Rate coefficients for the attachment reactions of electrons with c-C_7F_{14}, CH_3Br, CF_3Br, CH_2Br_2 and CH_3I determined between 200 and 600 K using the FALP technique

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Abstract. The rate coefficients, β, for the attachment reactions of electrons with c-C_7F_{14}, CH_3Br, CF_3Br, CH_2Br_2 and CH_3I have been determined under truly thermal conditions at temperatures in the range 200–600 K using the flowing afterglow/Langmuir probe technique. The β values (in units of $cm^3\,s^{-1}$) at 300 K are 6.8×10^{-8}, 6×10^{-12}, 1.6×10^{-8}, 9.3×10^{-8} and 1.2×10^{-7} respectively. The β for all of the reactions increase with temperature and approach the theoretical maximum value of β at high temperatures. From Arrhenius plots, activation energies for the reactions have been determined to be 40, 300, 80, 50 and 25 meV respectively. All of the reactions, except for that with c-C_7F_{14} (for which electron attachment is apparently non-dissociative), proceed by exoergic dissociative attachment producing halogen atomic negative ions. The data are compared with previous data where these are available.

1. Introduction

Electron attachment reactions have been studied for decades using a variety of techniques. Much of the early work has been reviewed in the books by Christophorou (1971) and by Massey (1976), and since their publication many research papers (see later) have reported measurements of attachment rate coefficients, henceforth designated by β in units of $cm^3\,s^{-1}$.

However, few studies of the temperature variation of β have been carried out especially under thermalised conditions (i.e. for equal electron and gas temperatures). In a very recent paper (Smith *et al* 1984), we reported measurements of β at several temperatures within the range 200–600 K for CCl_4, CCl_3F, CCl_2F_2, $CHCl_3$, Cl_2 and SF_6. These attachment reactions were studied in a thermalised flowing afterglow plasma medium using our flowing afterglow/Langmuir probe (FALP) apparatus. The values obtained at 300 K were in most cases in reasonable agreement with the previous values (see Smith *et al* 1984). From the temperature variation of β, we were able to estimate the activation energies, E_a, for some of the attachment reactions and again these are in reasonable agreement with previously reported values.

Subsequently, we improved our Langmuir probe technique and this now allows us to determine β values some two orders of magnitude smaller. In this paper, we report

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our measurements of β at several temperatures for c-C_7F_{14}, CH_3Br, CF_3Br, CH_2Br_2 and CH_3I. These reactions have not previously been studied as extensively as those for species included in our initial study (except for C_7F_{14}) and consequently the β values—even at 300 K—are not so well established. Both absolute values of β and the activation energies for the reactions were obtained in this study.

2. Experimental

A description of the FALP apparatus has been given in previous papers in relation to studies of ionic recombination (Smith and Church 1976, Smith and Adams 1983) and electronic recombination (Alge *et al* 1983). A full description of its application to the determination of attachment coefficients, including details of data analysis, is given in our recent paper (Smith *et al* 1984). Briefly, the attaching gas is introduced at a measured flow rate into a flowing afterglow plasma (carrier gas helium), and the change in the axial electron density gradient, $\partial n_e/\partial z$, in the plasma resulting from the loss of electrons to form negative ions is monitored using a Langmuir probe. Prior to the addition of the attaching gas, the only positive ions present in the plasma are He^+ and Ar^+ ions (the latter ions are formed when Ar is added to the plasma to remove metastable helium atoms) and then $\partial n_e/\partial z$ is due only to ambipolar diffusion. However when the attaching gas is added, then another unwanted electron loss process is possible because ion–molecule reactions can result in the conversion of the non-recombining He^+ and Ar^+ atomic ions to the rapidly recombining molecular ions (derived from the attaching gas). The large dissociative recombination coefficients for molecular ions may therefore contribute to the observed increase in $\partial n_e/\partial z$, thus resulting in erroneous β values. To avoid this potential problem, the experiments are carried out at the smallest values of n_e possible (the recombination loss rate is proportional to $n_e n_{m^+}$, where n_{m^+} is the density of the molecular positive ions, Smith *et al* 1984). For gases which have large β, this problem does not arise since only very small amounts of attaching gas are added to the plasma and thus there is an insignificant conversion of He^+ and Ar^+ ions to molecular ions.

The lower limit of β which can be measured is determined by the smallest n_e which can be accurately measured. Improvements to our Langmuir probe data acquisition technique have enabled us to measure n_e down to 10^7 cm^{-3} and thus to determine β values as small as about 10^{-11} cm^3 s^{-1} (note that in no way do these improvements in technique diminish the accuracy of our previous measurements of β for other molecules (Smith *et al* 1984)).

