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Rate constants of electron attachment to chlorobenzenes measured by atmospheric pressure nitrogen corona discharge electron attachment ion mobility spectrometry

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ABSTRACT

Using atmospheric pressure nitrogen corona discharge electron attachment ion mobility spectrometry (APNCD-EA-IMS), the rate constants of electron attachment to 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene and α,α,α-trichlorotoluene have been determined at ambient temperature as a function of the average electron energy in the range from 0.35 to 0.65 eV based on the experimental measurements of the negative ion mobility spectra. The rate constants are in the order of magnitude of $\sim 10^{-9}$ cm^3 molecule^{-1} s^{-1}. The ability of the dichlorobenzene isomers to capture the electrons has been found to decrease following the order of 1,2-chlorobenzene, 1,3-chlorobenzene and 1,4-chlorobenzene, which is different from previously reported results in the literature. For electron attachment to 1,2,4-trichlorobenzene and α,α,α-trichlorotoluene, the experimental measurements show that α,α,α-trichlorotoluene has a higher rate constant than 1,2,4-trichlorobenzene.

1. Introduction

Electron attachment to chlorine-containing molecules is a very effective reaction and often responsible for the negative ion formation in a variety of processes such as electric discharge, plasma reactions and gas lasers [1–3]. The rate constant of electron attachment can be measured by well-developed techniques including high-Rydberg collision ionization, rare-gas photoionization, crossed-beams and beam gas, flowing-afterglow Langmuir-probe, Cavalleri electron density sampling, and electron swarm [4–7]. In addition, ion mobility spectrometry (IMS) or ion mobility spectrometry coupled with mass spectrometry (IMS-MS) has been employed to measure the rate constant of electron attachment reactions. The conventional experimental procedure is to monitor the signal intensity of ions or electrons at different number densities of attachment gas, and the rate constant can be extracted from the plot of the intensity of ions or electrons as a function of the number density of attachment gas [8–10]. Recently, Tabrizchi et al. [11] developed a technique to determine the rate constant for electron attachment reaction by the so-called negative ion mobility spectrometry. This technique essentially is one kind of electron attachment ion mobility spectrometry. The thermal electrons are produced at atmospheric pressure by a corona discharge in pure nitrogen gas. When the ion shutter on the IMS apparatus opens, the electron packet will rapidly travel through nitrogen buffer gas in the drift region. If a reagent gas is added to the drift region, due to electron attachment reactions, the negative ions can be generated on the path of the electrons, thus a special spatial distribution of ions will be formed in the drift region. As a result, in the ion mobility spectrum, a negative ion intensity evolution with the drift time can be observed from which the rate constant information can be conveniently extracted using only the single concentration of the attachment gas. This method has been successfully applied to the rate constants measurement of electron attachment to chlorinated methane CCl_4, $CHCl_3$, and CH_2Cl_2 [11].

For electron attachment to chlorobenzenes, early in 1966 the dissociative electron attachment to benzene derivatives including three dichlorobenzene isomers was studied by the swarm-beam method [12]. The rate constants were reported to increase following the order of 1,4-, 1,2-, and 1,3-$C_6H_4Cl_2$ over the mean electron energy 0.14–0.35 eV. Recently, dissociative electron attachment to these dichlorobenzene isomers was investigated in the electron energy range from 0 to 2 eV and in the gas temperature range from 391 to 696 K using a crossed electron–molecular beam apparatus [13]. The temperature experiments demonstrated that the Cl^- ion peak at close to zero electron energy has an activation energy of

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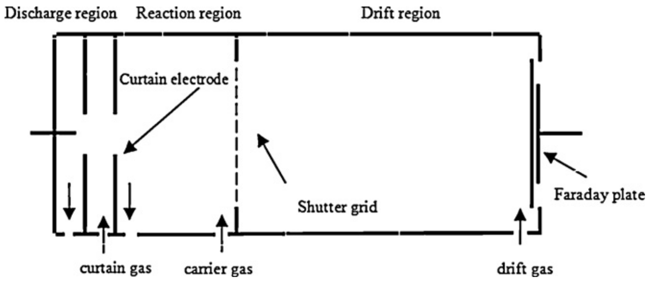

Fig. 1. Schematic diagram of the atmospheric pressure nitrogen corona discharge electron attachment ion mobility spectrometer (APNCD-EA-IMS).

