

Chapter 5

Conclusion

In this work the interaction of low energy electrons with organic molecules in the energy range 0–20 eV has been studied. Thereby we focused on molecules containing the following functional groups: alcohols, carboxylic acids, carboxylic acid esters and ketones. The intention was to study if we can identify characteristic reaction patterns following electron attachment for each of the four groups of molecules. Within these groups we wanted to investigate the influence of fluorination by the comparison of non-fluorinated and fluorinated compounds. Furthermore, we were interested how a molecular surrounding can change the electron induced processes. Therefore the organic molecules were studied as isolated compounds in the gas phase, in molecular clusters and in molecular films with respect to electron interaction. The main results will be summarized in the following.

Alcohols: Electron attachment to alcohols leads to the loss of hydrogen and the formation of the dehydrogenated alkoxy anion. Dehydrogenation following electron capture is a frequently observed reaction for various molecules like DNA bases or amino acids. The driving force for this process is the considerable stability of the formed anion RO^- . While the formation of OH^- is a quite efficient process for ethanol, it is not observed for trifluoroethanol. For the partly fluorinated molecule the abstraction of the stable molecule hydrogen fluoride together with the loss of hydrogen becomes a process with high efficiency.

Carboxylic acids: The carboxylic acids show as well the loss of hydrogen and the formation of the carboxylate anion as a common reaction channel. For formic acid it is demonstrated by experiments with deuterated isotopomers that the loss of hydrogen almost exclusively occurs at the O–H-site. Hence the dehydrogenation is a site-selective process.

The loss of hydrogen is also operative in molecular clusters. Here, either the single carboxylate anion or the solvated anions of the structure $R-COO^- \cdot M$ with $R = -H, -CF_3$ is detected. Additionally, an intracluster intermolecular chemical reaction that leads to the formation of water is operative. The reaction product can be observed via the ion-molecule complex $R-COO^- \cdot H_2O$. For CF_3COOH this complex is formed with the highest intensity of all anionic complexes while for formic acid the loss of hydrogen is still more efficient. Moreover, CF_3COOH forms the trifluoroacetic acid anhydride. In this case the anhydride anion is formed by the abstraction of a neutral water molecule. As both of the complexes related to water formation are formed exclusively from the dimer, one can assume that the specific conformation of a stable hydrogen bonded dimer is a necessary requirement for this reaction. Another chemical reaction leads to the formation of an anion that can be assigned to the dimer subjected to the abstraction of HF. In a non-dissociative process the intact molecular anions are formed by evaporative attachment. The observation of the monomer anion indicates a positive electron affinity.

In the condensed phase, product formation proceeds via a resonant and a non-resonant reaction channel. The resonant reaction pathway leads to the formation of water at low electron energy in similarity to clusters. As an additional product of the low energy resonance CO_2 is observed. Furthermore, there are indications for the formation of an CF_x and an AF-compound, where x is the number of fluorine atoms that is likely to be two. A possible structure for the AF-compound may be HF as it is an energetically favorable reaction channel. The non-resonant process at high energy leads as well to the formation of CO_2 . In comparison with the resonant process different fluorinated products are formed. While in the resonant process the CF_3 -group further decomposes, it is still present after the non-resonant interaction. The formation of water may also be operative in this case.

Carboxylic acid esters: Experiments with carboxylic acid esters clearly show that the substitution of the O–H-hydrogen by a hydrocarbon chain cannot block the bond rupture that leads to the formation of the stable carboxylate anion. Furthermore, the esters show a quite particular electron induced reactivity in that they do not abstract HF from partly fluorinated molecules. In this case the abstraction of a halocarbon molecule is favored which is most likely due to a considerably high electron affinity of the formed radical CF_2COO . A reaction pathway that is only observed for $\text{CF}_3\text{COOCH}_2\text{CF}_3$ is the hydrogen transfer from the C–H-position to the O–H-position which leads to the formation of CF_3COOH^- . The results also demonstrate the influence of fluorination as only the esters that are fluorinated in the ester chain form the corresponding alkoxy anion $\text{CF}_3\text{CH}_2\text{O}^-$.

In the cluster experiment the tendency to stabilize intact molecular anions by evaporative attachment is observable. For $\text{CF}_3\text{COOCH}_2\text{CF}_3$ even the monomer anion is detected which is an indication for a positive electron affinity. Surprisingly, the solvated complexes for the carboxylate anion of the structure $\text{RCOO}^- \cdot \text{M}$ were only observed for the acetic acid ester. In case of the trifluoroacetic acid esters the formation of the complex $\text{CF}_3\text{COO}^- \cdot \text{R–F}$ with the formation of a halocarbon R–F via an intracuster chemical reaction is favored.

The ester clusters do not show any indication for the formation of water or the corresponding neutral molecule which would be an ether. This can be considered as a further indication that the formation of water in the acid clusters is only possible because of the specific configuration due to hydrogen bonds.

Ketones: The different acetone molecules also show a tendency to abstract stable molecules. In acetone H_2 is abstracted while in 1,1,1-trifluoroacetone the more stable compound HF is formed. These abstraction processes most likely lead to the formation of chain-like or cyclic anionic structures. Hexafluoroacetone does not show the abstraction of neutral molecules because the formation of the corresponding reaction product F_2 is energetically not very favorable. For this molecule the formation of anionic complexes of the structure $\text{F}^- \cdot \text{M}$ is observed.

The comparison of the non-fluorinated acetone, the partly fluorinated trifluoroacetone and the perfluorinated hexafluoroacetone shows the influence of fluorination on the ability to stabilize the excess charge on the intact molecule. While

acetone does not form a corresponding anion, it is observed for trifluoroacetone as a result of evaporative attachment in the cluster experiment. Hexafluoroacetone forms the intact molecular anion in the gas phase as well as in the cluster experiment. For this molecule the presence of self-scavenging processes is demonstrated.

In the following some general conclusions are summarized:

- A molecular surrounding can lead by evaporative attachment to the formation of the intact molecular anions.
- Efficient fragmentation pathways for isolated molecules can be suppressed for molecular clusters in favor of complex intermolecular chemical reactions.
- The stronger intermolecular interactions via hydrogen bonds in carboxylic acids allow specific reaction channels like the formation of water in clusters and in molecular films.
- Various organic molecules show the tendency to the loss of hydrogen by the formation of stable anions (alcohols, acids, acetones).
- Esterification of an organic acid cannot generally block the bond cleavage leading to the formation of the carboxylate anion.
- The abstraction of stable molecules is a favorable reaction pathway. Especially partly fluorinated molecules show the tendency to abstract HF.
- Within the group of ketones the abstraction of stable molecules can lead to the formation of chain-like or cyclic anionic structures.
- A higher degree of fluorination increases the tendency to stabilize the excess charge on the intact molecule (acetones, esters)

In the future it would be interesting to extend these studies to further functional groups like aldehydes or carboxylic acid chlorides. Furthermore, an investigation of the studied compounds in the condensed phase (e.g. by means of HREELS) can give information on the neutral co-products of dissociative electron attachment.