The rapidity of many of the attachment reactions included in this study required the introduction of very small flow rates of the attaching gases into the afterglow plasma and this required that the gases were diluted with helium to facilitate accurate measurement of flow rates. For the gases used in this study, the mixtures typically consisted of 1–2% of the attaching gas except for the CH_3Br which had to be introduced as the 'neat' vapour because of the relatively small β for this species. Mixtures of different relative concentrations were used to check for consistency in their preparation.

Measurements were carried out at 205, 300, 452 and 585 K (except for CH_3Br which could not be studied at 205 K because of its very small β at this temperature). We estimate that the derived values of β are accurate to ±15% at 205 and 300 K and to ±20% at 452 and 585 K (for details see our previous paper (Smith *et al* 1984)).

3. Results and discussion

3.1. General comments

The values of β obtained for $c\text{-}C_7F_{14}$, CH_3Br, CF_3Br, CH_2Br_2 and CH_3I in this study are given in table 1 together with some values previously obtained at 300 K by other workers. The values of β cover the wide range from 1.8×10^{-7}–6×10^{-12} cm^3 s^{-1} and a variation of β with temperature was apparent for all gases studied. Hence the data are also presented in the form of Arrhenius plots in figure 1 from which activation energies, E_a, for the attachment reactions can be obtained. These E_a are also given in table 1 together with previously obtained values. Also included in figure 1 is β_{max} ($\approx 5 \times 10^{-7}(300/T)^{1/2}$ cm^3 s^{-1}), the theoretical maximum value of β which is derived from the theoretical maximum cross section for the attachment process as formulated in terms of the electron de Broglie wavelength (Warman and Sauer 1971). Notice that all of the measured β are significantly smaller than β_{max} over the available temperature range and thus none of the gases used in this study are such efficient electron scavengers at thermal energies as SF_6 and CCl_4 (Smith *et al* 1984). A more sophisticated theoretical estimate for β_{max} has been given by Klots (1976) which takes into account the polarisability of the attaching molecule. Values of β_{max} so derived are somewhat smaller than those indicated by the simpler relationship for β_{max} given above.
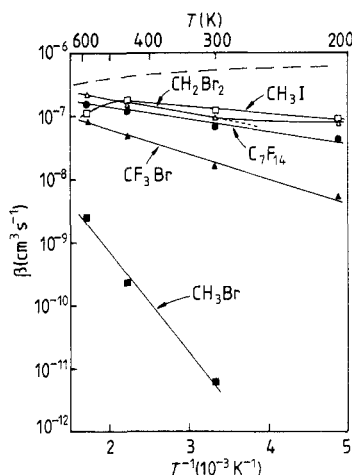
Figure 1. Arrhenius plots for the attachment reactions of electrons with the molecules indicated. The activation energies, E_a, derived from these plots are given in table 1. The broken curve represents $\beta_{max} = 5 \times 10^{-7}$ $(300/T)^{1/2}$ cm^3 s^{-1} (see text).

Below, we discuss briefly the β and E_a values obtained for each molecular species and compare them with the limited amount of previous data. That the E_a for these reactions are appreciable implies a sensitivity of β on temperature and as such the measured β can be used as an indicator of the experimental conditions (i.e. the electron (T_e) and gas (T_g) temperatures, mean electron energy, energy distribution etc).

Whilst the present FALP values of β were obtained under truly thermalised conditions, this is not the case for many of the other previous values given in table 1 (which ostensibly relate to 300 K), and we suggest that this in some cases explains the rather

Table 1. Electron attachment coefficients, β, and activation energies, E_a, obtained in the present FALP study at 205, 300, 452 and 585 K. The total estimated absolute errors in β are $\pm 15\%$ at 205 and 300 K and $\pm 20\%$ at 452 and 585 K (except for the very small β for CH_3Br at 300 K for which it is $\pm 50\%$). The E_a values are considered to be accurate to within $\pm 20\%$. Some values of β at 300 K and some E_a values obtained by other workers using the techniques indicated are also given.

