



## Research paper

## Thermal electron attachment to chlorinated alkenes in the gas phase



K. Wnorowski\*, J. Wnorowska, B. Michalczuk, A. Jówko, W. Barszczewska

Department of Chemistry, Siedlce University, 3 Maja 54, 08-110 Siedlce, Poland

## ARTICLE INFO

## Article history:

Received 4 July 2016

In final form 1 November 2016

Available online 2 November 2016

## Keywords:

Activation energy

Electron attachment

Rate coefficient

Chlorinated alkenes

Pulsed Townsend technique

## ABSTRACT

This paper reports the measurements of the rate coefficients and the activation energies of the electron capture processes with various chlorinated alkenes. The electron attachment processes in the mixtures of chlorinated alkenes with carbon dioxide have been investigated using a Pulsed Townsend technique. This study has been performed in the temperature range (298–378) K. The obtained rate coefficients more or less depended on temperature in accordance to Arrhenius equation. The activation energies ( $E_a$ 's) were determined from the fit to the experimental data points with function  $\ln(k) = \ln(A) - E_a/k_B T$ . The rate coefficients at 298 K were equal to  $1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ,  $2.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ,  $1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ,  $4.4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ,  $2.9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and  $7.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and activation energies were: 0.27 eV, 0.26 eV, 0.25 eV, 0.21 eV, 0.55 eV and 0.42 eV, for *trans*-1,2-dichloroethylene, *cis*-1,2-dichloroethylene, trichloroethylene, tetrachloroethylene, 2-chloropropene, 3-chloropropene respectively.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Low energy electron attachment to halogenated alkenes has been extensively studied for many years. The interest to this group of compounds is mainly due to their atmospheric and environmental significance [1,2]. Additionally their participation in electron transfer reactions that occur with metal containing molecules catalyzed by biologically relevant compounds, like vitamin B12 were well documented [3,4].

The fragmentation of chlorinated derivatives of ethylene under low energy ( $\sim 10$  eV) electron impact were studied previously by Christophorou et al. by using a time-of-flight mass spectrometer [5]. The beam studies have shown three types of fragment negative ions: i.e.  $\text{Cl}^-$  (the most abundant),  $\text{Cl}_2^-$  and  $(\text{M}-\text{Cl})^-$  where M means the parent molecule. The  $\text{Cl}_2^-$  yield is rising when any chlorine atoms in  $\text{Cl}_2^-$  comes from two adjacent carbon atoms and the most intense  $\text{Cl}^-$  peak shifts to higher energy in the order:  $\text{C}_2\text{Cl}_4$ ,  $\text{C}_2\text{HCl}_3$ ,  $1,1\text{-C}_2\text{H}_2\text{Cl}_2$ , *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$  and *cis*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ . It has been clearly established for tetrachloroethene that the  $\text{C}=\text{C}$   $\pi$ -orbital is definitely involved in the formation of the long-lived parent negative ion at about thermal electron energy [5].

Formation of stable negative ion fragments in the series of fluoroethylenes [6] and fluorochloroethylenes [7] were studied by using dissociative electron attachment spectroscopy. For all investigated molecules of fluoroethylenes ( $\text{C}_2\text{H}_3\text{F}$ ,  $\text{C}_2\text{H}_2\text{F}_2$ ,  $\text{C}_2\text{HF}_3$  and  $\text{C}_2\text{F}_4$ ) rich fragmentation patterns (among others  $\text{F}^-$ ,  $\text{C}_2^-$ ,  $\text{HF}_2^-$ ,

$\text{C}_2\text{HF}^-$ ) were observed. It is interesting that in tetrafluoroethylene the formation of the negative ion ( $\text{CF}_2^-$ ) by cleavage of the double bond  $\text{C}=\text{C}$ , as a result of the perfluoro effect was noticed [8]. For all fluorochloroethylenes ( $\text{C}_2\text{Cl}_4$ ,  $\text{C}_2\text{FCl}_3$ ,  $1,1\text{-C}_2\text{F}_2\text{Cl}_2$ , mixture of geometric isomers of  $1,2\text{-C}_2\text{F}_2\text{Cl}_2$  and  $\text{C}_2\text{F}_3\text{Cl}$ ) was found low-lying resonances ( $<4$  eV) associated with various dissociation channels. The  $\text{Cl}^-$  was observed as the most abundant negative fragment ion with resonance energy decreases if fluorine(s) atom(s) was replaced by chlorine(s) in the molecule. The measurements of the thermal electron attachment rate coefficient of *c*- $\text{C}_4\text{F}_8$  and *2*- $\text{C}_4\text{F}_8$  were carried out using swarm method [9]. Obtained value of  $k$  for *2*- $\text{C}_4\text{F}_8$  ( $4.2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ) is in good agreement with value reported by Sauers ( $4.8 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ) [10].