482 meV for 1,2-$C_6H_4Cl_2$ and 59 meV for 1,4-$C_6H_4Cl_2$. The experiments also show that, at ambient temperature, the Cl^- ion yields exhibit peaks only at 0.49, 0.39, and 0.32 eV for 1,2-, 1,3- and 1,4-$C_6H_4Cl_2$, respectively. However, there are no rate constants to be reported in the crossed-beam experiment.

In the present work, electron attachment to chlorobenzenes was investigated by using an atmospheric pressure electron attachment ion mobility spectrometer with nitrogen corona discharge as electron source. First, electron attachment to CH_2Cl_2 was studied so as to check the validity of the experimental measurement procedure. Subsequently the rate constants of electron attachment to 1,2-$C_6H_4Cl_2$, 1,3-$C_6H_4Cl_2$, 1,4-$C_6H_4Cl_2$, 1,2,4-$C_6H_3Cl_3$ and α,α,α-$C_6H_5CCl_3$ were determined in an electron energy range from 0.35 to 0.65 eV. In the case of 1,3-$C_6H_4Cl_2$ there exists a discrepancy between the present experimental value and that reported in the literature. We will discuss the difference in the rate constants for electron attachment to dichlorobenzene isomers or trichlorobenzene derivatives.

2. Experimental

The electron attachment experiments were accomplished on an atmospheric pressure nitrogen corona discharge electron attachment ion mobility spectrometer (APNCD-EA-IMS), which had been constructed at Hefei laboratory. Its design is basically identical to that reported by Tabrizchi et al. [11,14]. Fig. 1 is a schematic drawing of the apparatus. The drift tube has a total length of 17 cm and the internal diameter of 4 cm. Thermal electrons were generated by negative corona discharge through nitrogen gas at atmospheric pressure. The discharge electrodes are in the geometry of point to plate and the corona discharge voltage is around 3 kV. There is a curtain electrode mounted in parallel to the discharge plate electrode so as to form an 8 mm wide space, where flowing curtain gas like nitrogen can prevent the attachment gas from diffusing into the discharge region to quench the discharge. The voltage supplied between the discharge and the curtain electrodes drags the electrons formed in the discharge area into the reaction region. The reaction and drift regions consist of metal ring electrodes and insulating Teflon spacers. The high voltage through an electric resistance network on the metal rings generates a weak homogeneous electric field along the central axis of the drift tube. In order to examine the rate constants of electron attachment at different electron energies, the electric field in the drift region can be varied in the range of 260–500 V cm^{-1}, which corresponds to an average electron energy from 0.35 to 0.65 eV. Electric fields outside the range between 260 and 500 V cm^{-1} were not adopted, because the lower electric fields produce too weak ion signal and the higher fields may induce a destructive spark. An ion shutter of the Bradbury–Nielson type was used and in the present experiment its open time was 200 μs. The ions collected on the Faraday plate were measured by a current amplifier (Keithley 428) which was interfaced to a computer data processing system.