Molecule	Electron attachment coefficient β ($cm^3\,s^{-1}$)						Activation energy (meV)	
	205 K	300 K	452 K	585 K		Previous values at 300 K	This work	Previous results
$c\text{-}C_7F_{14}$	0.45	0.68	1.3	1.6	$\times 10^{-7}$	$0.82^a, 0.98^b, 0.798^c,$ $0.52^d, 0.40^e, 0.56^f$	40	73^c
CF_3Br	0.53	1.6	4.9	7.7	$\times 10^{-8}$	1.36^g	80	
CH_2Br_2	0.81	0.93	1.6	2.2	$\times 10^{-7}$	0.32^g	50	52^k
CH_3Br	—	0.06	2.3	25	$\times 10^{-10}$	$33^g, 10^h, 0.07^i, 0.049^j,$ 0.036^d	300	247^k
CH_3I	0.85	1.2	1.8	1.1	$\times 10^{-7}$	0.25^g	25	26^k

[a] Asundi and Craggs (1964); total ion current.
[b] Mahan and Young (1966); microwave.
[c] Chen *et al* (1968); pulse sampling.
[d] Mothes *et al* (1972); ECR.
[e] Davis *et al* (1973); drift–dwell–drift.
[f] Christodoulides and Christophorou (1979); swarm.
[g] Blaunstein and Christophorou (1968); from analysis of data due to Lee (1963).
[h] Christodoulides and Christophorou (1971) at an electron energy of 0.05 eV; swarm.
[i] Bansal and Fessenden (1972); microwave.
[j] Bansal and Fessenden (1972); from analysis of data due to Wentworth *et al* (1969).
[k] Wentworth *et al* (1969); pulse sampling.

large differences in the β values obtained for some reactions. The reasonably good agreement between the E_a determined using the pulse technique of Wentworth *et al* (1969) and the FALP technique (see table 1) is a clear indication of the thermalised conditions in both experiments.

3.2. Comments on the individual reactions

3.2.1. $c\text{-}C_7F_{14}$. This is the cyclic compound perfluoromethylcyclohexane. We deal with this species first since it has been studied more extensively than the others in the present group (see table 1). It is also unique in the group in that the reaction proceeds via a three-body process in which, first the excited parent negative ion is formed, which then can either autoionise or be stabilised in collision with a helium bath gas atom (Mahan and Young 1966)

$$c\text{-}C_7F_{14} + e \longrightarrow (c\text{-}C_7F_{14}^-)^* \xrightarrow{\text{He}} c\text{-}C_7F_{14}^-.$$
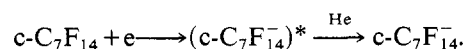
However, we are not able to definitely confirm that $C_7F_{14}^-$ was the only product ion since the large mass of this negative ion ($m/e = 350$ amu) was above the range accessible with our quadrupole mass filter. However we are able to state that no negative ion with m/e less than 300 amu was a reaction product. The β at 300 K for the reaction

is several times smaller than β_{max}, increasing towards β_{max} at the higher temperatures. Since the mean time for collisions of $(C_7F_{14})^*$ with helium atoms (about 10^{-7} s) is much shorter than the autoionisation lifetime (about 10^{-3} s; Naff *et al* 1968), then we feel justified in interpreting the increase in β with temperature in terms of an activation energy for the initial electron attachment step. Thus from the linear Arrhenius plot in figure 1, $E_a = 40$ meV ($\equiv 4$ kJ mol^{-1}). This is appreciably smaller than the value previously determined by Chen *et al* (1968), although it is not clear from their paper if the 73 meV given in table 1 actually refers to an activation energy in the normal (Arrhenius) sense. There is evidence from previous studies for an increasing β with increasing T_e (Davis *et al* 1973) and for an increasing cross section, σ, for electron attachment with increasing electron energy, E_e, reaching a peak near to $E_e \simeq 0.15$ eV (Mothes *et al* 1972). The earliest values of β at 300 K (see table 1) are grouped near to 8×10^{-8} cm^3 s^{-1} and more recent values are nearer to 5×10^{-8} cm^3 s^{-1}. The present value at 300 K is (tantalisingly!) between these at 6.8×10^{-8} cm^3 s^{-1}.

3.2.2. CH$_3$Br. This reaction, in common with the remaining reactions in the group, proceeds via exoergic dissociative electron attachment:

$$CH_3Br + e \rightarrow CH_3 + Br^- + 0.36 \text{ eV}$$
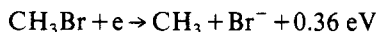
Br$^-$ was the only observed product ion at each temperature. A remarkable increase in β occurs between 300 and 585 K indicating a large E_a for the reaction. Our β at 300 K is subject to rather a large uncertainty ($\pm 50\%$) since it is close to threshold for our measurements. This inevitably places an appreciable error on the derived E_a (from figure 1) but nevertheless it is in reasonable agreement with that obtained by Wentworth *et al* (1969) (see table 1). Clearly, derived values of β for this reaction will be very sensitively dependent on departures from thermal equilibrum. Significantly, relatively large values were obtained from the non-thermal experiments ($> 10^{-9}$ cm^3 s^{-1}, see table 1) which were thought to relate to 300 K. However, the data obtained from thermal experiments including the present value, indicate a 300 K value of about 5×10^{-12} cm^3 s^{-1} i.e. some five orders of magnitude smaller than β_{max}. There is experimental evidence for a peak in σ at a small value of E_e (about 0.05–0.35 eV) and $T_g = 300$ K (Mothes *et al* 1972, Stockdale *et al* 1974). Detailed investigations of the variation of β and σ as a function of T_e, E_e and T_g are necessary to identify the critical parameters which determine the course of this interesting reaction.

