounts of attaching gas to the plasma and the measurement of the axial gradients of n_e provides values of β. Note that the temperature of the attaching gas molecules prior to their interaction with electrons remains constant at T_g due to their multiple collisions with the carrier gas atoms. Details of this technique, the procedures used for the determination of T_e, and the analysis of the raw experimental data to obtain values of β as a function of T_e (and T_g) are given in our previous articles [8,27].

The n_e in the afterglow must be relatively low for attachment studies (n_e in the range 10^7–10^9 cm^{-3} is required, depending on the rate of the attachment reaction [6]). The upper limit to the initial n_e is imposed by the fact that it must be much less than the number density of the attaching molecules, n_m, to ensure that the attaching gas is not significantly depleted by electron attachment. Also, n_e must be small enough that recombination of electrons with positive ions does not occur [6].

3. Results and discussion

Attachment of electrons to $CHCl_2Br$, CCl_2Br_2, and $CHClBr_2$ has been studied at a fixed of T_g of 300 K and increasing T_e up to 5000 K, and at a fixed T_g of 540 K and increasing T_e up to 4000 K. The reduced range of T_e at the higher T_g is a consequence of the more rapid diffusive loss of plasma along the FALP flow tube at this higher carrier gas temperature. The kinetic data obtained under truly thermalised conditions (i.e. $T_g = T_e$) are presented in Table 1. In all three reactions, Br^- is the dominant product ion at all temperatures, but the fraction of Cl^- increases with increasing T_g, i.e. the product ion branching ratios $R = [Cl^-]/([Cl^-] + [Br^-])$, increase with T_g. Minor fractions of diatomic halogen negative ions are also observed as products. The variations of R with T_e are more varied and we attempt to explain these variations in terms of the ideas presented in Sec. 1. Similarly, the β values for all three reactions are greater at 540 K than at 300 K, but the variations of β with T_e are more varied and need to be explained. We now consider the kinetic data for each reaction separately before making some further general comments on the results of these studies.

3.1. $CHCl_2Br$

The measured β values at both T_g values over the accessible ranges of T_e are shown in Fig. 1(a) and the corresponding product ion percentages are shown in Fig. 1(b). The reaction proceeds thus:

$$CHCl_2Br + e \rightarrow Br^- + CHCl_2 \quad (5a)$$

$$\rightarrow Cl^- + CHClBr \quad (5b)$$

$$\rightarrow Cl_2^- + CHBr \quad (5c)$$

The overall β for the reaction increases by about three times as T_g increases from 300 K to 540 K, at which its

