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Thermal electron capture by some halopropanes

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Abstract

Thermal electron attachment rate constants for $CF_3CHClCH_3$, $CF_2ClCFClCF_3$ and $CBrF_2CH_2CH_2Br$ have been measured with electron swarm method. Corresponding rate constants are equal to 7.6×10^{-11}, 5.5×10^{-9} and $1.5 \times 10^{-8} \, cm^3 \, molecule^{-1} \, s^{-1}$, respectively. The dissociative electron attachment (DEA) spectra for nine haloalkanes have been determined using negative ion mass spectrometry. The correlation between rate constants, position of the DEA peaks and vertical attachment energy (VAE) available in literature has been demonstrated.
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Keywords: Dissociative electron attachment; Electron swarm; Negative ion mass spectra; Halopropanes; Rate constants

1. Introduction

This paper deals with electron capture processes by halocarbons in the gas phase. There are three main experimental techniques to investigate these processes. The thermal electron capture rate constants and activation energies can be measured using various swarm experiments. The dependence of the cross section for dissociative electron attachment (DEA) on electron energy can be obtained in the beam experiment. The vertical attachment energy (VAE) can be obtained from electron transmission spectroscopy (ETS). These data describe the same process and should be interconnected. This follows from the fact that the rate constant for the thermal electron capture strongly depends on the extent of overlap between the shape and position of DEA cross section peak and the Maxwell–Boltzman distribution of both electron and molecules energies. The DEA peak energy position and cross section, in turn, depend on VAE and partly on an auto-detachment rate.

Moreover, different authors investigate different compounds. Because of a large number of different halocarbons, up to last time there were scarce compounds with all three sets of data available. Again, the data from various laboratories sometimes differ strongly, in the case of swarm experiment the difference in the rate constants quite often is of more than an order of magnitude and new data and some theoretical analysis are required to find the correct values.

First serious attempt to connect these data was made by Christophorou (1996). He has plotted logarithm of the rate constant for thermal electron attachment ($\log(k_{th})$) as a function of VAE and obtained crudely linear dependence for a large set of halocarbons available at that time. Further, Aflatooni et al. (1998, 2000) and Aflatooni and Burrow (2001) have demonstrated that there exists a good correlation between the peak cross section for DEA and VAE for chloro- and chlorofluoroalkanes. They have also calculated the thermal attachment rate constants from their beam data and have shown that they correlate well with the swarm ones and that the $\log(k_{th})$ is a linear function of VAE (Gallup et al., 2003). Recently, Pshenichnyuk et al. (2006) compared DEA and VAE for a set of chloro- and bromoalkanes.

In 1998, the Siedlce group proposed an approach to correlate the thermal attachment rate constants with molecular structure (Foryś and Szamrej, 1998; Szamrej, 1998). It was demonstrated that $\log(k_{th})$ depends linearly on

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electronic polarizability of the attaching center (α_{center}) (see Section 3). It has been also shown that activation energy of the process diminishes with α_{center} and this has been connected with a relative bond change in the transient negative ion as calculated using AM1 method. We have further developed this approach and applied it to much larger group of halocarbons (Rosa and Szamrej, 2000; Pezler and Szamrej, 2001; Barszczewska et al., 2001a, b). We have demonstrated that also VAE depends on α_{center} and using swarm data we have confirmed the cited above finding of Burrow that $\log(k_{th})$ is a linear function of VAE (Barszczewska et al., 2003). In the recent paper we have extended this approach on bromoalkanes (Barszczewska et al., 2004).

This work is a continuation of the program to measure systematically the rate constants for thermal electron capture by haloalkanes using electron swarm method and DEA spectra using NIMS. Up to date, the measurements concentrated mostly on halomethanes and haloethanes. In previous papers, we have presented for the first time the rate constants for 1- and 2-chloropropanes and all four isomers of dichloropropane (Barszczewska et al., 2003), 1- and 2-bromopropanes (Barszczewska et al., 2004) as well as some chlorobromopropanes (Barszczewska et al., 2005).

Here we present the swarm rate constants for further halopropanes. The DEA peaks were measured for nine halocarbons. On this basis and available literature data, we discuss the interdependence of α_{center}, k_{th}, DEA and VAE.

2. Experimental section

This work presents joint effort of Siedlce and Ufa groups to measure rate constants and NIS for the same compounds using the same samples.

An electron swarm method with ionization chamber and carbon dioxide as a carrier gas has been applied for the measurements of the electron capture rate constants. The experimental procedure has been described in detail previously (Rosa et al., 2001). In brief, an experimental set-up consists of an ionization chamber with two parallel electrodes, a preamplifier, a fast oscilloscope with a digital memory connected with a computer and a computer-controlled power supply.

The electron swarm was produced by an ionization of the carrier gas with an α-particle in the plane parallel to electrodes. In carbon dioxide electrons are swiftly thermalized (Szamrej and Foryś, 1989). The electron swarm moves to the collecting electrode under the influence of a uniform electric field causing the change in collecting electrode potential, which increases linearly as electrons move to the electrode in pure CO_2. In the presence of electron acceptor, it declines from linearity due to removal of electrons. The preamplifier output potential is registered on the oscilloscope and saved in a computer memory. The analysis of the peak shape gives the rates of the electron capture at given acceptor concentration and hence the corresponding rate constant.

The electron capture negative ion mass spectrometry has been used to determine the dependence of the electron attachment process relative cross section on the electron energy. We could not measure absolute cross section, so the main result is the energy position of the maximum and the shape of the peak.

Negative ion mass spectra have been obtained using a modified MI-1201 mass spectrometer described in detail in previous papers (Pshenichnyuk et al., 2003; Asfandiarov et al., 2003, 2004). Schematically, the device consists of an anion source (tungsten filament, electron optics and reaction chamber), magnetic analyzer and detection system. In the experiment, an electron beam of the defined energy moved through an equilibrium flow of molecules in the reaction chamber at a pressure ca. 10^{-5} Torr.

The negative ions formed were separated according to the mass to charge ratio using $90°$ magnetic sector analyzer and registered by detection system.

