

Electron driven processes in chlorodifluoroacetic acid methyl ester^{*}

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Received 31 January 2014 / Received in final form 29 April 2014

Published online 29 July 2014

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Abstract. Dissociative electron attachment to gas phase 2-chloro-2,2-difluoroacetic acid methyl ester (CClF₂COOCH₃) is studied by means of a crossed beams apparatus. Effective cleavage of the C-Cl bond is observed within a broad resonance in the energy range 0–1 eV and visible via the appearance of the light fragment Cl⁻. In chlorodifluoroacetic acid cleavage of the C-Cl bond was observed not only via the Cl⁻ anion formation but predominantly via expulsion of the neutral chlorine atom leading to the formation of the (M-Cl)⁻ anion. Similar to the previously studied esters CF₃COOCH₃ and CF₃COOC₂H₅ [I. Martin, J. Langer, E. Illenberger, *Z. Phys. Chem.* **222**, 1185 (2008)], we observe reaction due to the cleavage of the ester bond resulting in the formation of the closed shell (M-CH₃)⁻ anion.

1 Introduction

The investigation of collisions between electrons and neutral molecules is of high importance in fundamental sciences such as radiation chemistry, astrophysics, chemistry of the upper atmosphere, materials science and plasma physics [1]. Owing to many industrial applications dissociative processes received a great deal of interest in recent years, among them dissociative electron attachment (DEA).

In this respect a particular attention has been paid to organic compounds, e.g., organic acids such as formic acid (HCOOH) [2] and acetic acid (CH₃COOH) [3]. A main goal of various studies was to unravel the molecular mechanism of electron induced decomposition, which in both of these molecules is characterised by a pronounced resonance at very low energy peaking at 1.25 and 1.5 eV, respectively. This resonance decomposes into the closed shell anion (M-H)⁻ by the loss of a neutral hydrogen atom. Studies of formic acid and its partly deuterated isotopomers have shown that hydrogen abstraction occurs from the -COOH site [4]. However, according to the theory there are two possible mechanisms that can be implicated. The first mechanism concerns the initial localisation of the excess charge at the π^* orbital of the carboxylic group [5] followed by the π^*/σ^* coupling prior to dissociation that requires a symmetry-breaking molecular deformation. Another mechanism assumes localisation of the excess charge

directly at the O-H site involving a σ^* orbital of the hydroxyl group [6], however, at extreme conditions with respect to energy and autodetachment lifetime of the resonance (the resonance energy and width has been predicted to be as large as 5.3 and 5.8 eV, respectively). More recent experimental studies on various deuterated isotopomers of formic acid indicate that a direct electron attachment into σ^* orbital is more favorable than the initial localisation of an excess electron at the π^* orbital of the carboxylic group [7].

In the case of halosubstituted organic acids the respective resonances of (M-H)⁻ (where M is the neutral molecule) are shifted to lower energy with respect to those observed from non-halogenated organic acids. In addition, due to the high electron affinity of the halogen atoms further and often more intense fragments are generated at this low energy domain. As an example, in the case of CF₃COOH [8] the loss of HF is observed as the second most dominant decomposition channel at around 1 eV, while for the chloro-containing compounds namely CClF₂COOH [9,10] and CCl₃COOH [10] there are two complementary fragments Cl⁻ and (M-Cl)⁻, which are produced within the highest intensity already at energy close to 0 eV.

In this contribution we will present the results from low energy electron driven reactions in methyl ester of 2-chloro-2,2-difluoroacetic acid (CClF₂COOCH₃) and compare with those obtained from various pure and halo-substituted organic acids. As will be demonstrated in the following, methyl ester of chlorodifluoroacetic acid effectively captures electrons resulting in the formation of both shape and core excited resonances, which decompose into CClF₂COO⁻, CClFCOO⁻, CF₂COO⁻, (CClFCOOCH₂)⁻, CF₂⁻, CH₃O⁻/CF⁻, Cl⁻, F⁻ and O⁻.