In general, electron attachment to chlorobenzene molecules M proceeds via the dissociative electron attachment process (1).

$$e + M \xrightarrow{k} Cl^- + (M\text{–}Cl) \tag{1}$$

If the number density of attachment gas $[M]$ is far larger than that of electrons $[e]$, the reaction (1) will obey the pseudo-first-order approximation. The electron density $[e]_t$ can be expressed as Eq. (2).

$$[e]_t = [e]_0 \exp(-k[M]t) \tag{2}$$

where $[e]_0$ is the initial electron density. After differentiation, Eq. (2) is transformed to Eq. (3).

$$-d[e]_t = k[M][e]_0 \exp(-k[M]t)dt \tag{3}$$

When the ion shutter opens for a short time t_g, a packet of electrons will travel rapidly through nitrogen gas in the drift region, and the Cl^- ions are formed via dissociative electron attachment reactions. According to Eq. (3), the spatial distribution of chlorine ions $[Cl^-]_x$ along the drift region can be derived on the basis of the charge conservation.

$$[Cl^-]_x = k[M]t_g[e]_0 \exp\left(-k[M]\frac{x}{w}\right) \tag{4}$$

where w is the electron drift velocity and x is the distance from a point in the drift region to the ion shutter. The distance x can be written in the following form.

$$x = \nu_d(t_p - t_d) = \frac{L}{t_p}(t_p - t_d) = L\left(1 - \frac{t_d}{t_p}\right) \tag{5}$$

In Eq. (5), ν_d is the ion drift velocity, t_p is the ion transit time from the shutter to the Faraday plate, and t_d is the drift time of the ions from the point located at x in the drift region to the Faraday plate. Thus, Eq. (4) is further converted to Eq. (6)

$$[Cl^-]_x = k[M]t_g[e]_0 \exp\left(-k[M]\frac{L}{w}\left[1 - \frac{t_d}{t_p}\right]\right) \tag{6}$$

When nitrogen is used as drift gas, normally it is very difficult to completely remove water impurity inside. Thus, the Cl^- ions formed in the drift region can be converted to the clusters ions $Cl^-(H_2O)_n(M)_m$ via the following ion reactions.

$$Cl^- + nH_2O + mM \xleftrightarrow{K} Cl^-(H_2O)_n(M)_m \tag{7}$$

In Eq. (7), K is the balance constant, and the relation of ionic density between Cl^- and the cluster ions is $[Cl^-(H_2O)_n(M)_m] = K[Cl^-][H_2O]^n[M]^m$. The ions detected on the ion mobility spectrometry will be $Cl^-(H_2O)_n(M)_m$, and the corresponding ionic current i should be

$$i = K[H_2O]^n k[M]^{m+1} t_g[e]_0 \exp\left[-\frac{k[M]L}{w}\left(1 - \frac{t_d}{t_p}\right)\right] \tag{8}$$

The drift time ratio t_d/t_p is a constant (x/L) for the ions Cl^- and $Cl^-(H_2O)_n(M)_m$. Thus, the t_d and t_p in Eq. (8) can adopt the counterpart drift times of $Cl^-(H_2O)_n(M)_m$ when the Cl^- ions are converted to the $Cl^-(H_2O)_n(M)_m$ ions. From Eq. (8), the logarithm of the ionic current i exhibits a linear relation versus the ionic drift time t_d, and the slope of the straight line is relevant to the rate constant k of electron attachment.

$$\ln\, i \propto \frac{k[M]L}{wt_p}t_d \tag{9}$$

If the attachment gas concentration $[M]$, the drift time t_p at the peak of cluster ions, the drift tube length L and the electron velocity w are all known, the electron attachment rate constant k can be extracted.

In the present experiment, the chlorobenzene vapour samples were introduced to the reaction or drift region of the ion mobility

