



Kinetics of low energy electron attachment to some fluorinated alcohols in the gas phase



K. Wnorowski*, J. Wnorowska, J. Kopyra, B. Michalczyk, I. Szamrej, W. Barszczewska

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

ARTICLE INFO

Article history:

Received 7 September 2013

In final form 21 November 2013

Available online 28 November 2013

ABSTRACT

Thermal electron attachment processes in the mixtures of $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$, $(\text{CF}_3)_2\text{CHOH}$ and $\text{CH}_3\text{CH}(\text{OH})\text{CF}_3$ with carbon dioxide have been investigated using an electron Pulsed Townsend technique. Measurements were carried out in the temperature range (298–413) K. The obtained rate coefficients depended on temperature in accordance to Arrhenius equation. From the fit to the experimental data points with function $\ln(k) = \ln(A) - E_a/k_B T$ the activation energies (E_a 's) were determined. The rate coefficients at 298 K are equal to $3.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, $5.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, $1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, $3.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $2.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and activation energies are: 0.37 eV, 0.25 eV, 0.28 eV, 0.20 eV and 0.23 eV, respectively for $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$, $(\text{CF}_3)_2\text{CHOH}$ and $\text{CH}_3\text{CH}(\text{OH})\text{CF}_3$.

© 2013 Elsevier B.V. All rights reserved.

Introduction

The studies of electron attachment processes are very important for understanding the electron-molecule interactions, negative ions formation, basic processes occurring in plasmas [1,2]. Those investigations are important also from the environmental protection point of view, especially if processes of the organofluorine contaminations in the earth atmosphere are considered.

The concentration of the man-made organofluorine compounds has substantially increased during the past few decades. The fate of perfluoroalkyl substituents, such as the trifluoromethyl groups, are of particular interest. Up to now most evidences suggest that such groups resist defluorination, although they can confer significant biological activity. Certainly, some volatile fluorinated compounds can be oxidized in the troposphere yielding nonvolatile compounds, such as trifluoroacetic acid.

In recent years the interest was turned to fluorinated alcohols, which are applied more often and often. For example, they are used as pharmaceuticals, inhalation anesthetics, herbicides, polymers, refrigerants, etchants, lubricants, heat transfer fluids, and so on [3,4]. Recently fluoroalcohols have been suggested as substitutes for chlorofluorocarbons (CFCs) too. Fluoroalcohols have been marketed as replacements for the stratospheric ozone depleting CFCs, however they may be equally hazardous to the environment. In spite of fluoroalcohols have zero ozone depletion potential (ODP), they still must be considered as possible greenhouse gases contributing to global warming stemmed from the strong IR activity of the

C–F bonds [5,6]. For these reasons the further information on the degradation mechanisms are required.

To our knowledge, only the electron attachment processes to ethanol and trifluoroethanol have been previously studied in gas phase by using electron-molecule crossed beam technique [7,8]. The formations of negative ions have been measured in the energy range from 0 to 19 eV [7]. These studies showed that gaseous trifluoroethanol generates the ionic fragments: $\text{CF}_3\text{CH}_2\text{O}^-$, $\text{C}_2\text{F}_2\text{HO}^-$, C_2FO^- , CF_3^- and F^- while for ethanol only ions: O^- , OH^- and $\text{CH}_3\text{CH}_2\text{O}^-$ were observed. Additionally, the fluorination considerably increases the cross section for dissociative electron attachment. The ethanol forms exclusively products of simple bond cleavage while the fluorinated alcohol shows a tendency to abstract the stable molecule hydrogen fluoride. Independently, almost at the same time, Allan and co-workers investigated the electron attachment processes to some alcohols (among others $\text{CH}_3\text{CH}_2\text{OH}$) [8]. They confirmed results presented by Illenberger and co-workers [7] and additionally new weaker processes at lower energies (<3 eV) were identified. Furthermore they showed large D/H isotope effect on dissociative electron attachment to molecule.

This Letter is a continuation of the systematical studies on the rate coefficients (k 's) and activation energies (E_a 's) of thermal electron captures by various molecules using Pulsed Townsend technique. In our previous papers we have presented results concerning some halocarbons [9,10] and perfluoroethers [11]. We have demonstrated then the linear dependence between $\log(k)$ and E_a . We have found also that the activation energy is the main factor determining the rate coefficient for thermal electron capture. At present we have started the electron capture studies on the new group of compounds – fluorinated alcohols. Below,

* Corresponding author.

E-mail address: karolw@uph.edu.pl (K. Wnorowski).

we present the data on the thermal electron attachment to $\text{CH}_3\text{-CH}_2\text{OH}$, $\text{CF}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$, $(\text{CF}_3)_2\text{CHOH}$ and $\text{CH}_3\text{CH}(\text{OH})\text{CF}_3$.

Experiment

The experiments were carried out with Pulsed Townsend (PT) technique apparatus. A schematic view of the apparatus is shown in Figure 1. This technique allows us to study electron attachment processes at elevated temperature. The experimental apparatus and measurement procedure has been already described in detail previously [9], therefore we will give only a brief description. The experimental setup consists of the stainless steel chamber of 700 cm^3 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 heated using heating jackets produced by Watlow Company. Electronic control enables us to stabilize the temperature within $1\text{ }^\circ\text{C}$. 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 to the collecting electrode (anode) due to uniform electric field, through the gas mixture containing buffer gas and an electron acceptor. 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 computer memory.