The gases: 1,3,1,1-dibromodifluoropropane was from ABCR (98%), 2,1,1,1-chlorotrifluoropropane and 1,2-dichlorohexafluoropropane were synthesized in the Institute of Organic Chemistry in Warsaw. They were purified by the vacuum freeze-pump-thaw technique. The other gases (used in beam experiment) were from Aldrich Co.

All the rate constants were measured at room temperature (293 ± 3 K).

The dependence of the electron capture rate on the 2,1,1,1-chlorotrifluoropropane concentrations at different concentrations of carbon dioxide is shown in Fig. 1. One
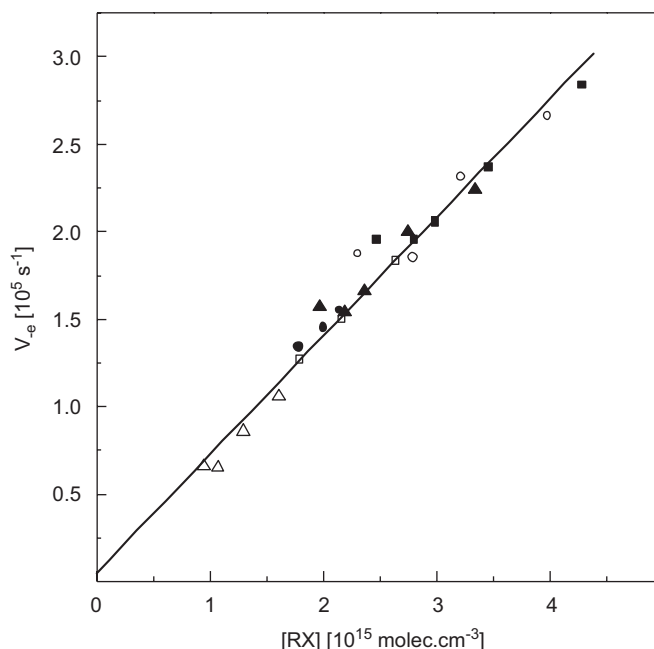

Fig. 1. The rate of electron disappearance from the swarm for $CH_3CHClCF_3$ as a function of halocarbon concentration at a few concentrations of carbon dioxide: ■—3.15, ○—2.94, ▲—2.48, ●—2.26, □—1.99, △—1.19 × 10^{19} molec. cm^{-3}.

can see that it does not depend on carbon dioxide pressure, which again shows that CO_2 does not contain impurities influencing the rate constants. Also, we did not observe peaks from impurities in the beam experiment.

3. Results and discussion

The swarm rate constants for 1,1-difluoro-1,3-dibromopropane, 1,1,1-trifluoro-2-chloropropane and 1,1,1,2,3,3-hexafluoro-2,3-dichloropropane have been measured. The obtained rate constants are presented in Tables 1 and 2 together with available literature data for haloalkanes, which are necessary for further discussion.

The negative ions spectra (NIS) have been measured for nine halocarbons. The example spectra for 2,1,1,1-chlorotrifluoropropane and 2,1,1,1-bromotrifluoropropane are shown in Fig. 2.

The positions of maxima of the DEA peaks are collected in Tables 1 and 2 together with the available literature ones. Also, literature data for VAE have been included for forthcoming discussion.

Let us start the discussion with bromopropane isomers. As can be seen from Table 2, changing a position of bromine atom in bromopropane from 2 to 1 causes an increase in the thermal electron capture rate constant by an order of magnitude (from 1.4×10^{-12} to 1.1×10^{-11} $cm^3 molec.^{-1} s^{-1}$) and in the same time lowering the peak position of NIS from 0.9 to 0.6 eV. This is understood if both LUMO and ground state potential energy curve crossing lies lower for 1-bromopropane than for 2-bromopropane. This is not quite evident as experimental VAE goes opposite way (1.23 and 1.3 eV, cf. Table 1). However, this difference seems not to be meaningful and should be rather caused by an experimental error. Fig. 3a

Table 1
Rate constants for thermal electron capture, k_{th}, positions of the maxima on negative ion spectra, E_{DEA}, and VAE for a set of chloro- and chlorofluoroalkanes

Molecule	α_{center} $(10^{-24} cm^3)$	k_{th} [a] $(cm^3 molec.^{-1} s^{-1})$	VAE (eV)	E_{DEA} (eV)	E_{DEA} [b] (eV)
Chloromethane	2.18	2×10^{-13}	3.4 [c,d]	0.8[d]	
Chloroethane	2.18	5×10^{-13}	2.41 [e]	1.55 [d]	
1-chloropropane	2.18	3.6×10^{-13}	2.4 [d]	1.5 [d]	
1-chlorobutane	2.18		2.39[f]	1.54d]	
1-chloropentane	2.18		2.26[f]	1.47[d]	
1-chlorooctane	2.18		2.24[f]	1.45[d]	
1-chlorononane	2.18		2.23[f]	1.34[d]	
2-chloropropane	2.18	3.8×10^{-12}	1.97 [e]	1.58 [d]	
2-chlorobutane	2.18		2.05[f]	1.51[d]	
t-butylchloride	2.18		1.8[f]	1.55[d]	
c-butylchloride	2.18		1.98[f]	1.19[d]	
c-pentylchloride	2.18		1.93[f]	1.52[d]	
c-hexylchloride	2.18		2.31[f]	1.43[d]	
dichloromethane	4.36	4.7×10^{-12}	1.01 [c,e]	0.43 [f]	
1,1-dichloroethane	4.36	2.1×10^{-11}	1.36 [e,f]	0.96 [f]	
1,2-dichloroethane	3.27	2.9×10^{-11}	1.7 [f]	0.37 [f]	
1,1-dichloropropane	4.36	5.7×10^{-11}	1.39 [e,f]	0.9[f],0.81[g]	
1,2-dichloropropane	3.27	8.1×10^{-12}	1.64 [e,f]	0.76 [f]	
1,3-dichloropropane	2.62	2×10^{-12}	1.91 [e,f]	1.14 [f]	
2,2-dichloropropane	4.36	6.3×10^{-12}	1.41 [e,f]	1.16 [f]	1,1
trichloromethane	6.54	2.7×10^{-9}	0.42 [c,e]	0.27[f]	
1,1,1-trichloroethane	6.54	1.4×10^{-8}	0.64 [e,f]	0.61 [f]	
1,1,2-trichloroethane	5.45	2×10^{-10}	0.94 [e]	0.36 [f]	0.3
1,1,1,2-tetrachloroethane	7.63	1×10^{-6}	0.63 [e]		0.1
1,1,2,2-tetrachloroethane	6.54	3.3×10^{-8}	0.5 [e]	0.2[g]	
Chlorodifluoromethane	3.30	1.1×10^{-13}	2.11 [c]	1.27 [c]	
Chlorotrifluoromethane	3.86	2.1×10^{-13}	1.83 [c]	1.4 [c]	
Dichlorofluoromethane	4.92	5.5×10^{-12}	0.94 [c]		
Trichlorofluoromethane	7.10	2.1×10^{-7}	0.47 [c]	0.15 [c]	
Dichlorodifluoromethane	5.48	1.6×10^{-9}	0.97 [c]	0.71 [c]	
Chloropentafluoroethane	4.98	4.8×10^{-9}			0. 6
1,1,1-chlorodifluoroethane	3.30	6×10^{-13}			1.2
2,1,1,1-chlorotrifluoropropane	3.02	7.6×10^{-11} [b]			0.7
1,1,1-trichlorotrifluoroetane	7.38	2.2×10^{-7}			0.0
1,1,2-trichlorotrifluoroethane	6.57	5.4×10^{-9}			0.3
1,2-dichlorohexafluoropropane	5.01	5.5×10^{-9} [b]			