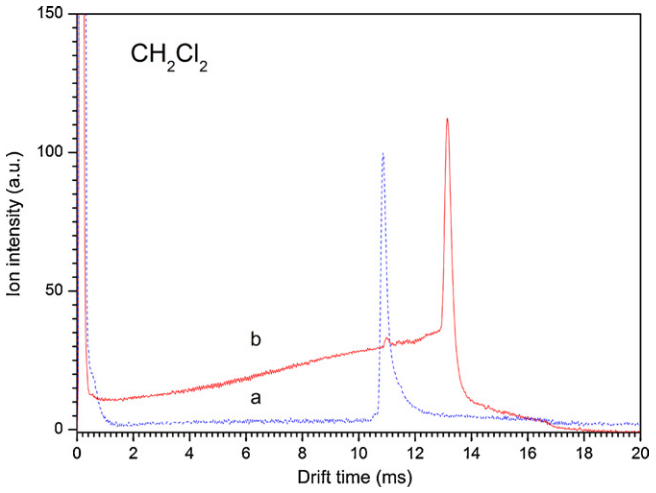

Fig. 2. The ion mobility spectrum of CH_2Cl_2: (a) the sample was introduced into the ionization region and (b) the sample was introduced into the drift region.

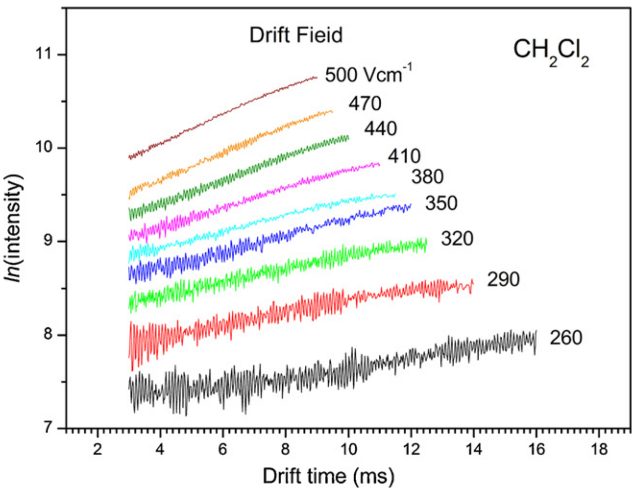

Fig. 3. Logarithm of the ion signal intensity in the incline region versus the drift time at various electric fields.

spectrometer. Their concentrations were generated by the conventional syringe pump introduction followed by further dilution with a calibrated buffer gas flow. A gastight syringe was used to prepare the saturation vapour of the sample. The emission rate of the sample from the syringe was obtained by means of the controlled pump speed and the saturation vapour pressure [15]. The purity of the buffer nitrogen gas is 99.9995%. CH_2Cl_2, 1,2-$C_6H_4Cl_2$, 1,3-$C_6H_4Cl_2$, 1,4-$C_6H_4Cl_2$, 1,2,4-$C_6H_3Cl_3$ and α,α,α-$C_6H_5CCl_3$ samples (Aladdin Co., Shanghai) are chemical reagents with a purity of >99.7% and were directly used without further purification. This experiment was carried out at the laboratory temperature (292 K) and ambient pressure (766 Torr).

3. Results and discussion

3.1. Dichloromethane

Electron attachment to CH_2Cl_2 has been widely studied by many investigators and the rate constants are easily available in the literature [11,16,17]. Therefore this electron attachment reaction was first studied to validate the ensuing measurement for other chlorobenzenes. Fig. 2 displays two ion mobility spectra recorded with CH_2Cl_2 introduction to (a) the reaction region and (b) the drift region, respectively. One can see that there is a very strong signal peak close to zero drift time in each spectrum, which originates from the electron packet. In the case of CH_2Cl_2 input to the reaction region, as shown in Fig. 2(a), only one ionic peak appears at the drift time of 10.8 ms. We ascribe the peak to the cluster ions $Cl^-(H_2O)_n$. When CH_2Cl_2 was introduced to the drift region, the observed spectrum in Fig. 2(b) exhibits two remarkable changes compared with Fig. 2(a). The ion peak has a shift from 10.8 to 13.2 ms, while a gradually increasing incline appears between the electron and ion peak. The ion peak shift to longer time indicates that larger cluster ions $Cl^-(H_2O)_n(CH_2Cl_2)_m$ achieved a thermal equilibrium via reaction (7) in the drift region and finally could be detected. The incline phenomenon is a result that the ions $Cl^-(H_2O)_n(CH_2Cl_2)_m$ were formed along the path of the electrons in the drift region under the circumstances of $[M] >> [e]$. Fig. 3 displays the logarithm of the ion signal around the incline versus the drift time at different electric fields from 200 to 500 V cm^{-1}. Indeed a linear relation exists, as predicted by Eq. (9). From the slope of the straight line, the electron attachment rate constants were obtained and the results are shown in Fig. 4. In the data treatment, the velocities and average energies of electron movement in nitrogen are taken from Ref. [18]. For comparison, Fig. 4 also gives the rate constants reported in the literature [11,16,17]. It can be noticed that the present experimental results are in good agreement with previous data, showing the validity of the present APNCD-EA-IMS experimental measurement.