The experiment was performed in such a way that each fluoroalcohols – carbon dioxide mixture was first introduced into the chamber at the highest applied total pressure (ca. $350\text{--}400\text{ Torr}$). 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 ($1.5 \times 10^{-17}\text{--}3.0 \times 10^{-17}\text{ V cm}^2\text{ molec.}^{-1}$), 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 in the range $298\text{--}413\text{ K}$. The whole experiment was carried out for a few different initial concentrations of fluoroalcohols in carbon dioxide.

Figure 2 shows the pulse which is the result of averaging of the 50 consecutive pulses. The electrons traversing in pure buffer gas (CO_2) induce change of the anode potential which increases linearly when electrons move to the collecting electrode. But in the

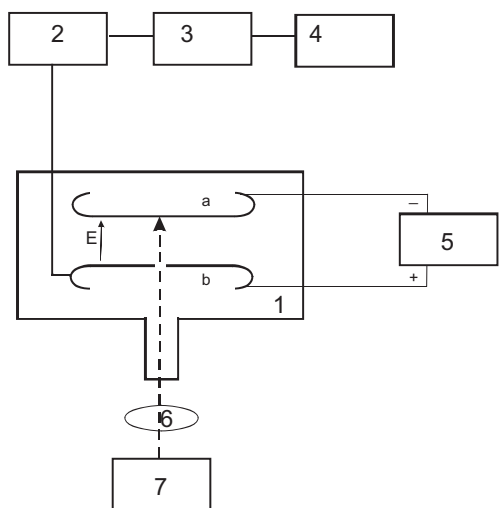


Figure 1. Schematic diagram of the experimental set up: (1) swarm chamber; (a) cathode, (b) anode; (2) preamplifier; (3) oscilloscope; (4) computer; (5) high voltage power supplier; (6) optical set up; (7) laser (E , uniform electric field).

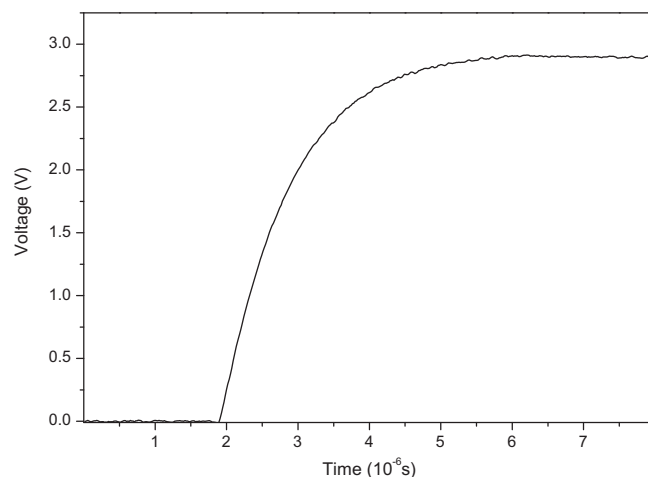


Figure 2. Averaged voltage signal for the mixture of $(\text{CF}_3)_2\text{CHOH}$ and CO_2 obtained at 298 K and $E/N = 1.8 \times 10^{-17}\text{ V cm}^2\text{ molec.}^{-1}$.

mixture: buffer gas – electron acceptor, as shown in Figure 2, the electrons are captured and increase a potential is no longer linear. The electron attachment rate coefficients were determined from the shape of the output signal of the electron pulse. The experimental curves as shown in Figure 2 were fitting using Eq. (I) [9]:

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

where: B – apparatus arbitrary constant, k – electron capture rate coefficient, N_a – electron acceptor concentration, t_1 – time constant of the preamplifier ($t_1 = RC = 400\text{ }\mu\text{s}$). Since all the values are known, except B and k these two parameters were simulated using a computer program as described in Ref. [9]

The examined compounds and appropriate purities are as follows: $\text{CH}_3\text{CH}_2\text{OH}$ (Applichem, 99.8%), $\text{CF}_3\text{CH}_2\text{OH}$ (Aldrich, 99%), $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$ (Appolloscientific, 98%), $(\text{CF}_3)_2\text{CHOH}$ (Aldrich, >99%) and $\text{CH}_3\text{CH}(\text{OH})\text{CF}_3$ (Aldrich, 97%). All compounds were purified by the vacuum freeze–pump–thaw technique. The CO_2 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 is chosen to give the rate of the process approximately 10^5 s^{-1} .

Results and discussion

The present data were obtained by using the swarm method, known as the Pulsed Townsend technique. We have measured the electron attachment rate coefficients (k 's) in the temperature 298 K for $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$, $(\text{CF}_3)_2\text{CHOH}$ and $\text{CH}_3\text{CH}(\text{OH})\text{CF}_3$ used as attaching gases diluted with carbon dioxide. The example results are shown in Figure 3 in terms of the rate coefficients vs. CO_2 concentrations. As shown for $(\text{CF}_3)_2\text{CHOH}$ (like for the other investigated in this letter molecules) k does not depend on the carbon dioxide or the electron acceptor concentration. This means that for all presented cases only the two-body electron attachment processes by a single molecule takes place. All rate coefficients obtained at 298 K are presented in Table 1 and to our knowledge they have been determined for the first time.

The rate coefficients for fluorinated alcohols are more than two orders of magnitude higher than for alcohols. We have observed the influence of numbers of fluorine substituents on increase the value of the rate coefficients. It seems that it is more reasonable to compare our data (fluorinated alcohols) to the data of fluorinated and perfluorinated alkanes or perfluoroethers. All of the aforementioned molecules contain fluorine atoms, but their

Download English Version:

<https://daneshyari.com/en/article/5381165>

Download Persian Version:

<https://daneshyari.com/article/5381165>

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