ECCL Short Term Scientific Mission
Scientific report

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Reference: Short Term Scientific Mission,
Beneficiary's Name and Institution: Thorben Hamann, Institut für Angewandte und Physikalische Chemie
Host's Name and Institution: Paul Scheier, Institut für Ionenphysik und Angewandte Physik
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Purpose of the visit

An ongoing research project in the group of Professor Swiderek is to find low-energy electron induced reactions for the functionalization of hydrocarbons. One example is the introduction of a functional group into an alkanethiole self-assembled monolayer (SAM) which would be a useful process in surface patterning.
The idea is to prepare an alkanethiole SAM, transfer it into the ultra-high-vacuum Chamber (UHV-Chamber), cool it down to very low temperatures (below 90 K), deposit a reactive second molecule on top of it and irradiate the sample with low-energy electrons to activate the compound. The electron irradiation would produce reactive fragments, for example radicals or anions, which can react with the hydrocarbon surface and activate it so that a second fragment carrying a functional group can recombine with an activated site on the surface.
Formamid appears to be an interesting candidate fur such reactions. Previous experiments with acetaldehyde have shown that methyl- and hydrogen radicals and neutral carbon monoxide (shown in figure 1 (a)) molecules are created during irradiation with low-energy electrons [1]. Similar reactions may occur in formamide, if the NH_2 radical recombines with a CH_2 radical site produced by hydrogen abstraction by the H radical. This would result in a NH_2 end group in the SAM (see figure 1 (b)). The first step is to find a suitable electron energy for the activation of formamide. The aim of this project was therefore to identify the dissociative electron attachment (DEA) channels in formamide. The group of Professor Paul Scheier in Innsbruck uses a crossed molecular and electron beam apparatus in which the electron beam can be tuned to different energies. These experiments can produce the

information we need to proceed with the next step, the transfer from the gas phase to the solid phase.

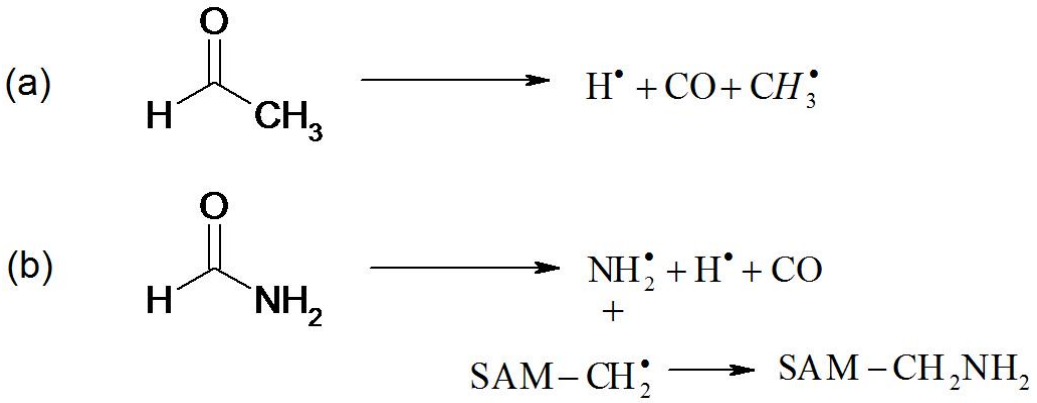

Fig. 1 Radicals produced with low-energy electron irradiation in acetaldehyde and formamide

Work carried out

The irradiation measurements with low-energy electrons were performed in a crossed molecular and electron beam apparatus with a base pressure of $2x10^{-7}$ mbar. The equipment was described elsewhere[2]. Liquid formamide [Fluka, puriss. p.a. , ACS reagent, ≥ 99.5% (GC/T)] was filled in a small metal container and connected to the inlet system via a metal tube. The whole inlet system and the container were continuously heated up to 55 °C. The inlet pressure of formamide varied between 1 and $2.1x10^{-5}$ mbar during the measurements. To identify some species with masses that can be assigned to different structures, two types of deuterated formamide were used: D_1-Formamide ($DCONH_2$) [Aldrich, 99 atom % D] and N,N-D_2-Formamide ($HCOND_2$) [synthesized before the experiment at the university of Innsbruck].

Main results

We found many species which were produced by the dissociative electron attachment (DEA) process. For a short overview we summarized the results in three intensities groups:

Strong Intensity: $(CN)^-$, H^-, $(NH_2)^-$ and $(CH_2NO)^-$
Medium Intensity: $(CNO)^-$ and O^-
Low Intensity: $(CHNO)^-$, $(NH)^-$, $(HCNH)^-$ and $(HCO)^-$.