The α_{center} values were calculated using $\alpha_F = 0.56$ and $\alpha_{Cl} = 2.18 \times 10^{-24} cm^3$ (from CRC Handbook of Chemistry and Physics, 1992–93).
[a]—Barszczewska et al., 2003; [b]—Present results; [c]—Aflatooni and Burrow, 2001; [d]—Pearl and Burrow, 1994; [e]—Aflatooni et al., 2000; [f]—Aflatooni and Burrow, 2000; [g]—Pshenichnyuk et al., 2006.

Table 2
Rate constants for thermal electron capture, k_{th}, positions of the maxima on negative ion spectra, E_{DEA}, and VAE for a set of bromoalkanes

Molecule	α_{center} (10^{-24} cm^3)	k_{th} [a] (cm^3 molec.$^{-1}$ s^{-1})	VAE (eV)	E_{DEA} (eV)
bromoethane	3.05	5.3×10^{-12}	1.26[c]	0.6[c,d]
1-bromopropane	3.05	1.1×10^{-11}	1.3 [c]	0.65[c]0.6 [e]
2-bromopropane	3.05	1.4×10^{-12}	1.23[c]	0.9[c] 0.9[e]
1,2-bromofluoroethane	3.33	5×10^{-11}		0.4[e]
1,2-bromochloroethane	4.14	4.5×10^{-10}	1.41[d]	0.2 [e]
1,2-dibromoethane	4.58	1.8×10^{-8}	1.06[d]	0.1[d]
2,1-bromochloropropane	4.14	3.5×10^{-10}[e]		0.3 [e]
1,3-bromochloropropane	3.49	2.5×10^{-10}[e]		0.4[e]
1,1,2,2,2-bromochlorotrifluoro ethane	6.07	7×10^{-8}[f]		0.05[e]
2,1,1,1-bromotrifluoropropane	3.89	4.1×10^{-10}[g]		0.3[b]
1,3,1,1-dibromodifluoropropane	3.66	1.5×10^{-8}[b]		

The α_{center} values were calculated using $\alpha_F = 0.56$, $\alpha_{Cl} = 2.18$ and $\alpha_{Br} = 3.05 \times 10^{-24}$ cm^3. (from CRC Handbook of Chemistry and Physics, 1992–93).
[a]—Barszczewska et al., 2004; [b]—Present results; [c]—Modelli and Jones, 2004; [d]—Pshenichnyuk et al., 2006; [e]—Barszczewska et al., 2005; [f]—Barszczewska et al., 2001; [g]—Szamrej et al., 2004.
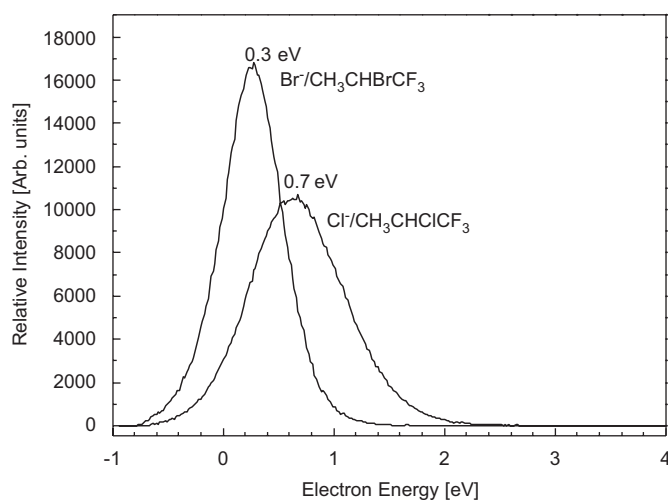
Fig. 2. Negative ion spectra for CH$_3$CHBrCF$_3$ and CH$_3$CHClCF$_3$.

shows the potential curves calculated using semi-empirical SCF PM3 method. One can see, that the calculated C–Br bond distance, 1.95 A ($\sim$1.93), as well as bond energy, 2.6 eV (2.9$\pm$0.2), and Br electron affinity, 3.8 eV (3.4) agree quite well (within 10%) with the experimental ones shown in parentheses (CRC Handbook of Chemistry and Physics, 1992–93). Usually, for comparison purposes in a series of compounds, equilibrium anion curves are considered as we have made it previously to analyze the elongation of the halogen–carbon bond due to formation of a negative ion in a set of chloro- and chlorofluoroalkanes (Barszczewska et al., 2004). However, the formation of the negative ion occurs fast enough to suppose that the structure of the excited negative ion on formation resembles rather that of the molecule than equilibrium one. Therefore, we have calculated Morse curves for both situations: 1° calculating the equilibrium structure for the negative ion and then the Morse curve for C–Hal bond at the rest of the ion "frozen" ("equilibrium anion" curve in Figs. 3a and 4) and 2° calculating the equilibrium structure for a neutral mole-

cule, changing its charge to −1 and again calculating the Morse curve at the rest of such anion "frozen" ("non-equilibrium anion" curve in Figs. 3a and 4). Because potential energy curves crossing for the molecule and the non-equilibrium anion in Fig. 3a is not clearly visible, we have enlarged this part in Fig. 3b.

