

Dissociative Electron Attachment to the Dichloropropanes

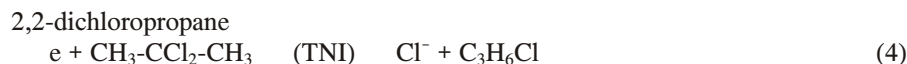
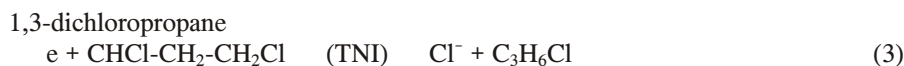
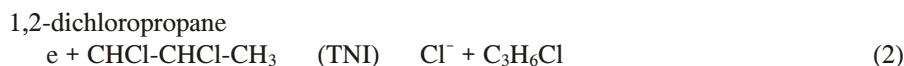
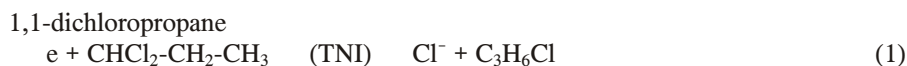
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Abstract: Measurements of relative partial cross sections for dissociative electron attachment to 1,1-, 1,2-, 2,2- and 1,3-dichloropropanes have been carried out in a crossed electron/molecule beams experiment in the gas phase at ambient temperature. Besides the s-wave attachment, two additional resonances at approximately 1 and 4 eV have been present in all isomers. The values of the partial cross sections for dissociative electron attachment have been estimated at the resonant energies.

1. Introduction

Dissociative electron attachment (DEA) reactions to the molecules play an important role in various fields of chemistry, physics, and in large number of technological applications [1]. Chlorinated hydrocarbons are of high importance for the atmospheric chemistry. These molecules are the source of the atomic chlorine in the upper atmosphere, which is responsible for the decomposition of the stratospheric ozone in a catalytic cycle [2]. To the most important sources of the chlorinated hydrocarbons belong the sea and the human activities, thus these molecules exist in the atmosphere in considerable amounts. In the present work we study the reaction of the DEA to four different isomers of dichloropropane:



TNI represents the transient negative ion. The DEA reactions is a two step process. In the first step the unstable transient negative ion is formed, which is subsequently decomposed into a fragment negative ion and neutral fragments. The study of DEA to different

isomers of dichloro-propane is also of fundamental interest. This molecule exists in four different isomers and thus we are able to study the effects of the chemical structure on the shape and magnitude of the partial cross section for DEA. The cross section for DEA to these molecules gives also valuable kinetic data applicable in many fields of the physics and chemistry.

DEA to these molecules have been previously studied using the swarm technique [3] and significant differences in the magnitude of the DEA rate coefficient have been reported. Additionally Aflatooni et al. [4] measured the resonance energies for whole class of dichloro-hydrocarbons and published the values of the total DEA cross sections for these molecules [5], however, without the mass spectroscopic analysis of reduced negative ions. In contrast to the study by Aflatooni et al. [5] in the present work we have measured partial cross section for DEA to the isomers of dichloropropane using mass spectroscopic analysis of the ions and in extended electron energy range.

2. Experiment

The present work has been carried out using the crossed electron/molecular beams apparatus. The apparatus has been described in detail in [6]; therefore we will give only a brief description. A schematic view of the apparatus is shown in Fig. 1. The electron beam is formed in a trochoidal electron monochromator (TEM) [7] with an electron energy resolution of about 60 meV full width at half maximum (FWHM). A well defined molecular beam with a narrow angular distribution function is formed by effusion of the molecules through a channel (4 mm long and 0.5 mm diameter). The pressure in the molecular beam source is measured by absolute pressure gauge (Barratron). The negative ions are formed at the crossing point of the two beams. The ions are extracted by a weak electric field into quadrupole mass spectrometer and the mass selected ions are detected as a function of the electron energy. The calibration of the electron energy scale and the estimation of the electron energy resolution are performed through the measurement of the electron attachment (EA) process SF₆⁻/SF₆. The ion yields were measured in the electron energy range from zero to 6 eV. The molecules studied in the present experiment are, under normal conditions, liquids and the purity of the samples has been 99 %. No additional cleaning of the samples has been carried out.

3. Results and Discussion

The Cl⁻ is the only negative ion detected in the present experimental study concerning DEA to the four isomers of dichloropropane molecule. Additional negative ions, e.g., parent molecular ions Cl₂ have not been detected within the sensitivity of the apparatus. The H⁻ could not be measured in the present experiment, because this ion is out of range of the mass spectrometer. The measured Cl⁻ ion yields for DEA to the isomers of the dichloropropane are presented in Fig. 2. All the curves exhibit three apparent peaks in the studied electron energy range from zero to 6 eV. The zero energy peaks indicate capture of s-wave electrons to the molecules, formation of transient negative ion (TNI) and subsequent dissociation of the molecular ion into Cl⁻ anion. The capture of s-wave electrons is typical for majority of the chlorinated hydrocarbons [5]. However, the zero energy peaks

