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Temperature dependence of low-energy electron attachment to $CHCl_3$

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Abstract

Dependence of the rate constants for electron attachment to $CHCl_3$ on mean electron energy from thermal to ~2 eV has been investigated at ambient temperatures between 300 and 600 K. The rate constant at thermal energy increases dramatically with temperature with an activation energy of 0.13 ± 0.01 eV, which is obtained by the Arrhenius plot of the present rate constants, while those at higher mean electron energies increase moderately with temperature. The attachment cross sections obtained by unfolding the rate constants show two peaks at 0 and 0.3 eV at 300 K, but only the zero-energy peak increases dramatically with temperature. The importance of vibrationally excited states in the deformation mode of $CHCl_3$ has been proposed to interpret the cross sections observed at 600 K. (Int J Mass Spectrom 205 (2001) 285–291) © 2001 Elsevier Science B.V.

Keywords: Electron attachment; Rate constant; Cross section

1. Introduction

A number of studies have demonstrated a pronounced effect of temperature on the electron attachment to molecules [1–5]. Recent studies [6–8] have revealed that the rate constants for dissociative attachment to some alkyl halides increase dramatically with ambient temperature in spite of the fact that the rate constants at room temperature decrease with the increase in the mean electron energy. Obviously, the elevation of buffer gas temperature and the increase of only mean electron energy in buffer gas at room temperature result in different effects on the electron attachment processes [9–11]. Vibrationally excited states may play an important role in the enhancement of the attachment rates with gas temperature. For an electron-attaching molecule in its ground vibrational state, a captured electron promotes the molecule to a negative ion state by a vertical transition. Thus the electron-energy dependence of the attachment cross section reflects the negative ion state in the Franck-Condon region. At elevated temperature from 300 to 600 K, the percentage of molecules in the vibrationally excited state increases ~20% in $CHCl_3$. Then for these molecules, the electron attachment occurs from these excited vibrational states. When the relevant molecule is oxygen, the change in the cross sections with temperature for the dissociative electron attachment can be understood from the change in the probability of the transition from vibrationally excited states to the upper repulsive negative ion state [2,3,12]. For a polyatomic molecule, however, it is not warranted that the potential energy curves can be

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

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approximated by a diatomic one, and we cannot make a straightforward predictable magnitude of the attachment cross sections at elevated temperature. The validity of the diatomic approximation for the dissociative attachment to polyatomic molecules has been demonstrated in some brominated hydrocarbons [13,14], and a similar interpretation has been a well accepted [15,16], but not proven, picture for the dissociative attachment to molecules. So far, however, no explicit attempt of the application of a nondiatomic picture has been made to interpret the attachment process except for N_2O [17] and some polyatomic molecules of which negative ions decompose into various fragments [18]. This is mainly because of the lack of the experimental results that necessitate the introduction of other interpretations for the initial attachment mechanism.

This study has focused on the electron attachment to $CHCl_3$, and the rate constants as a function of the mean electron energy at several gas temperatures between 300 and 600 K have been measured using the pulse-radiolysis microwave-cavity technique combined with microwave heating [7,8]. At room temperature, this molecule is known to undergo dissociative attachment for low-energy electrons, forming Cl^- ion [10,18,19]

$$e^- + CHCl_3 \rightarrow CHCl_2 + Cl^-, \tag{1}$$

with the maximum rate constant at the mean electron energy of ~0.3 eV [8]. The elevation of temperature leads to rapid increase in the rate constant [20], though at a temperature higher than 300 K, the dependence of the rate constants on the mean electron energy has not been known. Separate observation of the effects of gas temperature and the change in the mean electron energy may be important in deciding whether or not the diatomic approximation is truly effective in this case. The data obtained at each gas temperature have been converted to cross sections as a function of electron energy, and the effect of temperature on the initial electron attachment has been discussed.