^{*} Contribution to the Topical Issue “Electron and Positron Induced Processes”, edited by Michael Brunger, Radu Campeanu, Masamitsu Hoshino, Oddur Ingólfsson, Paulo Limão-Vieira, Nigel Mason, Yasuyuki Nagashima and Hajime Tanuma.

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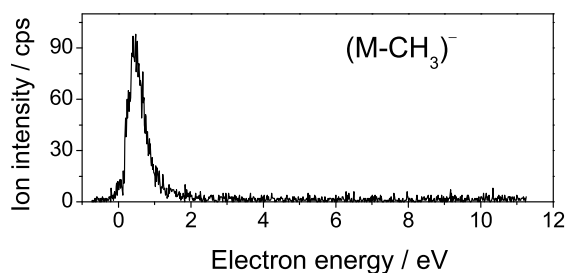


Fig. 1. Ion yield curve for the DEA reaction resulting from the cleavage of the ester bond thus generating the closed shell anion $(M-CH_3)^-$.

2 Experimental procedure

The experiments were carried out with an electron/molecule crossed beams apparatus. It consists of an oven, a trochoidal electron monochromator and a quadrupole mass spectrometer. Briefly, an incident electron beam of well-defined energy (FWHM ≈ 240 meV, electron current ≈ 10 nA) generated from a trochoidal electron monochromator orthogonally intersects with an effusive molecular beam. The molecular beam emanates from a capillary, which is directly connected to the collision chamber. The sample of 2-chloro-2,2-difluoroacetic acid methyl ester ($CClF_2COOCH_3$) is liquid under normal conditions and hence was introduced into the vacuum chamber via the inlet system both maintained at 320 K in order to obtain sufficiently high vapour pressure and prevent the molecules from condensation at the surface of the electrode. The pressure of the molecules in the gas phase was in the range of 10^{-6} mbar, as measured by an ionisation gauge mounted at one of the flanges.

The ions formed in the collision area are extracted from the reaction volume by a weak electric field (<1 V/cm) towards a quadrupole mass analyser and detected by single pulse counting techniques. The intensity of the respective anions is then recorded as a function of the incident electron energy. The electron energy scale was calibrated with respect to the formation of the SF_6^- ions from SF_6 , which exhibits a sharp peak located near 0 eV. The sample of chlorodifluoroacetic acid methyl ester was obtained from Aldrich with a stated purity of 99% and used after degassing in order to remove any remaining gases in the container.

3 Results and discussion

Figures 1–4 show ion yields obtained from dissociative electron attachment (DEA) to the target molecule namely 2-chloro-2,2-difluoroacetic acid methyl ester ($CClF_2COOCH_3$) in the energy range 0–12 eV. It appears that DEA to this molecule shows similar decomposition patterns as 2-chloro-2,2-difluoroacetic acid ($CClF_2COOH$). This not only concerns the composition of the generated anionic fragments but also the energy ranges where they are produced, i.e., 0–2 eV and 5–10 eV. However, a rough comparison of the anionic yields from both molecules at comparable experimental conditions clearly

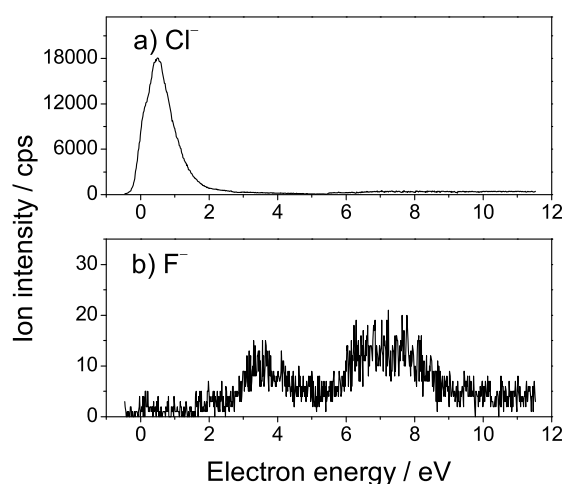


Fig. 2. Ion yield curves for the DEA reaction resulting in the formation of halogen anions: (a) Cl^- and (b) F^- .