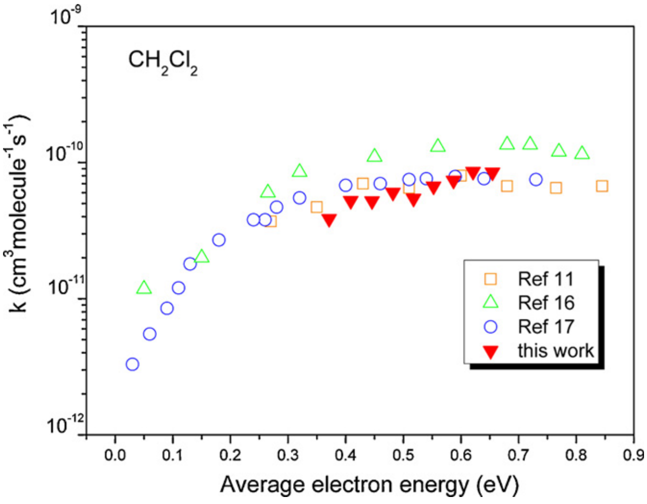

Fig. 4. The rate constants of electron attachment to CH_2Cl_2 as a function of average electron energies in nitrogen buffer gas at 292 K.

3.2. 1,2-, 1,3-, and 1,4-dichlorobenzene

Fig. 5(A)–(C) shows the ion mobility spectra measured for three dichlorobenzene isomers 1,2-, 1,3-, and 1,4-$C_6H_4Cl_2$, respectively. In analogy to the CH_2Cl_2 experiments, two different sample introduction modes were used. Traces a and b in Fig. 5 are the experimental results obtained by means of dichlorobenzene introduction to the reaction region and the drift region, respectively. When dichlorobenzene samples were introduced to the reaction region, the ion mobility spectra exhibit the similar behaviour with only one ionic peak at the drift time ~10.8 ms. When dichlorobenzene vapours were introduced to the drift region, the ion peaks were found to move towards longer drift times. The ion mobility spectra labelled as b in Fig. 5(A)–(C) were recorded at dichlorobenzene concentrations close to 950 ppb. The drift times of the ion peaks in the three spectra are 11.10, 11.28 and 11.35 ms for 1,2-, 1,3-, 1,4-$C_6H_4Cl_2$, respectively. These ions may be ascribed to the