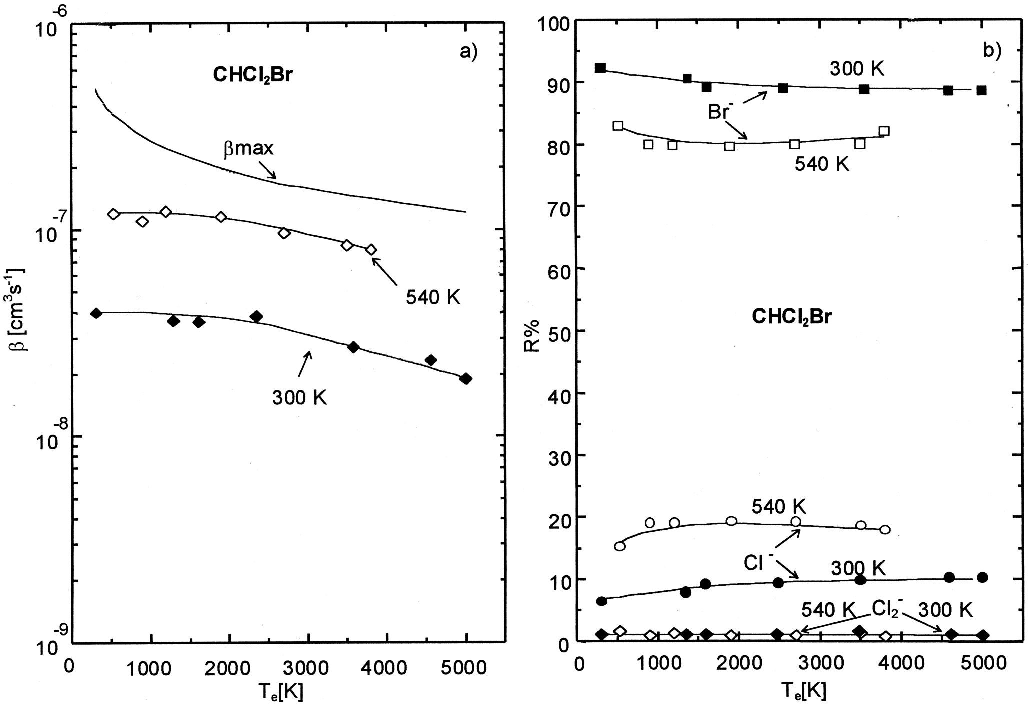

Fig. 1. (a) Overall rate coefficients, β, and (b) product ion distributions, R, for the attachment reaction of $CHCl_2Br$ as functions of the electron temperature, T_e, at the fixed attaching gas temperatures of 300 K and 540 K. Also indicated is the s-wave electron capture rate coefficient, β_{max}, as a function of T_e [see Eq. (1) in the text]. The small fractions of diatomic product ions, ~2%, are similar at the two T_g.

magnitude is approximately $0.3\beta_{max}$, as can be seen in Table 1 and Fig. 1(a). Following Eq. (2) and constructing a two-point Arrhenius plot, an activation energy E_a of 64 meV is indicated for the overall reaction (5) and the pre-exponential factor A is 4.7×10^{-7} cm^3 s^{-1}, i.e. closely equivalent to β_{max} at 300 K. These approximate results indicate that autodetachment from the nascent negative ion is not important. The major product ion is Br^- at all temperatures, but the fraction of Cl^- ions increases somewhat with increasing T_g and to a lesser extent with T_e. By combining the overall β and R values at each T_g, the partial rate coefficients for both reactions (5a) and (5b) can be obtained (see Table 1), noting that (5c) is only a very minor channel. Thus, from these partial rate coefficients at the two T_g, estimates can be obtained for the separate E_a for both Br^- and Cl^- production. The respective values are $E_a = 58$ meV, $A = 3.4 \times 10^{-7}$ cm^3 s^{-1} and $E_a = 114$ meV, $A = 2.1 \times 10^{-7}$ cm^3 s^{-1}. Clearly, the A value is acceptably close to β_{max}, especially when using the Arrhenius equation to describe the temperature variation of these partial rate coefficients. This procedure is often used, but is open to question.

The β values decrease with increasing T_e at both T_g by about a factor of 2 [see Fig. 1(a)]. This represents a slower decrease than that of β_{max}, which indicates that the decrease is not simply controlled by a decreasing capture efficiency by the attaching molecule as the electron energy increases [see Eq. (1)]. Rather, this indicates that the dissociation rate of the nascent negative ion increases somewhat as T_e increases and this, in turn indicates that partial vibrational heating of the ion by the incoming electron occurs. This deduction is supported by the fact that the branching into the ionic products [as indicated by R in Fig. 1(b)] changes only slowly, with T_e in common with the CCl_3Br reaction discussed in Sec. 1. This is most probably due to the short lifetime of the $(CHCl_2Br^-)^*$ nascent negative ion, which does not allow sufficient time for the additional (electron)