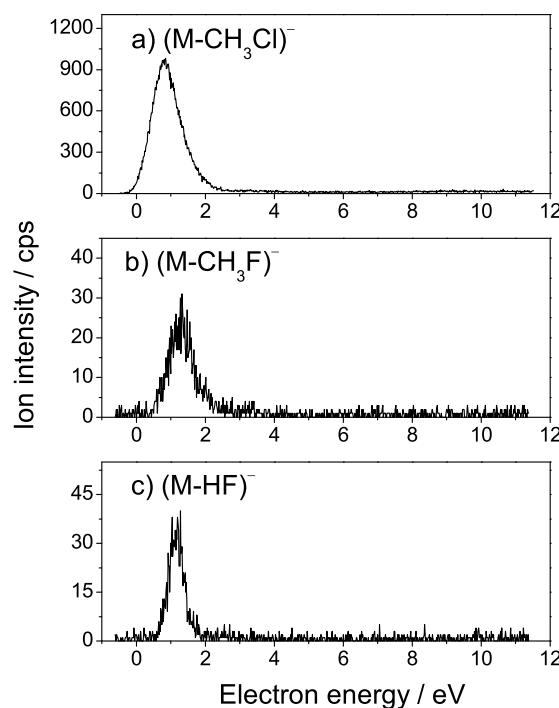


Fig. 3. Ion yield curves for the DEA reaction resulting in the formation of (a) $(M-CH_3Cl)^-$, (b) $(M-CH_3F)^-$ and (c) $(M-HF)^-$.

shows that the dissociative attachment cross section of the ester is at least one order of magnitude lower. In the following we will consider the fragmentation reactions of $CClF_2COOCH_3$ and discuss the results in the context of previously reported results from acetic acid and its derivatives.

3.1 Ester bond cleavage and formation of the $CClF_2COO^-$ anion

In general, in organic synthesis, esterification is considered to be a good means to block certain undesired reactions.

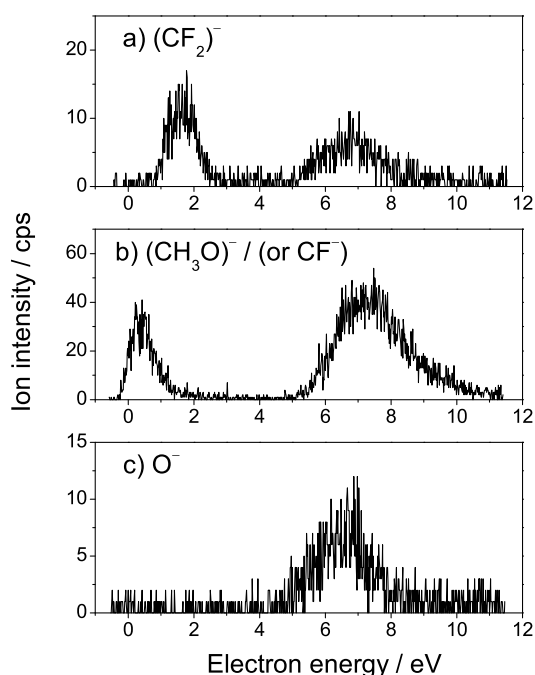
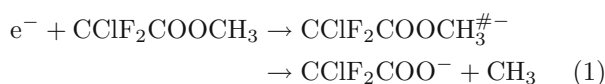


Fig. 4. Ion yield curves for the DEA reaction resulting in the formation of (a) CF_2^- , (b) CH_3O^- (and/or CF^-) and (c) O^- .