An inspection of Figs. 3a and b shows that the energy of the curve crossing for both the equilibrium and non-equilibrium structure of the negative ion lowers on going from 2- to 1-bromopropane, which is compatible with corresponding increase in the thermal electron attachment rate constant. The VAE value (for equilibrium configuration), with which DEA energy should be connected, also follows this pattern.

Similar curves for 1- and 2-chloropropane are shown in Fig. 4. They were calculated using SCF AM1 method, more suitable for chlorine containing compounds. One can see, that the calculated C–Cl bond distance, 1.78 A ($\sim$1.8), as well as bond energy, 3.6 eV (4.1$\pm$0.3), and Cl electron affinity, 3.6 eV (3.6) agree quite well (within 10%) with the experimental ones shown in parentheses (CRC Handbook of Chemistry and Physics, 1992–93). In this case the experimental thermal rate constants increase and compatibly VAE values diminish on going from 1- to 2-chloropropane (from 3.6×10^{-13} to 3.8×10^{-12} cm^3 molec.$^{-1}$ s^{-1} and from 2.4 to 1.97 eV, respectively) while changes in DEA energy seem to be in the error range (1.5 and 1.58 eV). This time the neutral–non-equilibrium anion curve crossing lies lower for 2-chloro- than for 1-chloropropane while that for equilibrium one lies higher. Thus, only supposition that non-equilibrium anion–neutral curve crossing energy is responsible for observed changes in thermal electron capture efficiency correctly describes both cases.

An addition of chlorine in position 3 in 1-bromopropane (CH$_2$ClCH$_2$CH$_2$Br) causes a lowering in the DEA peak energy from 0.6 to 0.37 eV. At the same time, this increases the rate constant by an order of magnitude (from 1.1×10^{-11} to 2.5×10^{-10} cm^3 molec.$^{-1}$ s^{-1}).

a

$D_e = 2.6 (2.9\pm0.2)$ eV

equilibrium anion

$EA(Br) = 3.8 (3.4)$ eV
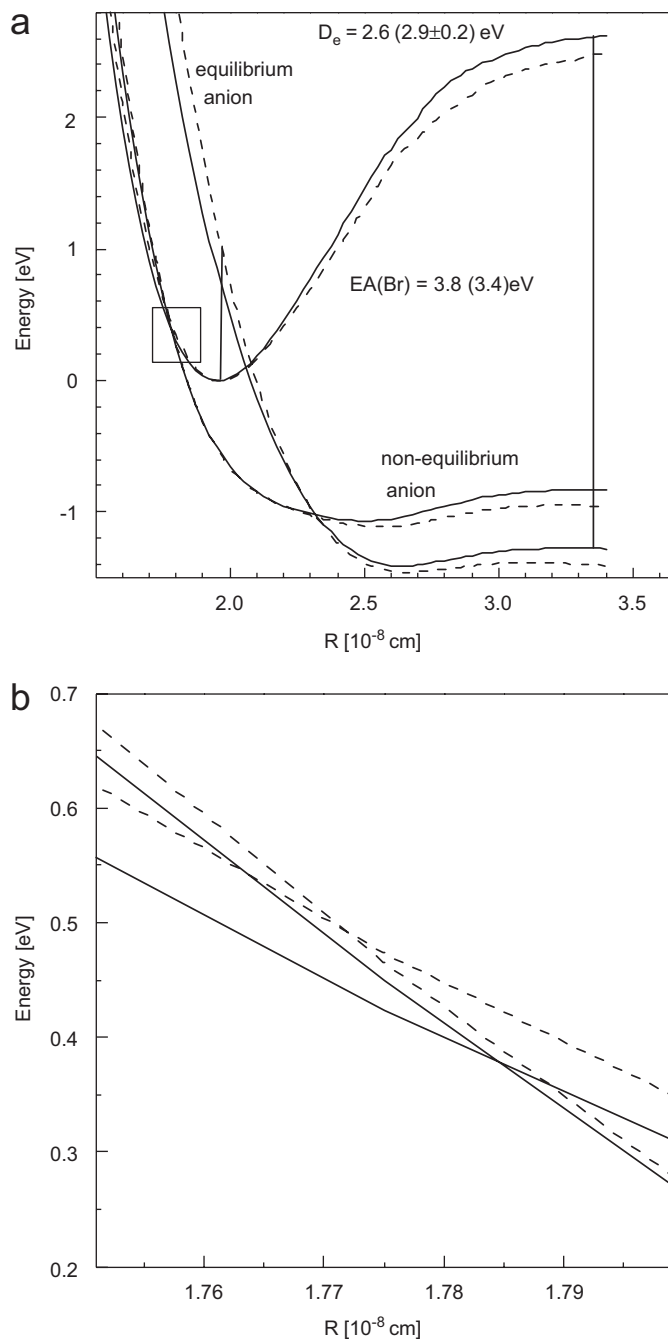
non-equilibrium anion

b

Fig. 3. (a) Morse curves for bromopropanes and their negative ions: 1-bromopropane—solid lines, 2-bromopropane—dash lines. (b) Potential energy curves crossing for molecules and non-equilibrium anions (marked area in Fig. 4a).

$D_e = 3.6 (4.1\pm0.3)$ eV

equilibrium anion

$EA(Cl) = 3.6 (3.6)$ eV

non-equilibrium anion

Fig. 4. Morse curves for chloropropanes and their negative ions: 1-chloropropane—solid lines, 2-chloropropane—dash lines.