3.2.3. CF$_3$Br. This reaction proceeds thus:

$$CF_3Br + e \rightarrow CF_3 + Br^- + 0.41 \text{ eV.}$$
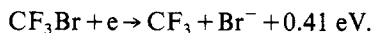
Again Br$^-$ is the only observed product at each temperature. This reaction also has an appreciable E_a causing β to increase by more than an order of magnitude for a temperature increase from 205 to 585 K. There are few previous data with which to compare our results. Spence and Schulz (1973) showed that the energy integrated cross section for the reaction did increase with increasing temperature of the CF$_3$Br molecules. Blaunstein and Christophorou (1968) re-interpreted the early data of Lee (1963) and showed that the mean σ decreases with increasing mean E_e, i.e. in the opposite sense to the change of β with temperature. They also derived a value for β at 300 K which is in good agreement with the present value (see table 1). Note the present data show that β quite rapidly approaches β_{max} as the temperature increases.

3.2.4. CH_2Br_2. This reaction proceeds thus:

$$CH_2Br_2 + e \rightarrow CH_2Br + Br^- + 0.65 \text{ eV}.$$

The reaction exhibits a small activation energy (see table 1). The E_a derived from our data (from the three highest temperature points) is within error in agreement with that due to Wentworth *et al* (1969). The 205 K point does not lie on the linear plot indicating that an Arrhenius plot is not appropriate over the complete temperature range. At the highest temperature, β has increased to within a factor of two of β_{max}. Spence and Schulz (1973) showed that the energy-integrated cross section for this reaction did not noticably change with increasing temperature of the CH_2Br_2 molecules and Blaunstein and Christophorou (1968), again from a re-interpretation of Lee's data, showed that the decrease in the mean σ with increasing E_e was much less rapid than for CF_3Br which is qualitatively consistent with the relative rates of change of β with temperature for the two species. However the derived value of β for CH_2Br_2 from Lee's data, is a factor of about three smaller than the present value and thus well outside the error limits of our measurements.

3.2.5. CH_3I. This reaction also proceeds by exoergic dissociative attachment

$$CH_3I + e \rightarrow CH_3 + I^- + 0.61 \text{ eV}$$
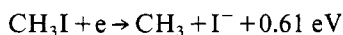
in this case I^- being the only observed product ion over the accessible temperature range. However, in this reaction, although our data indicate an increasing β between 200 and 452 K, the value at 585 K is smaller than at 452 K (the relative error in β is less than the $\pm 20\%$ appropriate to each absolute value). Of course, β must begin to decrease at some temperature; the observed decrease is only mildly surprising since β at the peak is within about a factor of two of β_{max}. The Arrhenius plot for the three lowest temperature data points indicates a small E_a which is in good agreement with that obtained by Wentworth *et al* (1969). The β derived by Blaunstein and Christophorou (1968) from Lee's data, ostensibly referring to 300 K, is several times smaller than the present value. The cross sections for this reaction have been investigated by Spence and Schulz (1973) and by Stockdale *et al* (1974).

4. Conclusions

The rate coefficients, β, for each of the attachment reactions included in this study are controlled by the presence of an activation energy barrier as is manifest by the increasing β values with increasing temperature. In the case of dissociative attachment, this is generally understood to occur as a result of the internal excitation of the reactant molecules—either thermally in collisions with the helium carrier-gas atoms or via electron collisional excitation—to a state which is crossed by a repulsive atomic negative ion/neutral radical potential curve (e.g. see Wentworth *et al* 1969). The c-C_7F_{14} reaction occurs via a three-body process in which an excited parent negative ion is formed and is stabilised in a collision with a helium atom. Nevertheless, the β for this reaction also increases with temperature in a similar manner to the other (dissociative) attachment reactions.

Where other truly thermal values of β are available, these and the derived E_a values are in good agreement with the present FALP data. However discrepancies are evident

between the thermal data and those obtained using non-thermal techniques, highlighting the differences between electron temperature, molecule temperature and electron energy in influencing the rate of electron attachment. Detailed studies of specific attachment reactions are required at several fixed molecule temperatures for varying electron energies in order to better understand the detailed mechanisms of this type of reaction.

Acknowledgment

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