However, in our experiments we observe the loss of methyl group from 2-chloro-2,2-difluoroacetic acid methyl ester. This leads to the formation of the chlorodifluorocarboxylate anion $\text{CClF}_2\text{COO}^-$ due to the cleavage of the O- CH_3 bond within the ester group, viz.:



with $\text{CClF}_2\text{COOCH}_3^{\#-}$ the transient negative ion that is formed in the initial stage of electron capture. As shown in Figure 1 the $\text{CClF}_2\text{COO}^-$ ion is formed at a peak maximum of 0.6 eV and thus at slightly lower energy than chlorodifluorocarboxylate anion from CClF_2COOH . The energy threshold for the appearance of the anionic fragments can be expressed as the difference between the bond dissociation energy ($D(\text{R-X})$) and the electron affinity ($\text{EA}(\text{X})$) of the neutral fragment on which the excess electron is localised. Assuming that the value of the electron affinity of the fragment CClF_2COO is the same for both $\text{CClF}_2\text{COOCH}_3$ and CClF_2COOH molecules, a comparison of the binding energy of the O-C bond (3.7 eV, representing an average O-C binding energy) and the O-H bond (4.86 eV; value given for non-halogenated organic acids namely formic acid and acetic acid [11]) indicates that formation of $\text{CClF}_2\text{COO}^-$ from the ester is energetically more favourable, which is consistent with our experimental observations.

3.2 Formation of the halogen anions

The ubiquitous reaction in the case of halo-containing molecules is formation of the halogen anions. Since the

presently studied molecule contains two different halogen atoms within the structure, as expected, we observe the formation of the two halogen anions namely Cl^- and F^- . While the predominant fragment Cl^- arising from the cleavage of the C-Cl bond is present in the very low energy domain (0–1.5 eV), the F^- anion is generated with appreciable lower intensity and preferentially at higher energy between 3–5 eV and 6–8 eV (Fig. 2). The positions of the resonances of Cl^- and F^- can be explained taking into account well-known thermochemical values such as binding energy of the C-X bond ($\text{BDE}(\text{C-Cl}) = 4.11$ eV, $\text{BDE}(\text{C-F}) = 5.72$ eV [12]) and electron affinity of the respective halogen atoms ($\text{EA}(\text{Cl}) = 3.61$ eV, $\text{EA}(\text{F}) = 3.40$ eV [13]). Thus for the Cl^- anion formation the thermodynamic threshold is 0.5 eV while for the F^- anion the threshold is 2.32 eV, which agrees reasonably well with our experimental findings.

The Cl^- ion is generated from at least two strongly overlapping resonances peaking at around 0 eV and 0.5 eV. The mechanism for its formation is not clear, but it may arise from low lying vibrational Feshbach resonances (VFR). In general, the fragment anion is generated in the same energy range as Cl^- from CClF_2COOH . However, the relative intensity of these overlapping resonances is different for both molecules. For the chlorodifluoroacetic acid the first peak at around 0 eV was much more intense than the second (shoulder) peak [9]. For the ester compound the situation is different and the second strong peak almost completely ‘swallows’ the first peak near 0 eV (Fig. 2).

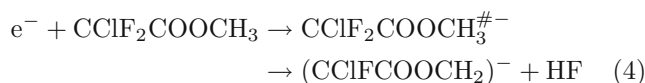
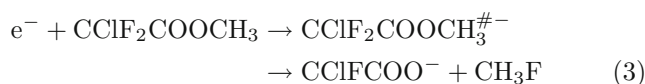
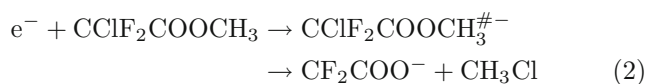
The F^- yield is visible via broad resonant features located near 2 eV, 3.5 eV and 7 eV. We can ascribe the low energy features to antibonding σ^* (C-F) shape resonances, while the broad structure at around 7 eV is due to a core excited resonance (with possible contributions of high energy shape resonances). Although the thermodynamic threshold for F^- formation, as mentioned above, is quite low and F is characterized by an appreciable electron affinity, the F^- ion intensity is much lower than Cl^- . As discussed in our earlier paper [10] this is due likely to significant difference in polarizability between Cl and F atoms (2.18×10^{-24} cm³ and 0.557×10^{-24} cm³, respectively [12]) which is an essential quantity determining the value of electron attachment cross section. This value increases downwards the 17th group and changes in the same line as the electron capacity [14], which is a quantity describing the ability of a halogen in a neutral molecule to accommodate extra charge.