Barszczewska et al., 2004) is three-orders of magnitude (7.1×10^{-9} and 6.6×10^{-12} cm^3 molec.$^{-1}$ s^{-1}). Thus, one can conclude that the shorter the distance between haloatoms the stronger the influence of the chlorine atom on the electron capture process by bromoalkane. This we will keep in mind in further discussion.

The rate constant for the thermal electron capture by CF$_2$ClCFClCF$_3$ is quite high (5.5×10^{-9} cm^3 molec.$^{-1}$ s^{-1}), as expected for fully halogenated propane. The DEA position and VAE value are still to be measured.

Now we will discuss the interdependence of k_{th}, DEA position and VAE value using quite large set of these values available now, which are collected in Tables 1 and 2. The rate constants values have been taken from Barszczewska et al., 2003, 2004; Szamrej et al., 2004. Where possible, we used the average values as calculated therein. There are only single values for VAE in each case while in some cases two or three data exist for DEA energy. The last ones do not differ meaningfully so for further discussion we use the mean values.

Fig. 5 shows the dependence of DEA position on VAE value. One can see that there exists general linear dependence extrapolating as expected to zero. The data lie in the same range of scattering for all three groups of compounds. The scattering can be explained on the grounds of difference between the autodetachment lifetimes for different negative ions as mentioned above. The connection between VAE and DEA has been first discovered by Burrow's group (Aflatooni et al., 2000). They have demonstrated then the exponential dependence of the DEA peak cross section on VAE for a set of chloroalkanes. Further they have extended this finding to a
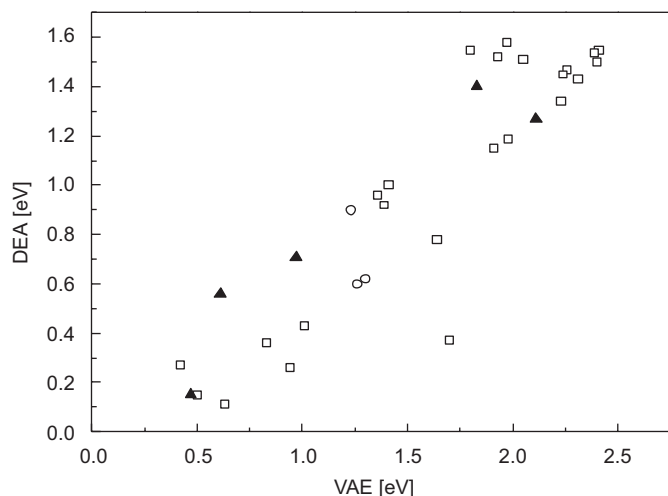
An addition of chlorine in neighboring position to Br in 2-bromopropane (CH$_2$ClCHBrCH$_3$) causes an increase in the rate constant by two-orders of magnitude (from 1.4×10^{-12} to 3.5×10^{-10} cm^3 molec.$^{-1}$ s^{-1}) and correspondingly an appreciable decrease in the DEA peak position from 0.9 to 0.3 eV. The ratio of the rate constants for CH$_2$BrCl (Sunagawa and Shimamori, 1997), the only available data for chlorine and bromine placed at the same carbon atom, and CH$_3$Br (Christophorou et al., 1984;

Fig. 5. The DEA peak position as a function of VAE value: □—chloroalkanes, ▲—chlorofluoroalkanes and ○—bromoalkanes.

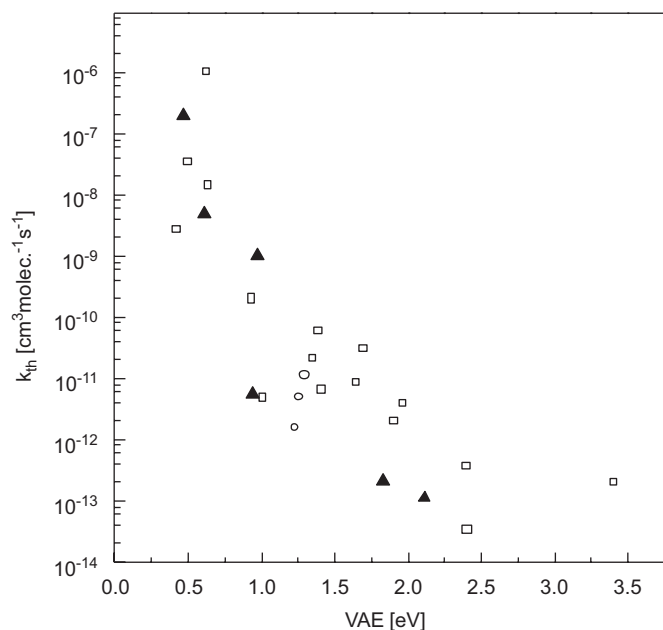
Fig. 6. The k_{th} plot vs. VAE value: □—chloroalkanes, ▲—chlorofluoroalkanes and ○—bromoalkanes.

larger set of chloroalkanes (Aflatooni and Burrow, 2000, 2001) and several chlorofluoromethanes (Aflatooni and Burrow, 2001).

Fig. 6 shows the dependence of the thermal electron attachment rate constant, k_{th}, on the VAE value. We observe the general linear dependence of $\log(k_{th})$ on VAE, with different slopes for chloro- and chlorofluoroalkanes. For bromoalkanes, there is too little data to discuss the functional dependence but still they lie in between the other data. Nevertheless, it shows that the potential curves crossing energy (cf. discussion on Figs. 3 and 4) which determines the activation energy of the thermal process ($\log(k_{th})$) depends linearly on VAE. Gallup et al. (2003), have calculated the thermal attachment rate constants from

their DEA peaks for a set of polychloroalkanes and obtained also similar linear dependence.

Fig. 7 shows the dependence of the thermal electron attachment rate constant, k_{th}, on the DEA position. We again observe the general linear dependence of $\log(k_{th})$ on DEA position with similar slopes for chloro- and bromoalkanes and rather different for chlorofluoroalkanes. In this case the correlation is much better which shows that the link between potential curves crossing energy which determines the activation energy of the thermal process ($\log(k_{th})$) and DEA position is more straightforward than that with VAE value.