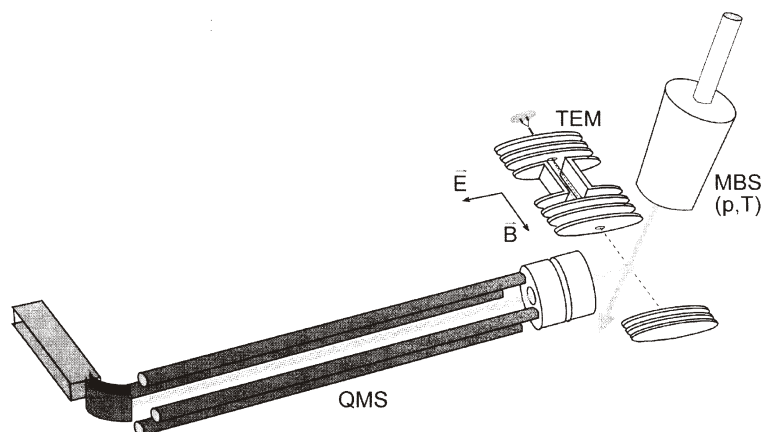


Fig. 1. Schematic view of the apparatus. TEM—trochoidal electron monochromator, MBS—molecular beam source, QMS—quadrupole mass spectrometer.

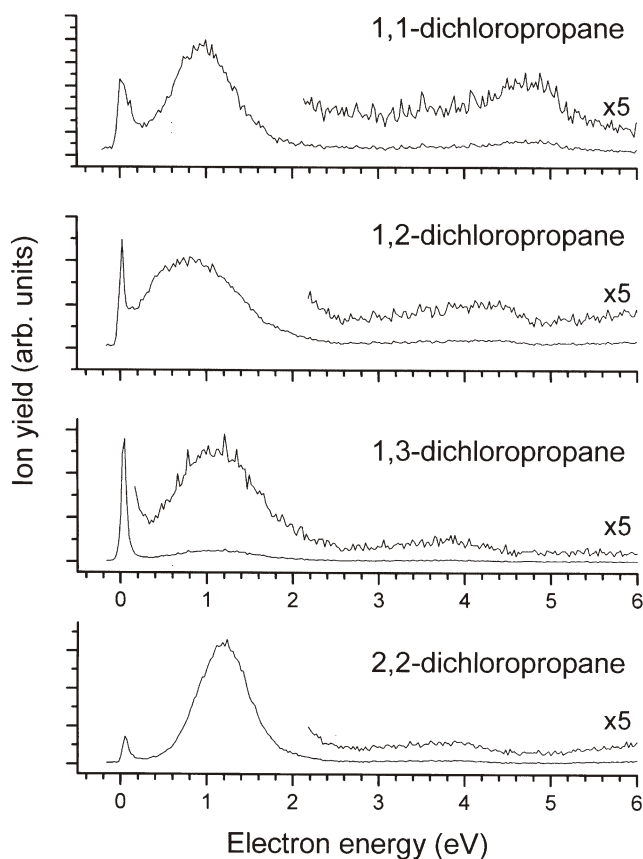


Fig. 2. The Cl^- ion yields for the particular isomers of the dichloropropane molecule.

Table 1. The resonance energies and the values of the cross sections as estimated for particular isomers of the dichloropropanes.

Molecule	Peak energy	Cross section	Peak energy	Cross section
	(eV)	(10^{-18} cm ²)	(eV)	(10^{-18} cm ²)
1,1-dichlorometane	0.95	30 3	4.9	2 0.2
1,2-dichlorometane	0.80	20 2	4.4	3 0.3
1,3-dichlorometane	1.10	4 0.5	3.8	0.5 0.2

may also originate (in the case of 1,3-dichloropropane) from impurities (such as CCl₄), which have extremely high cross sections for DEA at 0 eV and already trace amounts may substantially contribute to the ion yield at low electron energies. The shape of the zero energy peaks is given by the convolution of the cross section with the electron energy distribution function and the width of the peak is given by the width of the electron energy distribution function.

The second resonance is present in all the isomers at about 1 eV. We attribute these peaks to the resonances associated with the temporal occupation of the C-Cl * orbital of the molecules by the interacting electron. The exact peak energies and the present values of the partial cross sections are summarized in Tab. 1. The present values of the peak energies agree very well with those measured by Aflatooni et al. [5]. Also the present values of the partial cross sections for the reactions (1)–(4) agree within the error bars with the absolute total cross sections measured by Aflatooni et al. [5]. This indicates the fact that the formation of Cl⁻ ion contributes substantially to the total cross section. In the case of the DEA to 1,3-dichloropropane the zero energy peak is, in the present experiment, much larger than the second one. The strong electron attachment at 0 eV is in disagreement with the previous study [5]. We believe that this is due to presence of an impurity in the present sample (purity 99 %), because the value of the cross section at the second 1.10 eV resonance is in satisfactory agreement with the cross section estimated by Aflatooni et al. [5].

The resonances at high energies observed in the present study above 3 eV were not reported in the previous papers [4,5]. We tentatively assign these resonances to the processes associated with the excitation of the lowest electronic states of the molecules. The resonant energies and the magnitudes of the cross sections are summarised in Tab. 1. Generally the values of the cross sections at these resonances are about one order of magnitude lower than the cross sections at the low energy resonances at approximately 1 eV. In the present experiment we were not able to detect the neutral fragments of DEA reactions. We assume that at low electron energy resonances (at 0 and approximately 1 eV) only simple bond cleavage occurs, however, at high energy resonances fragmentation of the neutral products in several small fragments is possible.

Acknowledgments

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