Rate constants have been measured for electron attachment to bromoethylenes (1,2-dibromoethylene and tribromoethylene) in Xe buffer gas using the pulse-radiolysis microwave-cavity method combined with microwave heating [11]. For those compounds the maximum of the resonance peak of the cross section has been recorded at zero electron energy and no other peaks at higher energies were observed. Comparing the efficiency of the electron capture by bromoalkanes and bromoalkenes it has been found that the presence of an unoccupied  $\pi$  orbital does not much affect the efficiency of the low energy electron attachment.

In parallel to the experimental measurements of this group of compounds the calculations were carried out to evaluate the virtual orbital energies for the optimized geometries of the neutral states of these molecules and other related  $\pi$ -systems [12–14]. The electron attachment was explained in terms of the extent of  $\sigma^*/\pi^*$  mixing in the temporary molecular anion and the contribution from

\* Corresponding author.

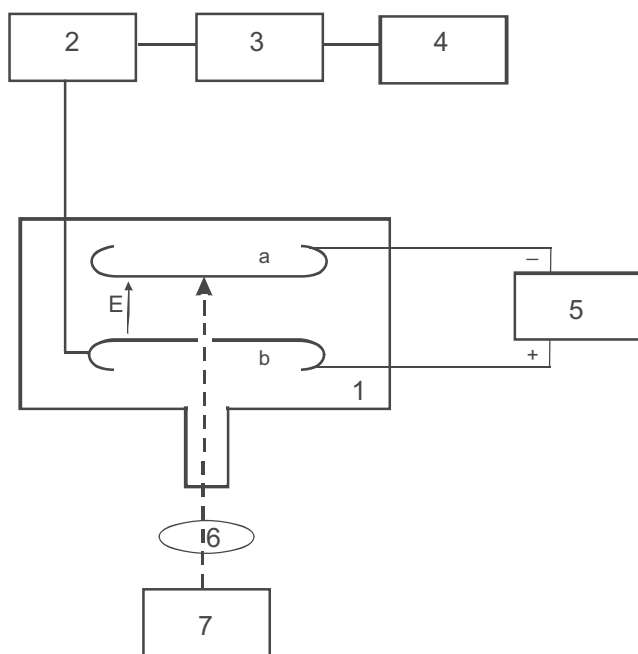
E-mail address: [karol.wnorowski@uph.edu.pl](mailto:karol.wnorowski@uph.edu.pl) (K. Wnorowski).

the C–Cl  $\sigma^*$  orbital diminish as the bridge connecting the C=C and C–Cl groups increases in length.

The aim of this paper is to study the kinetics of thermal electron attachment to some chlorinated alkenes (*trans*-1,2-dichloroethylene, *cis*-1,2-dichloroethylene, trichloroethylene, tetrachloroethylene, 2-chloropropene, 3-chloropropene) in carbon dioxide buffer gas by using the Pulsed Townsend method. In our previous papers we have presented results on some halocarbons [15,16]. Systematical studies on the rate coefficients ( $k$ 's) and activation energies ( $E_a$ 's) of thermal electron captures allowed us demonstrated the linear dependence between  $\log(k)$  and  $E_a$ .

## 2. Experiment

An electron swarm method with carbon dioxide as a carrier gas has been applied for the measurements of the electron capture rate coefficients and activation energies. A schematic view of the apparatus is shown in Fig. 1. This technique allows us to study electron attachment processes at elevated temperature (not only room temperature). The experimental apparatus and measurement procedure have been described in detail previously [15]. The experimental setup consists of the stainless steel chamber of 700 cm<sup>3</sup> volume with two parallel electrodes, a preamplifier, a fast oscilloscope with a digital memory connected to a computer and a computer-controlled power supply, an optical set and a Quantel Nd:YAG fast laser. The laser operates on fourth harmonics at 266 nm at the frequency of 10 Hz. The chamber can be warmed by using heating jackets produced by Watlow Company. Electronic control enables us to stabilize the temperature within 1 °C. The electron acceptor was introduced into the chamber with the excess of carbon dioxide as a buffer gas. An electron swarm is produced at the cathode using a 5 ns Nd:YAG laser. The electron swarm moved through the gas mixture to the collecting electrode (anode) due to uniform electric field. The drifting electrons create a pulse change in the potential of the collecting electrode. The pulse signal is amplified, registered on the oscilloscope and saved in the com-