Now we will discuss the relationship between these experimental results and the molecular characteristics of the compounds forming molecular negative ions. As it was briefly announced in Section 1, in the previous papers the idea has been formulated that the logarithm of the thermal attachment rate constant depends linearly on the electronic polarizability of the attaching center (Barszczewska et al., 2001a, b, 2003, 2004). We have explained this by supposing that the higher the polarizability the lower the crossing point of the Morse curves for neutral molecule and the intermediate parent negative ion.

To proceed farther we should repeat our definition of the attaching center. Namely, this is that part of the molecule, which is immediately connected with the attachment process. In the case of haloalkanes polarizability of the attaching center, α_{center}, is a sum of electronic polarizabilities of the halogen atoms calculated using additivity rule. We do not take into account polarizabilities of carbon and hydrogen atoms. For halogens placed at neighboring carbon atoms, the best correlation is obtained if we calculate first the summary polarizabilities at each carbon
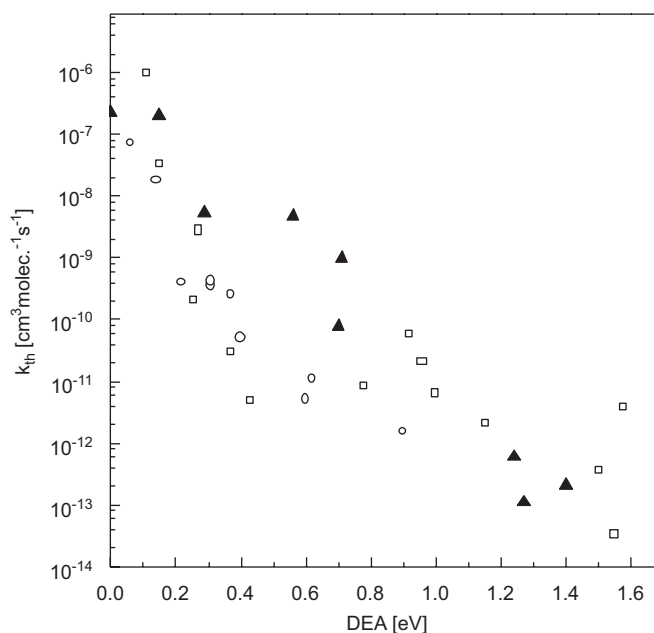

Fig. 7. The k_{th} plot vs. DEA position: □—chloroalkanes, ▲—chlorofluoroalkanes and ○—bromoalkanes.

and then take the higher value with coefficient 1 while the other one with coefficient 0.5. The polarizabilities of halogens in position 3; e.g., chlorine in $CH_2ClCH_2CH_2Br$, are taken with coefficient 0.2. The calculated α_{center} values are shown in Tables 1 and 2. This is compatible with the fact that the main anion in NIS is that with the highest α and electron capture occurs at the carbon atom with the highest summary α of the halogen atoms. Thus, the halogen atoms at other carbon do not take a part in the electron capture but only "help" this process proportionally to their proximity.

Fig. 8 shows that VAE strongly depends on the polarizability of the attaching center as defined above for both chloro- and chlorofluoroalkanes. There are only three values for bromoalkanes at the same α_{center} but still they lie in the same range as the data for other groups.
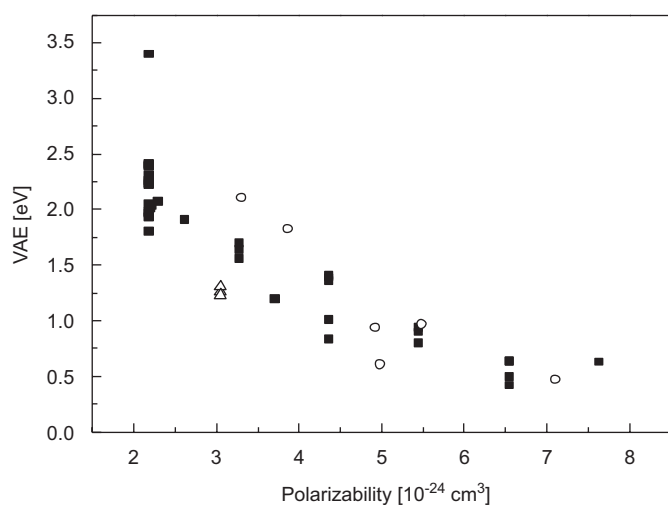
Figs. 9–11 demonstrate the dependence of DEA and k_{th} on α_{center} for chloroalkanes, chlorofluoroalkanes and bromoalkanes, respectively. In all cases, we observe clearly the exponential dependence of k_{th} and generally the linear one of DEA on α_{center}, similarly as that of VAE. Thus, we can state that in the first approximation or, in other words, on the large scale, the summary electronic polarizability of halogen atoms at the attaching center determines the position of the potential curve for the forming intermediate molecular anion. Hence it determines the VAE value, DEA position and the energy of the neutral and anion Morse curves crossing, the last corresponding the activation energy of electron capture by thermal electrons and thus the value of k_{th}. However, the scattering of the results cannot be explained purely by the experimental errors. We believe that it should be caused by other factors,