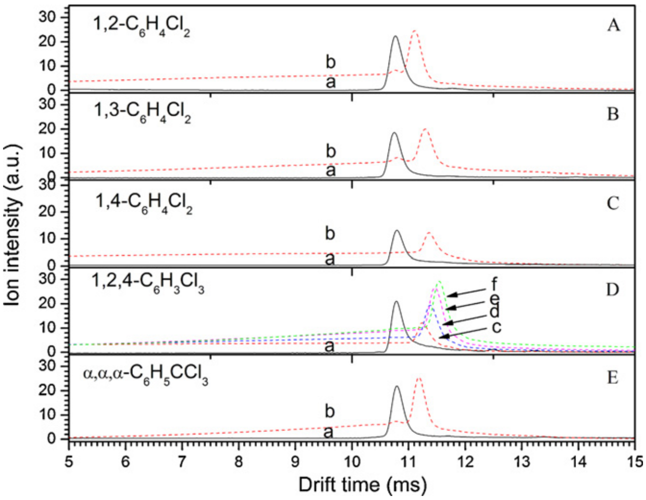

Fig. 5. The ion mobility spectra for 1,2-$C_6H_4Cl_2$, 1,3-$C_6H_4Cl_2$, 1,4-$C_6H_4Cl_2$, 1,2,4-$C_6H_3Cl_3$ and α,α,α-$C_6H_5CCl_3$. The samples were introduced into (a) the reaction region and (b) the drift region. In the case of introduction to the drift region, the concentrations of $C_6H_4Cl_2$ isomers and α,α,α-$C_6H_5CCl_3$ are close to 950 ppb and the concentrations of 1,2,4-$C_6H_3Cl_3$ are (c) 498, (d) 1302, (e) 2803 and (f) 2700 ppb.

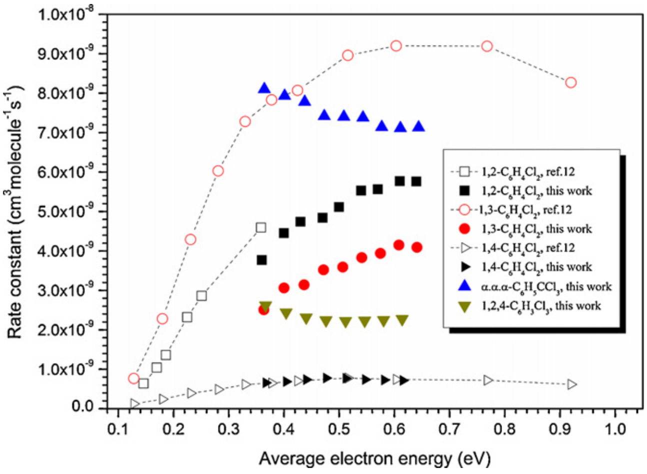

Fig. 6. The electron attachment rate constants for 1,2-$C_6H_4Cl_2$, 1,3-$C_6H_4Cl_2$, 1,4-$C_6H_4Cl_2$, 1,2,4-$C_6H_3Cl_3$ and α,α,α-$C_6H_5CCl_3$ in N_2 buffer gas at 292 K as a function of average electron energies.

cluster ions $Cl^-(H_2O)_n(C_6H_4Cl_2)_m$, formed in the drift region via reactions (1) and (7).

As described in Section 1, the rate constants of electron attachment to 1,2-, 1,3- and 1,4-$C_6H_4Cl_2$ were measured at electric fields ranging from 260 to 500 V cm^{-1}, which covers an average electron energy between 0.35 and 0.65 eV. The rate constants determined are displayed in Fig. 6 which also includes the rate constants of electron attachment to 1,2-, 1,3- and 1,4-$C_6H_4Cl_2$ measured using the swarm-beam method by Christophorou et al. [12].

For 1,2-$C_6H_4Cl_2$, the rate constants reported in the literature [12] increase in the electron energy range between 0.14 and 0.36 eV. The present measurement extends the upper boundary of the electron energy region from 0.36 up to 0.65 eV, particularly at around 0.36 eV our experimental datum of 3.8×10^{-9} cm^3 $molecule^{-1}$ s^{-1} is reasonably close to the reported value of 4.6×10^{-9} cm^3 $molecule^{-1}$ s^{-1} by Christophorou et al. [12].

The present work shows that, in the average electron energy range from 0.35 to 0.65 eV, electron attachment to 1,3-$C_6H_4Cl_2$ has a rate constant between 2.5×10^{-9} and 4.2×10^{-9} cm^3 $molecule^{-1}$ $^{-1}$, which is below that of 1,2-$C_6H_4Cl_2$. However, in the same electron energy region, the rate constant reported for 1,3-$C_6H_4Cl_2$ by Christophorou et al. [12] is in the range of 7.8×10^{-9} to 9.2×10^{-9} cm^3 $molecule^{-1}$ s^{-1}, which are larger than that for 1,2-$C_6H_4Cl_2$.