**Fig. 1.** Schematic diagram of the experimental set up: (1) swarm chamber, (a) cathode, (b) anode, (2) preamplifier, (3) oscilloscope, (4) computer, (5) high voltage power supplier, (6) optical set up, (7) laser ( $E$ , uniform electric field).

puter memory. The experiment was performed in such a way that each chloroalkenes–carbon dioxide mixture was first introduced into the chamber at the applied total pressure (ca. 350–400 Torr). Always 50 pulses were registered for a given  $E/N$  and averaged. The procedure was repeated usually for five  $E/N$  values in the rather wide range of reduced field ( $1.5 \times 10^{-17}$ – $3.0 \times 10^{-17}$  V cm<sup>2</sup> molec.<sup>-1</sup>), where electrons in carbon dioxide are in thermal equilibrium with gas molecules. Next, the mixture was heated to a higher temperature and the measurement procedure was repeated for other temperature in the range (298–378) K. The whole experiment was carried out for a few different initial concentrations of attaching gas in carbon dioxide.

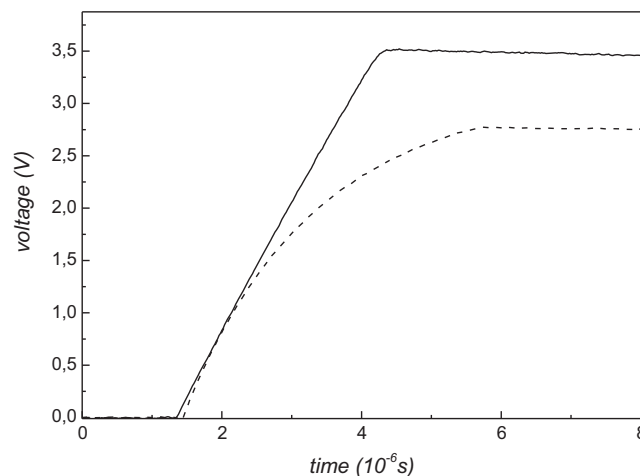
Fig. 2 shows the example pulses which are the result of averaging of the 50 consecutive pulses for carbon dioxide and mixture of *trans*-1,2-dichloroethylene–carbon dioxide. The electrons traversing in pure buffer gas (CO<sub>2</sub>) induce change of the anode potential which increases linearly when electrons move to the collecting electrode. But in the mixture: buffer gas – electron acceptor, as shown in Fig. 2, the electrons are captured and increase of the potential is no longer linear. The electron attachment rate coefficients were determined from the shape of the signal output of the electron pulse. The experimental curves as shown in Fig. 2 were fitting using Eq. (1) [15]:

$$V(\tau) = B \cdot [\exp(-k \cdot N_a \cdot \tau) - \exp(-\tau/t_1)] \quad (1)$$

where  $B$  – apparatus arbitrary constant,  $k$  – electron capture rate coefficient,  $N_a$  – electron acceptor concentration,  $t_1$  – time constant of the preamplifier ( $t_1 = RC = 400 \mu\text{s}$ ). Since all the values are known, except  $B$  and  $k$  these two parameters were simulated using a computer program as described in Ref. [15].

The examined compounds and appropriate purities were as follows: *trans*-1,2-dichloroethylene (98%), *cis*-1,2-dichloroethylene (97%), trichloroethylene (99.5%), tetrachloroethylene ( $\geq 99.9\%$ ), 2-chloropropene (98%), 3-chloropropene (99%) and were delivered from Sigma Aldrich.

All compounds were purified by the vacuum freeze-pump-thaw technique. The CO<sub>2</sub> with a quoted purity 99.998% was from Fluka and was used as delivered. The applied pressure of the electron attaching gases depends on their efficiency in capture electrons and was chosen to give the rate of the process approximately  $10^5 \text{ s}^{-1}$ .



**Fig. 2.** Averaged voltage signal for the pure CO<sub>2</sub> (solid line) and the mixture of *trans*-1,2-dichloroethylene and CO<sub>2</sub> (dashed line) obtained at 298 K and  $E/N = 2.7 \times 10^{-17}$  V cm<sup>2</sup> molec.<sup>-1</sup>.

Download English Version:

<https://daneshyari.com/en/article/5378502>

Download Persian Version:

<https://daneshyari.com/article/5378502>

[Daneshyari.com](https://daneshyari.com)