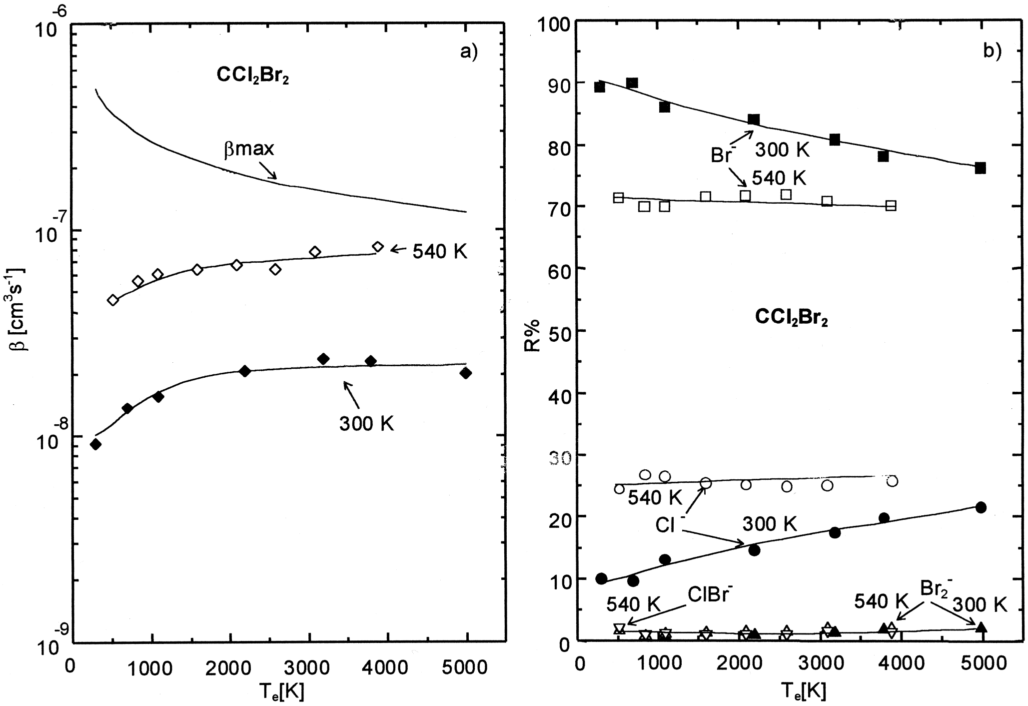

Fig. 2. (a) Overall rate coefficients, β, and (b) product ion distributions, R, for the attachment reaction of CCl_2Br_2 as functions of the electron temperature, T_e, at the fixed attaching gas temperatures of 300 K and 540 K. Also indicated is the s-wave electron capture rate coefficient, β_{max}, as a function of T_e [see Eq. (1) in the text]. There is little difference between the fractions of the molecular ions at the two T_g.

energy to be dispersed around the ion before fast unimolecular dissociation occurs. Unfortunately, detailed calculations based on our model outlined in Sec. 1 are not feasible without information on the molecular properties (bond strengths and frequencies).

A small but finite fraction of Cl_2^- ions were produced in this reaction at the T_g of 540 K (about 2% of the total ion products), with no change in this percentage being discernible with increasing T_e. Curiously, $ClBr^-$ ions are apparently not produced. Unfortunately, the thermochemical data needed to check the thermicities of these reactions are not available. Thus we cannot say if $ClBr^-$ production is endothermic in this reaction or if its absence is due to other constraints such as steric effects. Diatomic ions, including $ClBr^-$, were also produced in the attachment reactions of the other two chlorobromocarbons included in this study, these being especially obvious in the $CHClBr_2$, reaction discussed later. Diatomic halogen ion production in halocarbon attachment reactions has been observed previously [28]. For example, Br_2^- ions are a 15% product of the electron attachment reaction of CF_2Br_2 and Br_2^- ions are even produced in some 1,2 dibromoethane attachment reactions [28].

3.2. CCl_2Br_2

The measured β values at both T_g over the ranges of T_e are shown in Fig. 2(a) and the corresponding product ion percentages are shown in Fig. 2(b). The reaction proceeds thus:

$$CCl_2Br_2 + e \rightarrow Br^- + CCl_2Br \quad (6a)$$

$$\rightarrow Cl^- + CClBr_2 \quad (6b)$$

$$\rightarrow Br_2^- + CCl_2 \quad (6c)$$

$$\rightarrow ClBr^- + CClBr \quad (6d)$$

The overall β for the reaction increases by about five times as T_g increases from 300 K to 540 K at which its magnitude is only about $0.1\beta_{max}$, as can be seen in Table 1 and Fig. 2(a). The activation energy and the pre-exponential factor for the overall reaction (6) derived from these two data points are 96 meV and 3.7×10^{-7} cm^3 s^{-1}, respectively. The major product ion is Br^- at all temperatures, but the fraction of Cl^- ions clearly increases with increasing T_g and also with T_e at the lower T_g, as is clear in Fig. 2(b). Again, by combining the overall β and R values at each T_g, the partial rate coefficients for both reactions (6a) and (6b) can be obtained (Table 1), noting that (6c) and (6d) are both very minor channels. Thus, from these partial rate coefficients at the two T_g, estimates can be obtained for E_a for both Br^- and Cl^- production. The estimated values are $E_a = 82$ meV, $A = 2.0 \times 10^{-7}$ cm^3 s^{-1} and $E_a = 148$ meV, $A = 2.8 \times 10^{-7}$ cm^3 s^{-1}, respectively.