As for electron attachment to 1,4-$C_6H_4Cl_2$, the determined rate constant in the present experiment is in good agreement with the result obtained by Christophorou et al. [12]. One can see that the rate constant has a broad maximum around the electron energy of 0.5 eV.

Many studies [13,19–21] have shown that electron attachment to chlorobenzene derivatives proceeds via dissociative channel to produce Cl^- anions. The reaction mechanism is that electron is attached to the π^* molecular orbital on the benzene ring followed by intramolecular electron transfer to a C–Cl σ^* orbital, thus resulting in the Cl^- dissociation. In the present work, the differences in the rate constant for electron attachment to three dichlorobenzene isomers may be explained on the basis of the reaction energy and electron withdrawing induced effect.

The energy threshold (E_{th}) for Cl^- formation in the electron attachment reactions can be calculated using the bond dissociation energy D(C–Cl) and electron affinity EA(Cl) of Cl: $E_{th} = D(\text{C–Cl}) - \text{EA(Cl)}$. The experimental D(C–Cl) values of 1,2-, 1,3, and 1,4-$C_6H_4Cl_2$ were reported by Chen et al. [22] to be 3.998, 3.898, and 4.063 eV, respectively. However, Cioslowski et al. [23] thought that *this experimental D(C–Cl) value of 1,3-dichlorobenzene is most probably in error*. Their calculation at the BLYP/6-311G** level of theory gave a different result, *i.e.*, the D(C–Cl) values are incremental in the order of 1,2-, 1,3- and 1,4-$C_6H_4Cl_2$. Some other computations at a variety of theoretical levels [24–26] also obtained the same result. Based on these theoretical values for D(C–Cl), because the EA(Cl) is definite (3.61 eV) [27], the E_{th} values should exhibit an increase for Cl^- formation in electron attachment to dichlorobenzenes in the order of 1,2-, 1,3-, and 1,4-$C_6H_4Cl_2$. This will lead to the electron attachment reactions to be energetically more accessible following the order of 1,4-, 1,3-, and 1,2-$C_6H_4Cl_2$.

Forys et al. [28,29] investigated the thermal electron attachment rate constant dependence on the molecular structure for halogenated propane isomers. The rate constants difference, like $k(1,1\text{-}C_3H_3Br_2) > k(1,2\text{-}C_3H_3Br_2) > k(1,3\text{-}C_3H_3Br_2)$, was explained via a hypothetical summary polarizability only at the electron attaching centers in the molecule based on the concept of the electron withdrawing induced effect. Analogously, if the polarizability of a chlorine atom at the C1, C2, C3, and C4 position of benzene is expressed as P_1, P_2, P_3 and P_4, respectively, the position change of a chlorine atom in dichlorobenzene from C2 to C3 and C4 might cause a decrease in the polarizability: $P_1 > P_2 > P_3 > P_4$. Thus, for 1,2-, 1,3- and 1,4-$C_6H_4Cl_2$, their summary polarizabilities would have a relation: $P_1 + P_2 > P_1 + P_3 > P_1 + P_4$. This could result in a diminishing rate constant for electron attachment to 1,2-, 1,3- and 1,4-$C_6H_4Cl_2$: $k(1,2\text{-}C_6H_4Cl_2) > k(1,3\text{-}C_6H_4Cl_2) > k(1,4\text{-}C_6H_4Cl_2)$.