2. Experiment

The gas sample in a quartz cell placed inside a cylindrical microwave resonant cavity was irradiated by a 3-nsec X-ray pulse from a Febetron 706. An X-band microwave circuit having a frequency-discriminator unit with a balanced mixer was used for the detection of the microwave conductivity signal, which is proportional to the electron concentration. The signal was stored in a digital oscilloscope and transferred to a microcomputer for analysis. Electron temperature was varied by passing high-power microwaves from a Klystron (V-58) through the cavity. The outgoing power was monitored with a power meter directly at the outlet portion of the cavity. This circuit is similar to that used in previous studies of electron-energy dependence of electron attachment processes [7,8], but the cavity portion has been modified to enable variation of ambient temperature. The cavity operates with two-way modes, TE_{111} for electron heating and TE_{010} for detection of electron density, with the Q value of ~3000. The quartz cell was of crossed shape, tapered at both longitudinal ends to minimize the distortion of the high-power microwaves. One turn of platinum paste was plated on the outer surface of the cell perpendicular to the longitudinal axis of the cavity. Because of the heating with only one turn of the paste, some temperature gradient could be expected over the volume of the cell. Thus, to ensure the irradiation on the gas sample with less temperature gradient, the irradiation portion was confined, using lead for shielding, to a narrow area close to the center position of the cell. The elevation of temperature was made by applying the voltage to the paste up to 15 V, which allows variation of temperature between 300 and 600 K. The temperature of the sample was calibrated by a thermocouple inserted into the inside of the cell with the sample gas. The temperature variation with the position of the cell was ±2 K over the volume of the irradiation portion.

The gas handling system was of usual glass-type vacuum line and Ace-Teflon stopcocks with O rings for vacuum sealing were used. The gas pressures were measured with Baratron capacitance manometers. Xe (>99.999%, Teisan) was used as received. $CHCl_3$ (Takachiho Shoji) was used after degassing by freeze–pump–thaw cycles at 77 K.

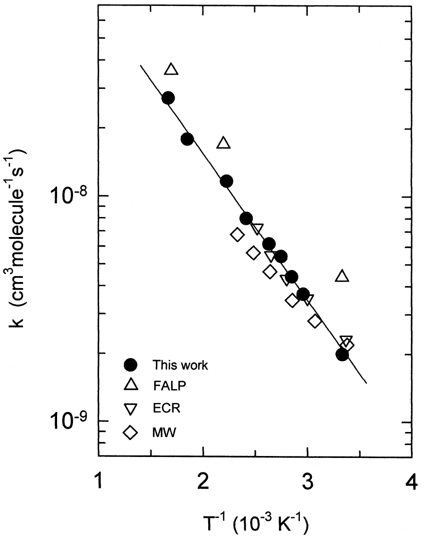

Fig. 1. Arrhenius plots of the rate constants for electron attachment to $CHCl_3$. The present results are shown as closed circles. Other data are found using the flowing afterglow Langmuir probe (FALP) method [20], the electron cyclotron resonance (ECR) [22], and the pulse radiolysis microwave cavity technique (MW) [21].

3. Results and discussion

For measurements, a trace amount of $CHCl_3$ (lower than 10^{-4} Torr) was added to 70 Torr of Xe, and the lifetime was measured for the first-order decay of electrons caused by an attachment reaction at different ambient temperatures from 300 to 600 K. The attachment rate constant (k_a) was obtained from the lifetime τ by a relationship $k_a = 1/(\tau[CHCl_3])$. Variation of the heating power allows determination of the rate constant as a function of the mean electron energy. The mean electron energies attained by applying heating microwaves to electrons in Xe have been obtained by a known relationship described in the previous paper [8].

As for the temperature dependence, the attachment rate constant for thermalized electron is observed to increase with increasing temperature. This is in agreement with a number of other studies, as illustrated in Fig. 1, which shows an Arrhenius plot of rate constants, where the values reported by other studies [20–22] are also included. The present results are in good agreement with those obtained by the electron cyclotron resonance (ECR) method [22] but are clearly lower than those obtained by the flowing afterglow-Langmuir probe (FALP) method [20]. At high gas temperature, the present values are slightly higher than those of the values of the microwave (MW) technique [21]. The errors in the present values of k are estimated to be ~10%. The slope of the straight line gives the activation energy of 0.13 ± 0.01 eV. The present activation energy can be compared to 0.10 [21,22], 0.11 [10], and 0.12 eV [20], reported previously.

