acta physica slovaca vol. 55 No. 5, 447 – 451 October 2005

LOW ENERGY ELECTRON INTERACTION WITH HALOETHANES[1]

J. Kopyra[2], W. Barszczewska, J. Wnorowska, M. Foryś, I. Szamrej
Chemistry Department, University of Podlasie, 3 Maja 54, 08-110 Siedlce, Poland

Received 18 April 2005, in final form 30 June 2005, accepted 8 July 2005

The dissociative electron attachment to chloro and fluoro derivatives of ethane have been measured using swarm technique. The rate coefficients have been estimated for first time for many of them and the values of the rate coefficients have been correlated to the DEA energies.

PACS: 52.20.-j

1 Introduction

This paper is a continuation of our effort to measure systematically the thermal electron attachment rate coefficients for halocarbons. The aim is to find out the connection between the structure of the molecule and its ability to attach the electron.

The knowledge of the kinetic data for the low energy electron interaction with halocarbons is very important especially for plasma processes and an environmental protection [1, 2].

Despite a large effort there is still a lack of systematic data which could serve as an experimental basis for verifying theoretical considerations why electrons in thermal equilibrium with the surrounding molecules capture electrons with different efficiencies. The systematic studies of the large homologous group of compounds could help to find general dependencies and the molecular parameters which control the attachment process.

Generally, there exist two approaches to systematize the available rate coefficients. One of them [3] demonstrates that thermal rate coefficients depend on the energy of the electron-attaching state, the other [4] that there is a dependence between rate coefficient and electronic polarizability of the electron attaching center.

2 Experiment

In our investigations the electron swarm method with ionization chamber has been applied as introduced by Christophorou [5]. We have made some modifications which allow to measure the kinetics of the thermal electron attachment process. The full experimental procedures used in these investigations have been described previously [4].

---

[1] Presented at Joint 15th Symposium on Applications of Plasma Processes (SAPP) and 3rd EU-Japan Symposium on Plasma Processing, Podbanské (Slovakia), 15 – 20 January 2005.

[2] E-mail address: kopyra@ap.siedlce.pl

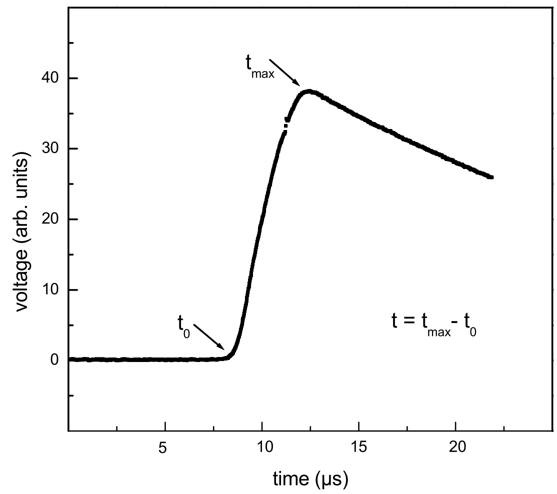

Fig. 1. Example averaged oscilloscope signal.

In brief, the experimental set-up employed for the measurements consists of an ionization chamber with two parallel electrodes, a preamplifier, a fast (50 ns) oscilloscope with digital memory connected with a computer-controlled Canberra-Packard dual $0-5$ kV HV power supply model 3125.

The electron swarm is generated by the ionization of the carrier gas molecules by high-energy α-particles in the plane parallel to the electrodes. The electrons are thermalised fast in elastic and inelastic collisions. The CO_2 was used as a carrier gas due to its very good thermalizing characteristics. Under the influence of the uniform electric field, E, the electrons are directed to the collecting electrode and detected by the time evolution of an electron pulse.

The changes of the electric potential on the collecting electrode are proportional to the number of electrons at a given distance. The presence of an electron acceptor decreases the electron number density. The rate of electron disappearance from the swarm depends on the electron attachment rate coefficient, k (cm^{3}molec.$^{-1}$s^{-1}). This rate coefficient is equal to the electron swarm drift velocity, W (cm s^{-1}), multiplied by the electron attachment coefficient, α. Drift velocity is easy to obtain from the oscilloscope pulse which is shown in Fig. 1. The drift velocity is equal to

$$W = \frac{d}{t}, \tag{1}$$

where d is the known distance between the α source and the collecting electrode, equal to 2 cm, and t is the drift time. Using this drift velocity the rate coefficient for the attachment process can be determined from the shape of the pulse.

The halogenated hydrocarbons were from: CH_3CH_2Cl $(99,7\%)$ Aldrich, CH_2ClCH_2Cl (r.g.) POCH, $CH_2ClCHCl_2$ (97%) Aldrich, $CHCl_2CHCl_2$ (98%) Aldrich, CH_3CHF_2 $(> 99,9\%)$ Merck, CH_3CF_3 (99%) ABCR, CH_2FCF_3 $(> 99\%)$ Aldrich.