3.3. *1,2,4-Trichlorobenzene and α,α,α-trichlorotoluene*

As in the case of dichlorobenzene, when 1,2,4-$C_6H_3Cl_3$ and α,α,α-$C_6H_5CCl_3$ samples were injected to the reaction region, in the ion mobility spectra only one ion peak occurred at the drift time of 10.8 ms (see Fig. 5). Similarly, when the trichlorobenzene derivative samples were fed to the drift region, the ion peak appeared at longer drift time. In Fig. 5(D), traces c, d, e and f are the ion mobility spectra recorded at 1,2,4-$C_6H_3Cl_3$ concentrations of 498, 1302, 2803 and 2700 ppb, respectively. It can be seen that the drift time of the ion peak increases with the 1,2,4-$C_6H_3Cl_3$ concentration. This shows that large cluster ions $Cl^-(H_2O)_n(1,2,4\text{-}C_6H_3Cl_3)_m$ can form via reaction (7), once the number density of 1,2,4-$C_6H_3Cl_3$ in the reaction region is high.

Table 1
Rate constant of electron attachment to 1,2,4-$C_6H_3Cl_3$ at 292 K and at 410 V cm^{-1}.

[1,2,4-$C_6H_3Cl_3$] (ppb)	t_p (ms)	Slope	k (10^{-9} cm^3 molecule^{-1} s^{-1})
498	11.30	0.04548	2.23
1302	11.44	0.12063	2.29
2083	11.54	0.19084	2.29
2700	11.60	0.24132	2.24

Table 1 lists the drift times of product ions with respect to the above mentioned four concentrations of 1,2,4-$C_6H_3Cl_3$. As shown in Eq. (9), the logarithm of the ionic current versus the drift time t_d indeed exhibits a linear dependence, and the slopes and rate constants were obtainable which are listed in Table 1. It can be seen that the rate constants k measured under the same drift electric field of 410 V cm^{-1} are nearly unchanged even though using different number densities of 1,2,4-$C_6H_3Cl_3$ in the experiments.

In order to compare with 1,2,4-$C_6H_3Cl_3$, electron attachment to α,α,α-$C_6H_5CCl_3$ was investigated and the ion mobility spectrum is given in Fig. 5(E). The rate constants of electron attachment were also determined and the results are displayed in Fig. 6. One can find that the rate constant for α,α,α-$C_6H_5Cl_3$ is about 3.3 times of that for 1,2,4-$C_6H_3Cl_3$. In the previous studies of electron attachment to chlorobenzenes [20], the cross-section for $C_6H_5CH_2Cl$ reaction was found to be about 20 times of that for C_6H_5Cl. This large difference in the reaction cross-sections has been attributed to the ring π^* orbital mixing with the C–Cl σ^* orbital that can promote the Cl^- dissociation. For the reaction system in the present work, we believe that the strong anti-bonding character of the C–Cl σ^* orbital in α,α,α-$C_6H_5CCl_3$ is the main reason for the higher rate constant compared to 1,2,4-$C_6H_3Cl_3$.

4. Conclusions

Using negative corona discharge in nitrogen gas at an atmospheric pressure as electron source, electron attachment ion mobility spectrometry technique has been applied to study electron attachment reactions to a series of chlorobenzene compounds at ambient temperature. Electron attachment to CH_2Cl_2 has been studied to demonstrate the validity of the experimental method. The rate constants for electron attachment to 1,2-$C_6H_4Cl_2$, 1,3-$C_6H_4Cl_2$, 1,4-$C_6H_4Cl_2$, 1,2,4-$C_6H_3Cl_3$ and α,α,α-$C_6H_5CCl_3$ were quantitatively determined in the average electron energy range from 0.35 to 0.65 eV, which follow the relations of k(1,2-$C_6H_4Cl_2$) > k(1,3-$C_6H_4Cl_2$) > k(1,4-$C_6H_4Cl_2$) and k(α,α,α-$C_6H_5CCl_3$) > k(1,2,4-$C_6H_3Cl_3$). The differences in the rate constants for electron attachment to dichlorobenzene isomers or to trichlorobenzene derivatives are discussed.

Acknowledgments

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