It is noteworthy that for previously studied chloro-containing organic acids (CClF_2COOH and CCl_3COOH [10]) the complementary anionic fragment (M-Cl^-) has been generated from DEA reactions. While for the CCl_3COOH molecule (M-Cl^-) was the second most intense anionic product, for CClF_2COOH it was in fact the most intense product. However, in the presently studied ester molecule this reaction is not operative. Instead, we observe the loss of neutral stable CH_3Cl molecule from the precursor anion that will be discussed in more details in the following section.

3.3 Loss of neutral stable molecules

Reactions driven by the loss of neutral stable molecules are quite frequently observed for organic compounds including those that contain halogen atoms. They have been recently reported for acetamide and some of its derivatives [15], pentafluoroaniline, pentafluorophenol [16] and various esters of trifluoroacetic acid [17].

Dissociative electron attachment to $\text{CClF}_2\text{COOCH}_3$ results in three such reactions generating the $(\text{CF}_2\text{COO})^-$ (m/z 94), $(\text{CClF}\text{COO})^-$ (m/z 110) and $(\text{CClF}\text{COOCH}_2)^-$ (m/z 124) anions (Fig. 3). These reactions require a cleavage of the two bonds namely the C-Cl or C-F bond and the O- CH_3 or C-H bond. Since the binding energy of these bonds is rather high these processes have to be driven by the gain of the energy from the formation of stable molecules. Thus bond raptures are most likely accompanied by the recombination of the two radicals to form CH_3Cl , CH_3F and HF , respectively, viz.,



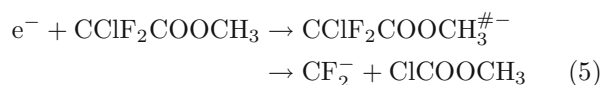
The formation of the fluoro-containing neutral counterparts (reactions 3 and 4) is visible via low intense resonant features in the energy range 1–1.5 eV (Figs. 3b and 3c). By contrast, the loss of CH_3Cl that is visible via a peak with a maximum at 0.8 eV is one of the most intense anionic fragment (Fig. 3a), i.e., the maximum count rate of $(\text{M}-\text{CH}_3\text{Cl})^-$ is more than 30 times that of $(\text{M}-\text{CH}_3\text{F})^-$ and $(\text{M}-\text{HF})^-$. By intuition the loss of HF should, in principle, be the most favourable reaction channel since the energy release through the formation of the H-F bond is 5.91 eV [12] while it is 4.99 eV [11] and 3.63 eV [11] for $\text{CH}_3\text{-F}$ and $\text{CH}_3\text{-Cl}$, respectively. Thus additional factors may play a role and we suggest that it may be, e.g., the lower electron affinity of CClFCOO and $\text{CClF}\text{COOCH}_2$ in comparison to CF_2COO and/or the activation barrier for the reactions to occur.

For the anionic fragment detected at m/z 94 and assigned to CF_2COO^- we cannot exclude the contribution of the anion that arise from the expulsion of the neutral CF_2 radical generating $(\text{ClCOOCH}_3)^-$. In fact, such a fragmentation reaction leading to ClCOOH^- has been reported from DEA to CClF_2COOH [9] in the energy range 0–1 eV albeit with low intensity.

3.4 Further DEA reactions

Finally, Figure 4 presents the anion yields of the fragments detected at m/z 50, 31 and 16. From stoichiometry, they can be attributed to the CF_2^- , $\text{CH}_3\text{O}^-/\text{CF}^-$ and O^- ions, respectively.

The fragment detected at m/z 50 (CF_2^-) arises from the cleavage of the C- C_α bond according to the DEA reactions:



This reaction requires the expulsion of the CF_2 group from the transient negative ion (TNI) with the excess charge localised at this light fragment. We suggest that CF_2^- generation is accompanied by the formation of chloroformic acid methyl ester in analogy to the decomposition reaction of CClF_2COOH into CF_2^- and ClCOOH [9] and CF_3COOH into CF_2^- and FCOOH [8]. CF_2^- as well as its neutral counterpart ClCOOCH_3 are known as thermodynamically stable species. Although, ClCOOCH_3 upon contact with moist air undergoes hydrolysis to methanol, hydrochloric acid and carbon dioxide ($t_{1/2}$ of ca. 15 min) [18]. While in CClF_2COOH the formation of CF_2^- was a very efficient process, for the ester under investigation the fragment anion is generated with only low intensity. In addition to the low energy resonance peaking at around 1.6 eV we observe some intensity at higher energies in the range 6–8 eV (Fig. 4) that was not reported from the earlier studies on halo-acids.