Fig. 8. The dependence of the VAE value on the polarizability of attaching center: □—chloroalkanes, ▲—chlorofluoroalkanes, ○—bromoalkanes.
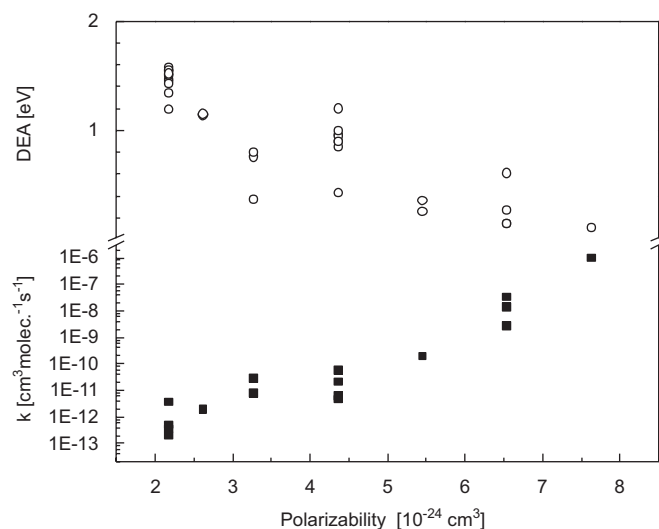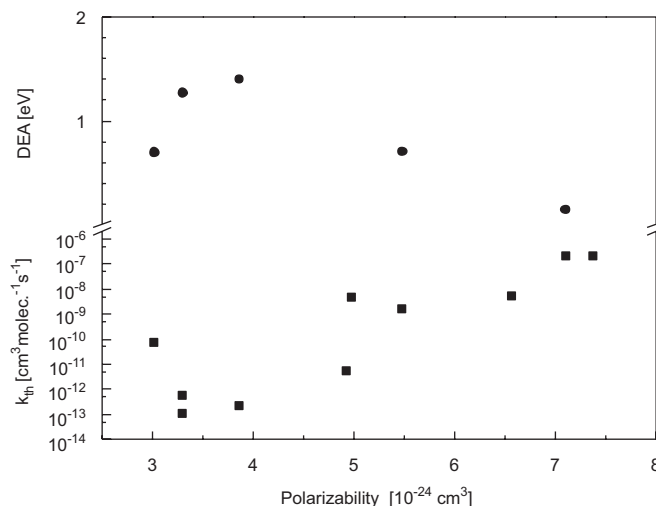

Fig. 10. The dependence of DEA (●) and k_{th} (■) on the polarizability of attaching center for chlorofluoroalkanes.

Fig. 9. The dependence of DEA (●) and k_{th} (■) on the polarizability of attaching center for chloroalkanes.
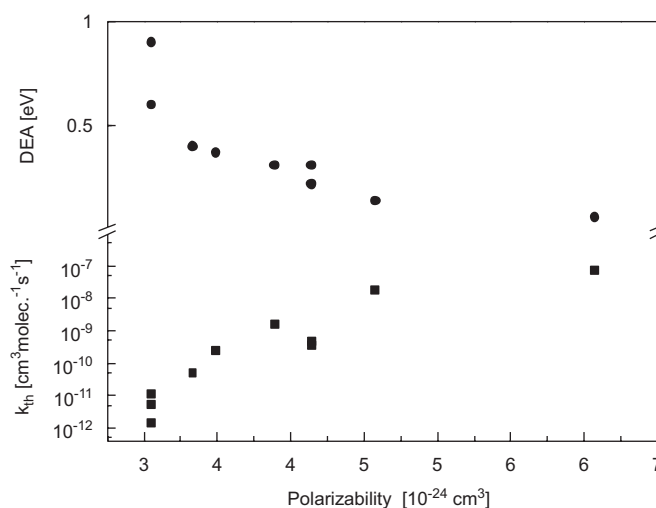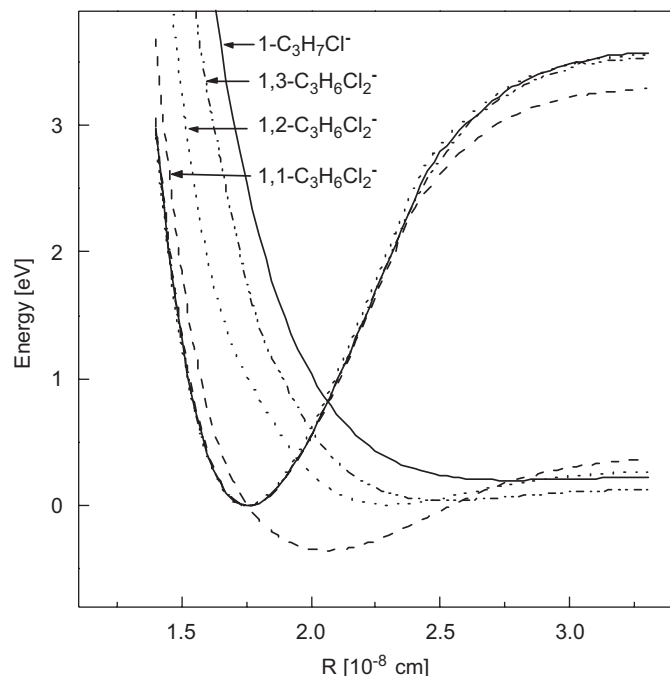

Fig. 11. The dependence of DEA (●) and k_{th} (■) on the polarizability of attaching center for bromoalkanes.

Fig. 12. Potential energy curves for molecules and negative ions: 1-C_3H_7Cl—solid, 1,1-$C_3H_6Cl_2$—dashed, 1,2-$C_3H_6Cl_2$—dotted and 1,3-$C_3H_6Cl_2$—dashed-dotted lines.

such as steric ones as in the case of halopropane isomers or the different lifetime of the resulting anion against autoionization.

In our previous papers, we have thoroughly analyzed the behavior of the negative ions in haloalkanes using AM1 and PM3 methods to justify the link between the α_{center} and effectiveness of the electron capture. We have demonstrated that additional electron in the intermediate anion causes elongation of the C–Hal bond, as in Figs. 3 and 4. This elongation diminishes from fluorine to bromine, accordingly to increasing α_{Hal}. This, in turn, increases k_{th} and lowers both DEA and VAE. Increasing the α_{center} by increasing the number of halogen atoms again strongly shortens the equilibrium distance causing the same effect. Fig. 12 shows that the bond length in the negative ion shortens and correspondingly crossing point goes down strongly when going from 1-C_3H_7Cl to 1,1-$C_3H_6Cl_2$. This figure shows also that the influence of the second chlorine atom decreases strongly with the distance from the first one, which justifies using coefficients 1, 0.5 and 0.2 for positions 1.1, 1.2 and 1.3, respectively.

4. Conclusions

New rate constants as well as negative ion mass spectra have been measured for halocarbons.

Interdependences between thermal electron capture rate constants, DEA and VAE for haloalkanes have been shown. All of them are linear and despite of the scattering the same for all analyzed compounds.