In our experiment we have used purified CO_2. As in all previous experiments, to purify the technical carbon dioxide we froze it with liquid nitrogen and pumped out volatile gases. To avoid the less volatile impurities we expounded CO_2 to the chamber from dry ice-methanol bath. We have checked its purity by introducing the gas to the chamber and measuring the rate of electron disappearance from the swarm as described above. It always corresponded to that of non-attaching gas. The other gases were purified by vacuum freeze-pump-thaw technique.

All measurements were carried out at room temperature (293K) in series with constant scavenger-to-carrier gas concentration.

3 Results and discussion

In this contribution we have investigated two groups of substituted haloethanes, with chlorine or fluorine atom(s) in the molecule. The summary of the swarm data are presented in Table 1.

From the representative data in Fig. 2 for $CHCl_2CH_2Cl$-CO_2 mixture it is clear that the value of the rate of electron disappearance depends only on halocarbon concentration. It means that only simple two-body attachment process occurs.

There are several reports on halogenated hydrocarbons regarding the kinetics of the electron attachment process [12-17] but only a few data for chloroethanes are available. The data presented in this paper are in good agreement with the ones obtained by others. Also, which is quite obvious, the rate coefficients increase with the number of substituted chlorine atoms.

Chloroethanes are known to undergo dissociative attachment with low energy electrons. Dissociation leads to the production of a neutral fragment and Cl^- ion [18]. For these substances the dissociative electron attachment (DEA) peak energy of a Cl^- formation decreases when increasing the number of substituted chlorine atoms in the molecule: C_2H_5Cl (1.55 eV [19]), CH_2ClCH_2Cl (0.37 eV [18]), $CHCl_2CH_2Cl$ (0.26 eV [20]), $CHCl_2CHCl_2$ (0.15 eV [20]). At the same time we observe increase in the thermal electron attachment rate coefficients (Table 1). Thus, taking into account both DEA peak energy and thermal electron attachment rate coefficient we can conclude that there is a strong correlation between these values.

To the authors' knowledge no other electron attaching data are available for the fluoroethanes

Tab. 1. Two-body thermal electron attachment rate coefficients.

Molecule	k ($\mathrm{cm^3 molec.^{-1} s^{-1}}$)	$k_{\mathrm{lit.}}$ ($\mathrm{cm^3 molec.^{-1} s^{-1}}$)
CH_3CH_2Cl	3.4×10^{-14}	$< 1.6 \times 10^{-15}$ [6], $\sim 1 \times 10^{-13}$ [7]
CH_2ClCH_2Cl	2.6×10^{-11}	3.2×10^{-11} [8]
$CH_2ClCHCl_2$	1.4×10^{-10}	3.1×10^{-10} [9, 10], 1.8×10^{-10} [11], 2.1×10^{-10} [3]
$CHCl_2CHCl_2$	3.2×10^{-8}	—
CH_3CHF_2	7.6×10^{-13}	—
CH_3CF_3	1.0×10^{-12}	—
CH_2FCF_3	3.7×10^{-12}	—

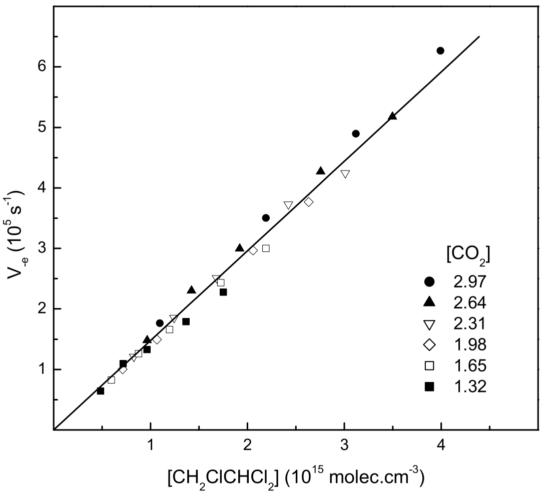

Fig. 2. The rate of electron disappearance for $CH_2ClCHCl_2$ as a function of halocarbon concentration at a few CO_2 concentration [10^{19} molec.cm^{-3}].

used in this study. Kinetics data for low energy electron attachment are available only for the fluoromethanes, i.e., CH_2F_2, CHF_3, CF_4, and perfluoroethane (C_2F_6). However, as we have shown earlier [21], there is a big difference between mechanism of the attachment process in halomethanes as compared with haloethanes or halopropanes [22, 23]. For almost all of them (except the ones with highest attachment coefficient as CCl_4 or $CHCl_3$) we have observed higher than second order kinetics. This was true also for CH_2F_2 and CHF_3 where we have observed the electron attachment not only to single, individual molecules but also to van der Waals dimers such as $(CH_2F_2)_2$ [24] and ($CHF_3 \times CO_2$) [24]. Moreover, the known rate coefficients for the two-body electron attachment to fluoromethanes are extremally small, less than 10^{-13} cm^{3}molec.$^{-1}$s^{-1} (CH_2F_2 - 3.5×10^{-14} [24], CHF_3 - 2.2×10^{-14} [24], CF_4 - $< 10^{-16}$ recommended in [3]). The reason for this is probably because the attachment by van der Waals dimers (homogeneous like for CH_2F_2 or heterogeneous like for CHF_3) is much more effective.