Another light fragment at m/z 31 can, in principle, be attributed to two isobaric anions, either to CH_3O^- or to CF^- . This fragment is visible via two resonances at energy 0–1 eV and 6–9 eV with the latter one being slightly more intense. The formation of the CF^- anion would require the scission of three bonds namely C-F, C-Cl and C-C. The total energy required to cleave these bonds would be around 12 eV that cannot be compensated by electron affinity of the CF radical, which is assumed to be >3.3 eV [13] (according to more recent ab-initio predictions electron affinity of CF is much lower and equals to 0.4 eV [19]). Thus the thermodynamic threshold for the formation of CF^- would be at least 9 eV. Based on these data and taking into account the lack of formation of the CF^- ion from DEA to CClF_2COOH we hence conclude that m/z 31 is attributed to the CH_3O^- ion. Indeed the presence of methyl group within carboxylic function will facilitate the formation of such fragment. However, we still have a situation that the threshold energy to form methoxide anion is around 2.8 eV (taking into account the $\text{CH}_3\text{C}(\text{O})-\text{OCH}_3$ bond energy of 4.34 eV [11] and electron affinity of 1.569 eV [20]) and thus higher than the peak maximum of low energy resonance. The explanation for the appearance of the fragment at energy slightly below 1 eV would be the formation of neutral stable counterpart(s) in order to supply the energy necessary for the reaction. On the other hand it is also possible that the introduction of electron withdrawing atoms in the alkyl chain weakens the $\text{C}(\text{O})-\text{OCH}_3$ bond and thus facilitates bond breaking.

Finally the fragment at m/z 16 is attributed to the O^- anion that is visible via a high energy structure with a peak maximum at around 6.5 eV. The formation of the anionic fragment, generated via core excited resonance, require either the cleavage of the double $\text{C}=\text{O}$

bond or the cleavage of two single bonds namely C-O and O-CH₃. Due to the lack of the thermodynamic values for the ester one cannot specify the exact value for the energy threshold. However, taking into account the available values for the acetic acid (i.e., $\Delta_f H^0(\text{CH}_3\text{COOH}) = -4,5 \text{ eV}$, $\Delta_f H^0(\text{CH}_3\text{COH}) = -1.8 \text{ eV}$ and $\Delta_f H^0(\text{O}^-) = 1.1 \text{ eV}$ [13]) we arrive with the energy threshold of 3.8 eV. This value should not change drastically when going from nonhalogenated acetic acid to its halo-containing ester hence we can assume that the appearance energy of the O⁻ anion is higher than the threshold energy.

4 Conclusions

In summary, in this contribution we show that the attachment of low energy electrons (<2 eV) to chlorodifluoroacetic acid methyl ester primarily leads to the formation of Cl⁻ and (M-CH₃Cl)⁻. Further reactions are generated with intensities lower by at least one order of magnitude. Some of these reactions proceed through complex routes such as rupture of the bonds and recombination of the radicals to form stable molecules as neutral counterparts. In addition our results show that esterification, which is considered to be a good means to block certain reactions, is not operative once the molecule is exposed to low energy electrons. This becomes obvious from the observation of the (M-CH₃)⁻ and CH₃O⁻ anions that are generated from the cleavage of the C(O)O-CH₃ or C(O)-OCH₃ bond within ester group.

This work has been supported by the Polish Ministry of Science and Higher Education. I wish to thank Małgorzata Biernacka, an undergraduate student, for her assistance in the initial stage of the measurements. This work was conducted within the framework of the EU/ESF COST Action CM1301 (Chemistry for Electron-Induced Nanofabrication, CELINA).

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