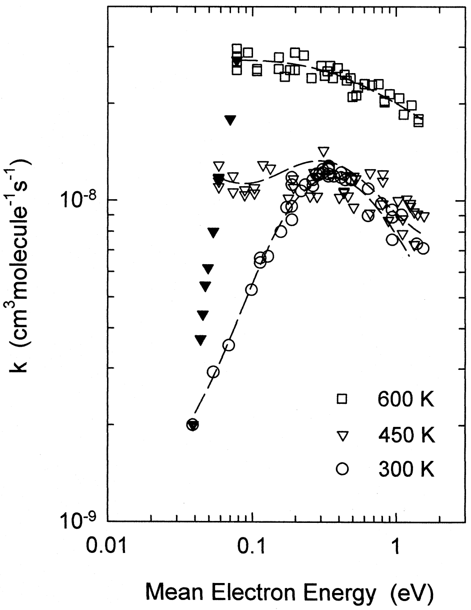

Fig. 2. Rate constants for electron attachment to $CHCl_3$ as a function of the mean electron energy at different ambient temperature. The mean electron energy is used in the form of $\langle\epsilon\rangle = (3/2)kT_g + E_{MW}$, where E_{MW} is the mean electron energy gained by microwave heating power and T_g is the gas temperature. The closed triangles are obtained from the values of this work in Fig. 1, using $\langle\epsilon\rangle = (3/2)kT_g$. The long dashed lines are used to make the unfolding procedure to obtain the cross sections; see text.

The mean electron energy dependence of the rate constants at 450 and 600 K obtained in the present experiment, along with our previous 300 K data [8], are shown in Fig. 2 (open symbols). Also included in Fig. 2 are the present values in Fig. 1 converted to the rate constants as a function of mean electron energy using $\langle\epsilon\rangle = (3/2)kT_g$, where T_g is the gas temperature (closed triangles). The mean electron energy is

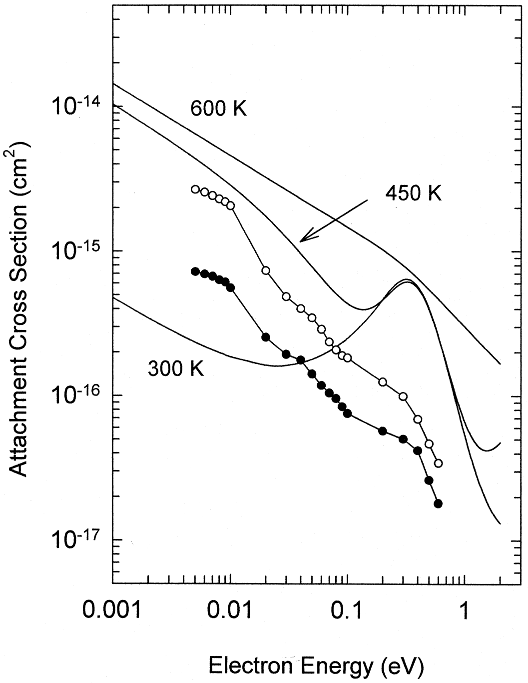

Fig. 3. Cross sections for electron attachment to $CHCl_3$ as a function of the electron energy at different ambient temperatures, derived by unfolding the rate constant data shown in Fig. 2. ●, [10] at 310 K; ○, [10] at 436 K.

used in the form of $\langle \epsilon \rangle = (3/2)kT_g + E_{MW}$, where E_{MW} is the mean electron energy gain from microwave heating power, calculated from the equation described in reference [8]. The E_{MW} for closed triangle data is equal to zero. It is seen that with the elevation of gas temperature, the rate constants in the low-energy region increase dramatically, while those at higher electron energies increase moderately. Furthermore, a peak observed at 0.3 eV at 300 K cannot be seen at 600 K.

Using an unfolding procedure [23,24], the rate constant data as shown in the long dashed lines in Fig. 2 have been converted to the attachment cross sections as a function of the electron energy at each temperature, shown in Fig. 3. In the unfolding procedure for the rate constants at elevated temperatures, the Maxwellian distribution function for the electron energy ϵ was used in the form of $f\ (\langle \epsilon \rangle,\ \epsilon) = 2\pi^{-1/2}(2\langle \epsilon \rangle/3)^{-3/2}\ \epsilon^{1/2}\ \exp(-3\epsilon/2\langle \epsilon \rangle)$. The cross sections at 300 K show a peak at 0.3 eV, which seems to remain at the same electron energy even at higher temperature, but another peak at zero eV becomes dominant with increasing temperature. This suggests that there are at least two different pathways for formation of negative ions, the one not affected much by elevation of temperature and the other showing a dramatic increase in the cross sections at higher temperature. At room temperature, the electron impact measurements have shown that the cross sections of electron attachment to $CHCl_3$ have double peaks at zero and at ~0.3 eV [10,19]. The peak at ~0.3 eV corresponds to the Cl^- formation [10,25] and, at zero eV, also corresponds to the Cl^- production [10], with the exothermicity of 0.2 eV. The present cross sections at room temperature are in good agreement with these previous data. The cross sections region between 310 and 436 K have been obtained by high-resolution crossed-beam technique [10].