The rate coefficients for thermal electron attachment processes presented in this report for fluoroethanes are two orders of magnitude higher than for fluoromethanes. Also for these compounds the rate coefficient increases with the number of substituted halogen atoms: difluoroethane < trifluoroethane < tetrafluoroethane. The difference in the rate coefficients between fluorine substituted methanes and ethanes shows that not only the number of fluorine atoms but also chain length influences the ability of accepting electron. This is in opposite to our previous finding for the case of 1-chloro- and 1-bromocompounds (from methane to propane) [22, 23] where there was no influence of the chain on the rate coefficients. Also for multi-substituted chloro- and bromo-derivatives the influence of the chain is much smaller (e.g. CH_2Cl_2 and CH_3CHCl_2 - 4.7×10^{-12} [22] and 2.1×10^{-11} cm^{3}molec.$^{-1}$s^{-1} [8], respectively).

In conclusion, we have measured the rate coefficients for seven chloro- and fluoro- substituted ethanes. We have found that, and as expected, the rate coefficients depend on the number of halogen atoms and that this dependence is much stronger in the case of chlorine than fluorine compounds.

References

[1] N. L. Alexandrov, K. V. Vakhrameev, S. V. Dobkin, E. E. Son: *Sov. Tech. Phys. Lett.* **18** (1992) 91

[2] N. L. Alexandrov, S. V. Dobkin, A. N. Konchakov, D. A. Novitskii: *Plasma Phys. Rep.* **20** (1994) 442

[3] L. G. Christophorou: *Zeitschr. Phys. Chem.* **195** (1996) 195

[4] A. Rosa, W. Barszczewska, M. Foryś, I. Szamrej: *Int. J. Mass Spectrom.* **205** (2001) 85

[5] L. G. Christophorou: *Atomic and Molecular Radiation Physics* (Wiley Interscience, New York, 1971)

[6] K. M. Bansal, R. W. Fessenden: *Chem. Phys. Lett.* **15** (1972) 21

[7] G. Datskos, L. G. Christophorou, J. G. Carter: *Gaseous Dielectrics VI* (Plenum Press, New York, 1991)

[8] L. G. Christophorou, R. A. Mathis, D. R. James, D. L. McCorkle: *J. Phys. D* **14** (1981) 1889

[9] D. Smith, P. Spanel: *Adv. Atom. Mol. Opt. Phys.* **32** (1994) 307

[10] D. Smith, C. R. Herd, N. G. Adams: *Int. J. Mass Spectrom. Ion Processes* **93** (1989) 15

[11] D. L. McCorkle, A. A. Christodoulides, L. G. Christophorou: *Gaseous Dielectrics IV* (Pergamon Press, New York, 1984)

[12] G. K. Jarvis, C. A. Mayhew, L. Singleton, S. M. Spyrou: *Int. J. Mass Spectrom. Ion Processes* **164** (1997) 207

[13] H. Shimamori, T. Sunagawa, Y. Ogawa, Y. Tatsumi: *Chem. Phys. Lett.* **232** (1995) 115

[14] T. Sunagawa, H. Shimamori: *J. Chem. Phys.* **107** (1997) 7876

[15] T. Sunagawa, H. Shimamori: *Int. J. Mass Spectrom. Ion Processes* **149/150** (1995) 123

[16] P. Cicman, A. Pelc, W. Sailer, S. Matejcik, P. Scheier, T. D. Märk: *Chem. Phys. Lett.* **371** (2003) 231

[17] P. Spanel, D. Smith: *Int. J. Mass Spectrom.* **205** (2001) 243

[18] K. Aflatooni, P. D. Burrow: *J. Chem. Phys.* **113** (2000) 1455

[19] D. M. Pearl, P. D. Burrow: *J. Chem. Phys.* **101** (1994) 2940

[20] W. Barszczewska, J. Kopyra, J. Wnorowska, I. Szamrej, N. L. Asfandiarov, S. A. Pshenichnyuk, S. A. Fal'ko: *submitted to J. Phys. Chem.*

[21] I. Szamrej, W. Tchórzewska, H. Kość, M. Foryś: *Radiat. Phys. Chem.* **47** (1996) 269

[22] W. Barszczewska, J. Kopyra, J. Wnorowska, I. Szamrej: *J. Phys. Chem. A* **107** (2003) 11432

[23] W. Barszczewska, J. Kopyra, J. Wnorowska, I. Szamrej: *Int. J. Mass Spectrom.* **233** (2004) 199

[24] I. Szamrej, H. Kość, M. Foryś: *Radiat. Phys. Chem.* **48** (1996) 69