The strongest signal is from the $(CN)^-$ species (see Fig. 2) and at this point we cannot be sure that there was no thermal dissociation of the formamide which would lead to HCN, besides other products, which produces after electron irradiation also $(CN)^-$.
It is clear, from the experiments with the deuterated formamide, that the hydrogen from the N side of formamide can be more easily abstracted than the hydrogen from the C side of the molecule.
Furthermore signals from the masses 44 und 1 were found and identified as $(CH_2NO)^-$ (mass 44, see Fig. 3) and H^- (mass 1, see Fig. 4).
The strong signal from mass 16 was identified as $(NH_2)^-$ at 6 and 7 eV, and (O^-) at 10 eV (see Fig. 5). The signals were identified by increasing the mass spectrometer resolution, so that it was possible to distinguish between the mass of O and NH_2 which is slightly higher because of the isotope ratio in nitrogen.

Projected publications/articles resulting or to result from the grant

We are planning one joint publication in the next months.

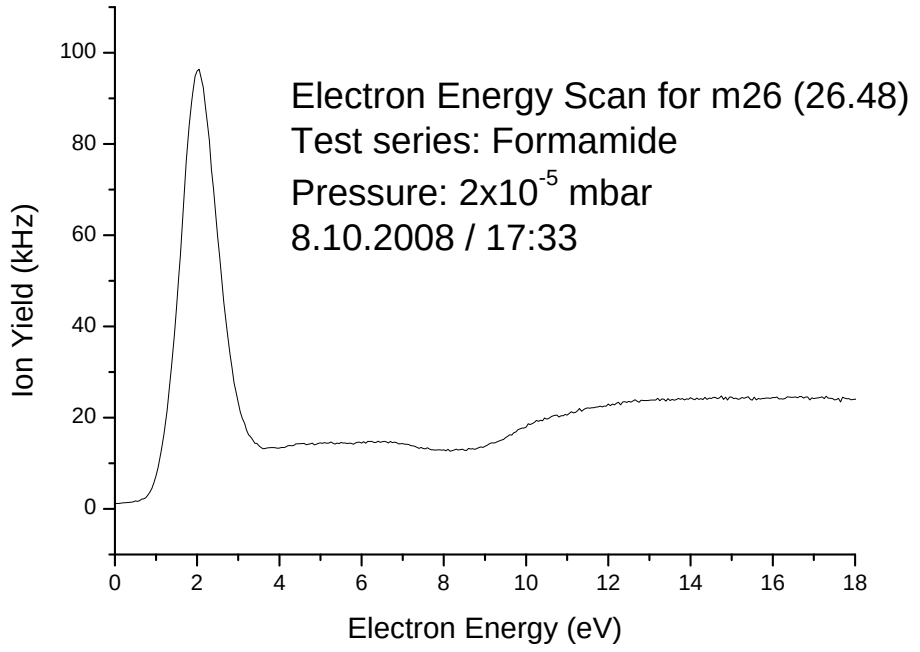

Fig. 2 Formamide: Electron Energy Scan mass 26

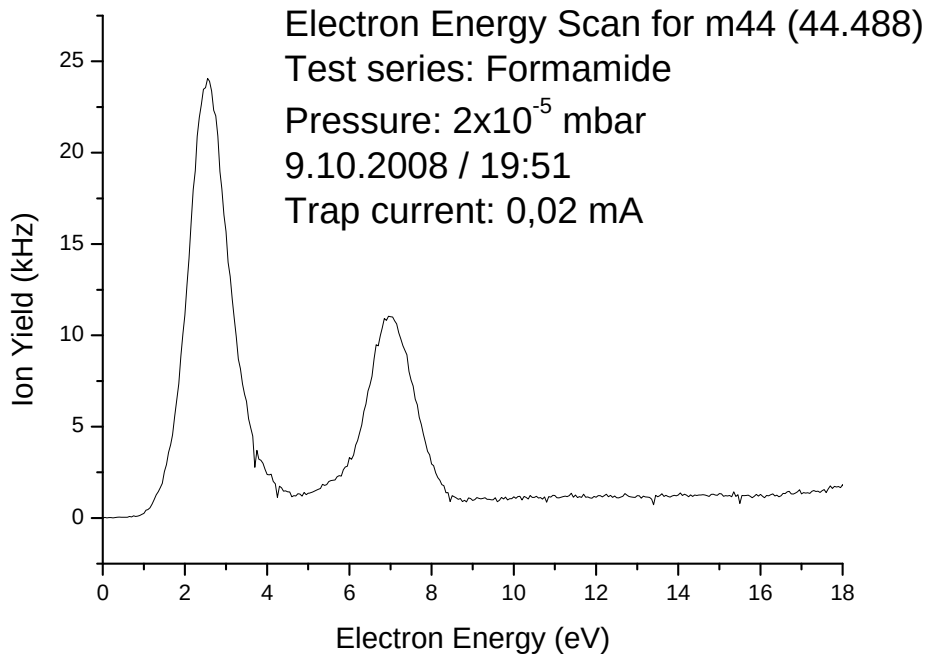

Fig. 3 Formamide: Electron Energy Scan mass 44

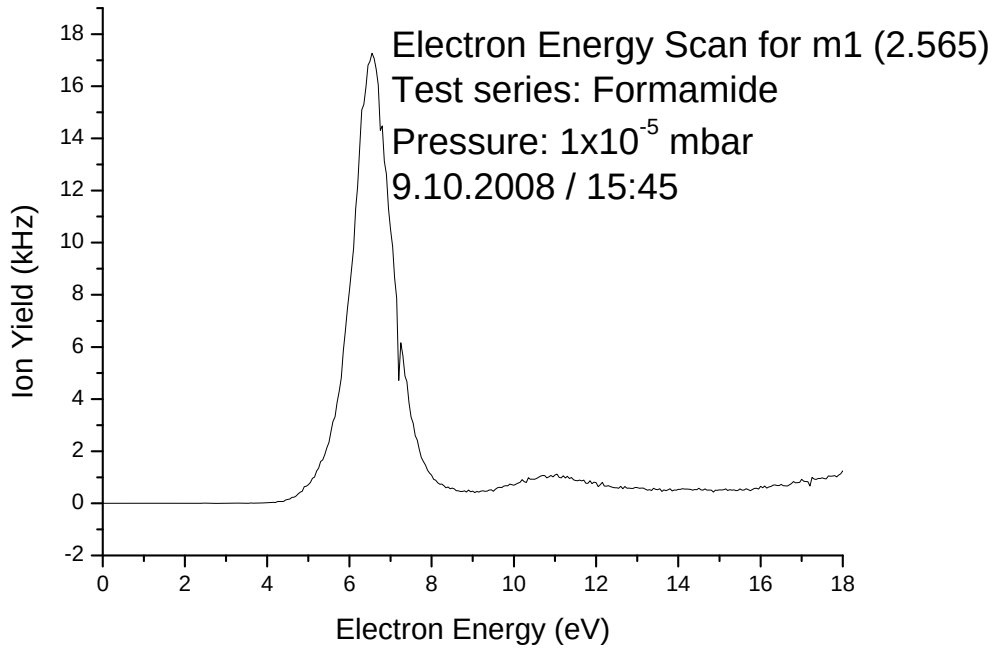

Fig. 4 Formamide: Electron Energy Scan mass 1

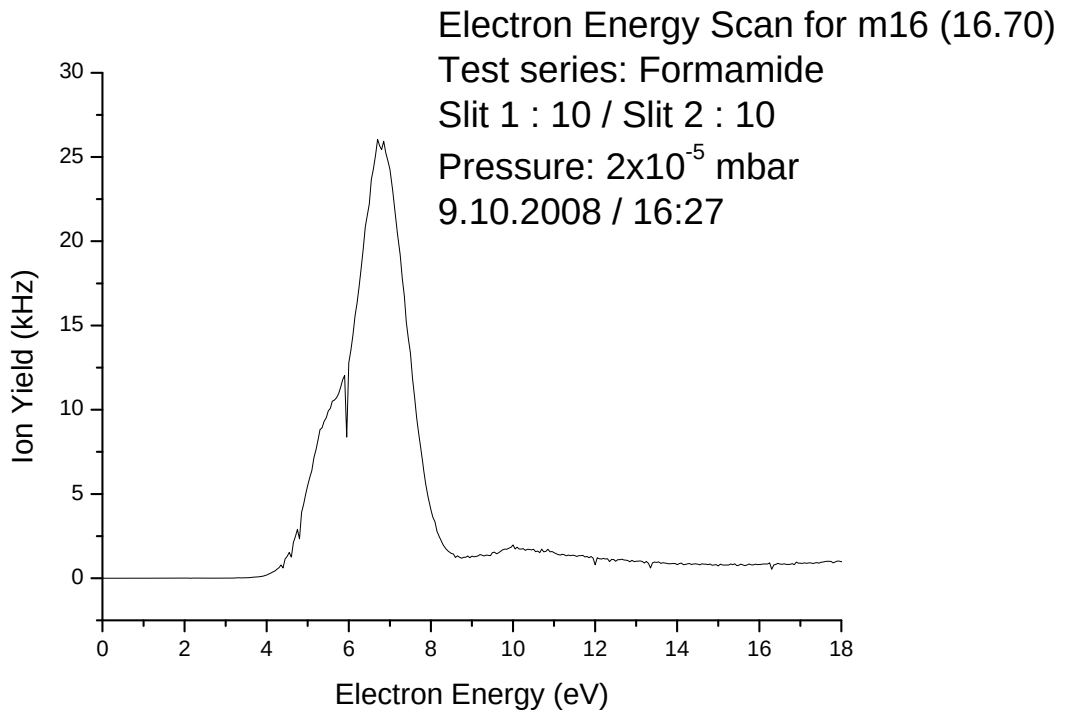

Fig. 5 Formamide: Electron Energy Scan mass 16

References

[1] E. Burean, P. Swiderek, *Surface Science* **2008**, *602*, 3194, doi: DOI: 10.1016/j.susc.2007.05.065.

[2] E. Alizadeh, F. Ferreira da Silva, F. Zappa, A. Mauracher, M. Probst, S. Denifl, A. Bacher, T. D. Märk, P. Limão-Vieira, P. Scheier, *International Journal of Mass Spectrometry* **2008**, *271*, 15, doi: DOI: 10.1016/j.ijms.2007.11.004.