The β values increase significantly with increasing T_e at both values of T_g, which is obviously against the expected trend of a reducing electron capture rate with T_e, as manifest by the reduction of β_{max}, also shown in Fig. 1(a). At a T_g of 540 K and a T_e of 4000 K, β is about 0.5 β_{max} and so at these temperatures the reaction is very efficient. So autodetachment from the nascent $(CCl_2Br_2^-)^*$ ion cannot be very important and this is supported by the A values given above. We take these observations to mean that significant heating of the nascent negative ion occurs by the incoming electron, which in turn implies that the lifetime of the nascent negative ion is adequately long to allow energy dispersal around the ion before dissociation occurs. This hypothesis is given further credence by the fact that the production of Cl^- ions is promoted by increasing T_e, as can be seen in Fig. 2(b).

Both Br_2^- and $ClBr^-$ are minority ion products in this reaction at T_g of 540 K, which indicates that production of both these ions is exothermic or at least not greatly endothermic in this reaction. We can say no more without the aid of appropriate thermochemical data.

3.3. $CHClBr_2$

The measured β values at both T_g over the ranges of T_e are shown in Fig. 3(a) and the corresponding product ion percentages are shown in Fig. 3(b). The reaction proceeds thus:

$$CHClBr_2 + \rightarrow Br^- + CHClBr \quad (7a)$$

$$\rightarrow Cl^- + CHBr_2 \quad (7b)$$

$$\rightarrow CHBr^- + CHBr \quad (7c)$$

The overall β for the reaction increases by less than a factor of 2 as T_g increases from 300 K to 540 K at which its magnitude is approximately $0.1\beta_{max}$, as can be seen in Table 1 and Fig. 3(a). As before, the derived activation energy and the pre-exponential factor for the overall reaction (7) are $E_a = 29$ meV, $A = 9 \times 10^{-8}$ cm^3 s^{-1}. Again, the major product ion is Br^- at all temperatures, but the fraction of Cl^- ions markedly increases with increasing T_g and very little with T_e. By combining the overall β and R values at each T_g, the partial rate coefficients for both reactions (7a) and (7b) can be obtained and these are included in Table 1. Thus, estimates can be obtained for the activation energies and pre-exponential A factors for both Br^- and Cl^- production. These are $E_a = 0.3$ meV, $A = 2.8 \times 10^{-8}$ cm^3 s^{-1} and $E_a = 131$ meV, $A = 2.2 \times 10^{-7}$ cm^3 s^{-1}, respectively. On this evidence there is little or no barrier to the production of Br^- ions. In contrast to the previous two reactions, sufficient diatomic ions, $ClBr^-$, are produced [see Fig. 3(b)] to allow estimates of E_a and A for reaction (7c). The values obtained are $E_a = 155$ meV, $A = 2.5 \times 10^{-7}$ cm^3 s^{-1}. Production of this ion is unequivocally exothermic.

The β values decrease quite slowly with increasing T_e at both T_g, certainly much slower than does β_{max} [see Fig. 3(a)] and again we take this to mean that the incoming electron partially heats the short-lived $(CHClBr_2^-)^*$ nascent molecular and promotes dissociation. The branching ratios shown in Fig. 3(b) indicate that the loser in this process is Br^- production and the winners are Cl^- and $ClBr^-$ production. These data also suggest that the $ClBr^-$ production is entirely at the expense of the majority Br^- ions even though little or no activation energy is required for Br^- production. This therefore implies that Br^- production is as efficient as it can be. It therefore