Dependences on polarizability are exponential for k_{th} and linear for DEA (the same has been observed for VAE), but different in shape for each analyzed group of compounds—chloro-, chlorofluoro- and bromoalkanes.

The explanation of the method we have used for calculating electronic polarizabilities of the attaching center has been made on the basis of shortening of the (C–Hal) bond in the anion caused by additional halogen atoms.

References

Aflatooni, K., Burrow, P.D., 2000. Total cross sections for dissociative electron attachment in dichloroalkanes and selected polychloroalkanes: the correlation with vertical attachment energies. J. Chem. Phys. 113, 1455–1464.

Aflatooni, K., Burrow, P.D., 2001. Dissociative electron attachment in chlorofluoromethanes and the correlation with vertical attachment energies. Int. J. Mass Spectrom. 205, 149–161.

Aflatooni, K., Gallup, G.A., Burrow, P.D., 1998. Dissociative electron attachment in chloroalkanes and the correlation with vertical attachment energies. Chem. Phys. Lett. 282, 398–402.

Aflatooni, K., Gallup, G.A., Burrow, P.D., 2000. Temporary anion states of dichloroalkanes and selected polychloroalkanes. J. Phys. Chem. 104, 7359–7369.

Asfandiarov, N.L., Pshenichnyuk, S.A., Fal'ko, V.S., Wnorowska, J., Wnorowski, K., Szamrej, I., 2003. Electron capture negative ion mass spectra of some Freon derivatives. Nukleonika 48, 83–88.

Asfandiarov, N.L., Pshenichnyuk, S.A., Fokin, A.I., Nafikova, E.P., 2004. Temperature dependence of mean autodetachment lifetime of molecular negative ion of p-benzoquinone molecule. Chem. Phys. 298, 263–266.

Barszczewska, W., Rosa, A., Kopyra, J., Szamrej, 2001a. Electron attachment processes in gas mixtures containing haloethanes. Res. Chem. Intermed. 27, 699–707.

Barszczewska, W., Kopyra, J., Wnorowska, J., Szamrej, I., Foryś, M., 2001b. Thermal electron capture by some halocarbons. In: Christophorou, L.G., Olthoff, J. (Eds.), Gaseous Dielectrics, vol. IX. Kluwer Academic/Plenum Publishers, New York, pp. 75–78.

Barszczewska, W., Kopyra, J., Wnorowska, J., Szamrej, I., 2003. Low energy electron attachment by chloroalkanes. J. Phys. Chem. A 107, 11427–11432.

Barszczewska, W., Kopyra, J., Wnorowska, J., Szamrej, I., 2004. Low energy electron attachment by bromoalkanes. Int. J. Mass Spectrom. 233, 199–205.

Barszczewska, W., Kopyra, J., Wnorowska, J., Szamrej, I., Asfandiarov, N.L., Pshenichnyuk, S.A., Fal'ko, S.A., 2005. Thermal electron capture by some chlorobromopropanes. Eur. Phys. J. D 35, 323–327.

Christophorou, L.G., 1996. The dependence of the thermal electron attachment rate constant in gases and liquids on the energy position of the electron attaching state. Z. Phys. Chem. 195, 195–215.

Christophorou, L.G., McCorkle, D.L., Christodoulides, A.A., 1984. Electron attachment processes. In: Christophorou, L.G. (Ed.), Electron–Molecule Interactions and their Applications, vol. 1. Academic Press Inc., Orlando, pp. 478–617.

CRC Handbook of Chemistry and Physics, 1992–1993. 73rd ed. CRS Press, Boca Raton, FL.

Foryś, M., Szamrej, I., 1998. The dependence of electron capture rate constants on some molecular parameters. J. Radioanal. Nucl. Chem. 232, 67–69.

Gallup, G.A., Aflatooni, K., Burrow, P.D., 2003. Dissociative electron attachment near threshold, thermal attachment rates, and vertical attachment energies of chloroalkanes. J. Chem. Phys. 118, 2562–2574.

Modelli, A., Jones, D., 2004. Empty level structure and dissociative electron attachment cross section in saturated and unsaturated bromohydrocarbons. J. Phys. Chem. 108, 417–424.

Pearl, D.M., Burrow, P.D., 1994. Dissociative attachment in selected monochloroalkanes. J. Chem. Phys. 101, 2940–2948.

Pezler, B., Szamrej, I., 2001. Geometry and energy changes in halomethanes due to electron capture. Res. Chem. Intermed. 27, 787–794.

Pshenichnyuk, S.A., Asfandiarov, N.L., Fal'ko, V.S., Lukin, V.G., 2003. Temperature dependence of dissociative electron attachment to molecules of gentisic acid, hydroquinone and *p*-benzoquinone. Int. J. Mass Spectrom. 227, 281–288.

Pshenichnyuk, S.A., Pshenichnyuk, I.A., Nafikova, E.P., Asfandiarov, N.L., 2006. Dissociative electron attachment in selected haloalkanes. Rapid Commun. Mass Spectrom. 20, 1097–1103.

Rosa, A., Szamrej, I., 2000. Thermal electron capture in the mixtures of halocarbons and environmental gases. J. Phys. Chem. A 104, 67–71.

Rosa, A., Barszczewska, W., Foryś, M., Szamrej, I., 2001. Electron capture by haloethanes in a carbon dioxide buffer gas. Int. J. Mass Spectrom. 205, 85–92.

Sunagawa, T., Shimamori, H., 1997. Low-energy electron attachment to brominated methanes. J. Chem. Phys. 107, 7876–7883.

Szamrej, I., 1998. The dependence of electron capture rate constants on electronic polarizability. In: Christophorou, L.G., Olthoff, J. (Eds.), Gaseous Dielectrics, vol. VIII. Kluwer Academic/Plenum Publishers, New York, pp. 63–72.

Szamrej, I., Foryś, M., 1989. Electron swarm method as a tool to investigate multi-body electron attachment processes. Radiat. Phys. Chem. 33, 393–400.

Szamrej, I., Foryś, M., Asfandiarov, N.L., 2004. Low energy electron attachment by haloalkanes. In: Christophorou, et al. (Eds.), Gaseous Dielectrics, vol. X. Springer, New York, pp. 29–33.