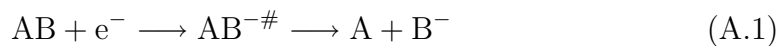


Appendix A

Abstract

In the present work the interactions of low energy electrons (0–20 eV) with organic molecules in different states of aggregation are studied. These processes play a particular role in radiation damage of DNA, in plasma chemistry as well as in atmospheric chemistry and in chemical reactions in the interstellar medium.

Besides elastic and inelastic electron scattering from the corresponding molecules, the electron can be resonantly captured and thus a temporary negative ion $AB^{-\#}$ (TNI) can be formed. The TNI can dissociate into the anion B^{-} and one or more radicals A. The overall process is called dissociative electron attachment (DEA):



The formed anions B^{-} can be detected by means of mass spectrometry and analyzed in dependency of the initial electron energy.

In this work we focus on the investigation of the influence of a molecular surrounding (like in molecular clusters and in molecular films) on the observed electron induced reactions. Furthermore, the assignment of characteristic fragmentation patterns to molecules that contain specific functional groups plays a central role. Additionally, the influence of fluorination can be studied within these groups by the comparison of fluorinated and non-fluorinated molecules. In this context we investigated four different groups of molecules: alcohols, carboxylic acids, carboxylic acid esters and ketones. Within these groups the fluorinated and non-fluorinated compounds of the structure R_1COR_2 with $R_1 = -CH_3, -CF_3$, respectively, were analyzed.

The results of these experiments clearly show differences between electron attachment to single molecules in the gas phase and to molecular clusters. A comparison of the electron attachment experiments for gas phase molecules and for clusters frequently shows a dramatically increased electron attachment cross section for clusters. Furthermore, a stabilization of the intact molecular anions by evaporative electron attachment is often observed. Stronger intermolecular interactions, like hydrogen bonds in carboxylic acids, lead to a particular configuration of the molecules and thus specific reactions become possible. In case of the carboxylic acids the formation of water in an intermolecular reaction in the dimer is observed. Efficient reaction channels in the gas phase can be suppressed in the cluster in favor of complex chemical reactions.

Alcohols, carboxylic acids and acetones show like various other organic molecules a strong tendency to the loss of hydrogen and the formation of stable anions. Within the carboxylic acid esters such a reaction is only observed for the acetic acid ester. Generally, the formation of the carboxylate anion is strongly favored in case of esters. The substitution of the O–H-hydrogen by a hydrocarbon group cannot suppress bond cleavage at this specific position.

Furthermore, the abstraction of stable, neutral molecules is a favorable reaction channel. Especially partly fluorinated compounds show a strong tendency to abstract hydrogenfluoride HF. The anionic products, formed by the abstraction of neutral molecules, often show chain-like or cyclic structures.

The fluorination of a molecule increases the probability to form a stable intact molecular anion. This is shown on the example of different acetones and carboxylic esters.

The obtained results clearly show a considerable influence on electron induced chemical reactions. On the example of carboxylic acids (with stronger intermolecular interactions via hydrogen bonds) it is demonstrated that complex chemical reactions can be induced at extremely low energy. Additionally, processes that are not possible in the gas phase can be observed for clusters due to efficient energy dissipation.