The potential-energy curves for the neutral $CHCl_3$ molecule and the negative ion $CHCl_3^-$ are shown in Fig. 4, right. The potential curve for the negative ion $CHCl_3^-$ can be drawn using a reflection method [14,26]. This is based on the assumption that, at room temperature, the neutral molecule is predominantly in the ground vibrational level and that the potential curve of the negative ion is repulsive in the Franck-Condon region. The state density of the ground vibrational level is assumed to be the square of the wave function of a harmonic oscillator. Using this negative ion potential curve, we can deduce the attachment cross sections at 600 K, taking into account the excited vibrational level ($v = 1$) for the symmetric stretching mode (see below), with the energy spacing of 0.083 eV [27]. The resulting cross sections are shown in Fig. 4, left. It is apparent that the calculated cross sections have a peak still at ~0.3 eV with slightly lower peak value. This is in accord with the present experimental cross sections at 0.3 eV but, evidently, disagrees with the cross sections showing a maximum at ~0 eV. As an alternative estimation of the negative ion potential for the diatomiclike system, Wentworth et al. [28–30] proposed a semiempirical equation with a modification of the Morse potential, employing either the experimental activa-

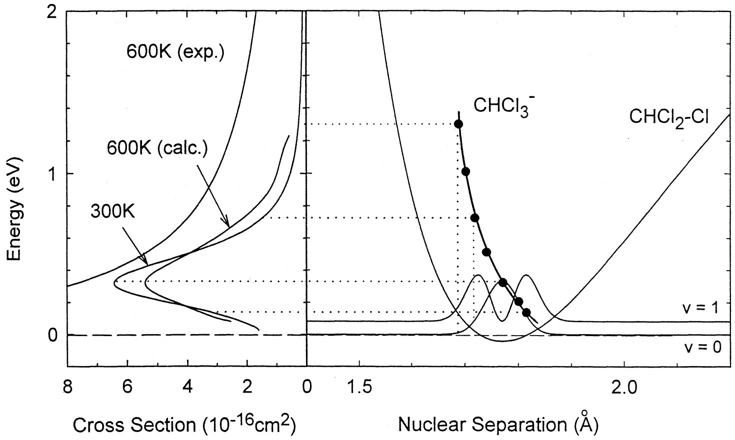

Fig. 4. Left: the cross section's electron attachment to $CHCl_3$. Right: the potential curve with diatomic approximation for the neutral $CHCl_3$ molecule drawn as a function of the C–Cl bond length using a Morse function [31] with the equilibrium internuclear distance of 1.77 Å and the dissociation energy of 3.51 eV [32] and the potential curve for the negative ion $CHCl_3^-$ drawn using a reflection method [14,26]. The probability distribution function for the vibrationally ground ($v = 0$) and excited ($v = 1$) states are derived using the wave functions for the harmonic oscillator. The curve for the negative ion (●●●) is drawn by reflecting the probability distribution function on the experimental cross sections at 300 K. The calculated cross sections at 600 K are obtained by re-reflecting the probability distribution function on the curve for the negative ion.

tion energy or the observed vertical attachment energy. It can be easily shown that the use of the activation energy 0.13 eV gives the maximum attachment cross section at 300 K at the electron energies of 0.8 eV, which are far above the present experimental result (0.3 eV), and that the fitting of the vertical attachment energy to 0.3 eV gives zero activation energy with the maximum cross section at zero electron energy, which is also in disagreement with the present data. From these considerations, we may conclude that the diatomic molecule approximation for the negative ion state is not appropriate for the zero-energy peak, supports the suggestion that it is from a different origin.