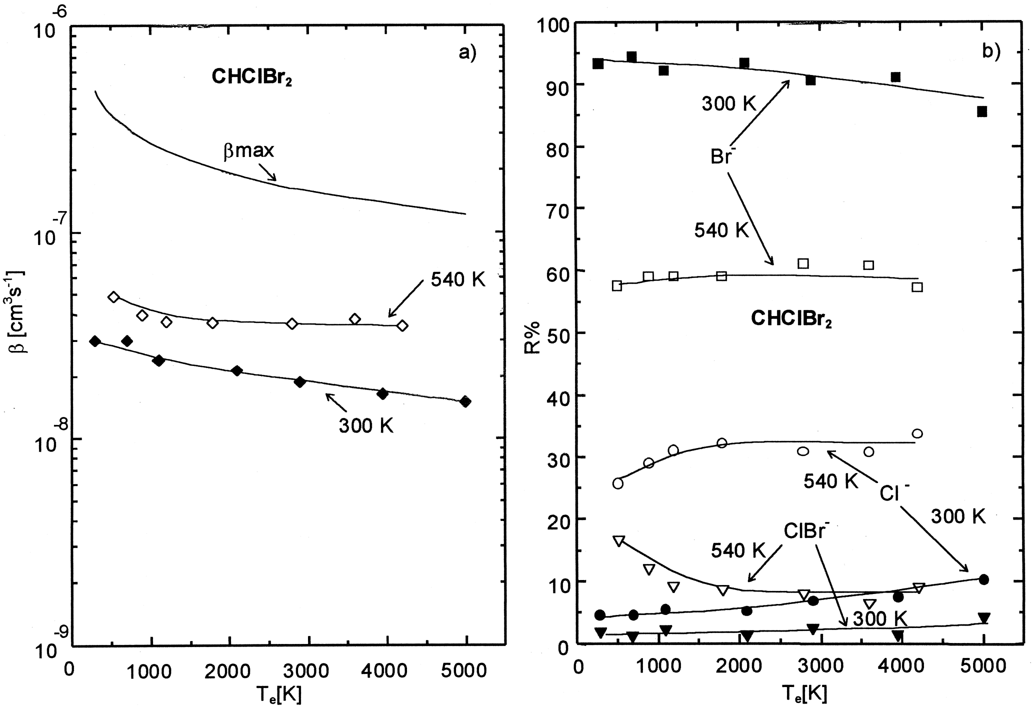

Fig. 3. (a) Overall rate coefficients, β, and (b) product ion distributions, R, for the attachment reaction of $CHClBr_2$ as functions of the electron temperature, T_e, at the fixed attaching gas temperatures of 300 K and 540 K. Also indicated is the s-wave electron capture rate coefficient, β_{max}, as a function of T_e [see Eq. (1) in the text]. Note the appreciable fraction of $ClBr^-$ product ions.

seems that the low β (low efficiency) for this reaction is largely due to the short lifetime against autodetachment of the nascent $(CHClBr_2^-)^*$ ions within the temperature range covered by the experiment. This premise is given some credence by the anomalously low value of A for the overall reaction of 9×10^{-8} cm^3 s^{-1} which falls well below β_{max} [see Fig. 3(a)].

4. Summary and concluding remarks

It is clear from these studies and previous similar studies that the rate coefficients and the product ion distributions for electron attachment reactions involving most halogenated alkanes are influenced significantly by the attaching gas temperature, T_g, and the electron temperature, T_e. It is equally clear that T_g has the dominant influence, at least in the thermal energy range and for moderate electron temperatures up to 5000 K. Such considerations are important when modeling negative ion production in “cool” plasmas such as the terrestrial atmosphere and some laboratory etchant plasmas. For these parallel T_g/T_e attachment studies, the FALP experiment is valuable, even though only limited T_g and T_e variations are possible.

In the T_g and T_e ranges covered by these experiments, the $CHCl_2Br$ and CCl_2Br_2 reactions apparently proceed initially by efficient electron capture, the rate of which decreases (as expected) as T_e increases. Then follows rapid dissociation along the appropriate reaction coordinate, the rates of which increase as the vibrational temperature of the nascent molecular ions increase as T_g and T_e increase. The major product ions are Br^- and Cl^-, the latter ion representing an increasing fraction of the products as T_g (and to a lesser extent T_e) increases, and diatomic halogen ions are minor products. The $CHClBr_2$ reaction is relatively inefficient even at a T_g of 540 K. This we attribute to the dominance of autodetachment, which renders the effective electron capture process inefficient. The major product is also Br^- in this reaction, but the molecular ion $ClBr^-$ is a 17% product at $T_g = T_e = 540$ K. It is worthy of note that even though there are clear differences in the overall rate coefficients for these three attachment reactions, the activation energies, E_a, for production of Cl^- ions are not very different, lying within the limited range 110–150 meV.

An interesting point to note is that as a result of different magnitudes of the activation energy barriers, the branching ratios for Cl^- and Br^- production in these dissociative attachment reactions depart from the respective simple statistical ratios. But, as more energy is provided to drive the dissociation reactions, either by the more efficient process of preheating the attaching molecules or by the less efficient molecular heating process resulting from the kinetic energy of the incoming electron, the branching ratios tend toward the statistical ratios.

To obtain greater insight into the nature of these attachment reactions it would be instructive if molecular beam studies were carried out similar to those for CCl_3Br [20]. Until then, our interpretation of the present FALP data must be open to debate.

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