Generally, it is known that varying gas temperature the vibrational excitation of some neutral molecules give major change on the electron attachment to this molecule [1–5]. It should be noted that the situation much resembles the temperature dependence of the cross sections for dissociative attachment to N_2O, for which a dramatic increase in the cross sections at low electron energies with increasing temperature has been observed [17]. The N_2O molecule is known to undergo dissociative attachment at 2.2 eV, forming $N_2 + O^-$, and the cross sections for this process are not much dependent on temperature. The dramatic dependence on temperature in the low-energy resonance has been interpreted by a pronounced increase of attachment to bend N_2O molecule with increasing temperature. As opposed to the linear N_2O molecule, for which the resonance energy of the attachment is rather high, in the bend N_2O molecule, the potential energy curve of the negative ion crosses at a position close to the minimum of the neutral curve, and therefore, very low energy electrons can attach to N_2O and the cross sections become large because of an increase in the survival probability of the transient negative ion. Next, we consider the vibrational excitation of $CHCl_3$. $CHCl_3$ is more complex than the triatomic N_2O molecule. On the basis of the IR (Raman) data [27], the $CHCl_3$ molecule possesses fundamental vibrational modes associated with CCl_3 deformation (the vibrational energy of 0.032 and 0.045 eV, e and $a1$ symmetry, respectively) and C–Cl stretching (0.083 and 0.094 eV for $a1$ and e, respectively). The excitation of the deformation modes is more effective than that of the C–Cl stretching by elevation of temperature. Thus, we suggest that the peak of the cross sections at 0.3 eV corresponds to the electron attachment to the local C–Cl stretching mode

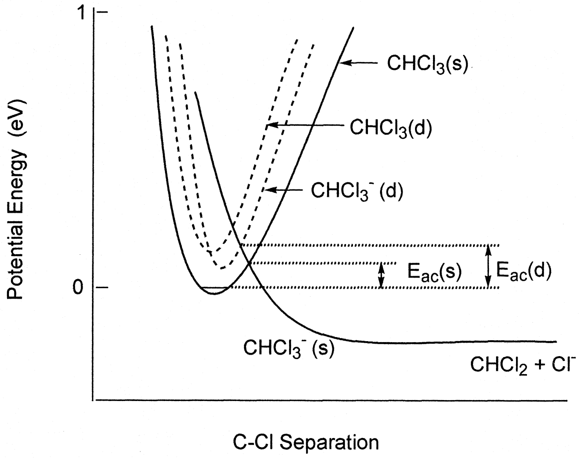

Fig. 5. Schematic representation of the potential energy curves for $CHCl_3$ and $CHCl_3^-$ as a function of the C–Cl separation. (s) denotes ordinary ground state molecule, and (d) corresponds to a vibrationally excited state in the deformation mode. The relative position of $CHCl_3$(d) relative to the ground state $CHCl_3$(s) and that of $CHCl_3^-$(d) relative to $CHCl_3$(d) are arbitrary, but the crossing point between $CHCl_3^-$(d) and $CHCl_3^-$(s) should be higher than that between $CHCl_3$(s) and $CHCl_3^-$(s) so that the activation energies are in a relation that $E_{ac}(d) > E_{ac}(s)$.

of $CHCl_3$, while that at 0 eV is related to the CCl_3 deformation modes. These are understandable with reference to Fig. 5, in which the potential energy curves of the neutral $CHCl_3$ and the negative ion $CHCl_3^-$ are shown as a function of C–Cl separation. In the figure, the curves of $CHCl_3$(s) and $CHCl_3^-$(s) represent the corresponding potential energies along the C–Cl dissociation coordinate, and those energies of $CHCl_3$(d) and $CHCl_3^-$(d) are shown schematically as a function of one of three-C–Cl-bond separation, where the attached electron may be delocalized over the three C–Cl bonds. The transition from $CHCl_3$(d) to $CHCl_3^-$(d) may have the threshold at zero electron energy, and the subsequent transition to the $CHCl_3^-$(s) curve leads to its dissociation into $CHCl_2$ and Cl^-. The energy E_{ac}(d) may correspond to the experimentally observed activation energy of ~0.13 eV, which can be higher than the energy E_{ac}(s) as the activation energy for direct attachment to a C–Cl bond in the stretching mode, which is estimated to be ~0.07 eV from the potential energy curves shown in Fig. 4b. We, thus, suggest that the lower activation energy cannot be observed experimentally because the attachment to the deformation mode possessing the high activation energy dominates at elevated temperature. Apparently, consideration of different vibrational modes in the initial attachment may be important in the interpretation of electron attachment to polyatomic molecules.

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