Low-Energy-Electron-Induced Hydroamination of an Alkene**

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The transformation of structurally simple molecules into functional materials is one of the ultimate challenges of chemical research. Introducing specific functional groups is an essential step towards this aim. Amino groups are particularly useful as they are versatile linkers that can be used to attach complex molecules.^[1] Hydroamination reactions are used in organic synthesis to add ammonia or amines to unsaturated hydrocarbons. They require specifically tailored catalysts because of the high activation barrier arising from electrostatic repulsion between the electron lone pair at the nitrogen atom and the electron-rich double or triple bond.^[2]

Low-energy free electrons provide an alternative approach to control chemical reactions. Dissociative electron attachment (DEA) leads to rupture of specific bonds depending on the energy of the incoming electron. A fine example demonstrating this selectivity has been provided by recent indepth investigations of electron-induced reactions of thymine in the gas phase.^[3] Similarly, DEA can trigger reactions leading to the modification or functionalization of surfaces.^[4,5] In these cases, the fragments produced by DEA form new bonds with an initially H-terminated silicon or diamond surface. Here we show that by proper tuning of the electron energy (E_0), low-energy-electron-induced reactions can also be used to introduce amino groups to an alkene using ammonia (NH₃) as a starting reagent.

The reaction described herein resembles a hydroamination except that the electron beam replaces the catalyst of the organic synthesis (Scheme 1). Ethylene (C_2H_4) was chosen to demonstrate the feasibility of our approach. To circumvent the electrostatic repulsion that prevents the reaction between neutral C₂H₄ and NH₃, multilayer films condensed on a cryogenic Au substrate were irradiated with electrons at E_0 somewhat above the ionization threshold but not high enough to produce extensive fragmentation.^[6] Ionization above the first threshold removes an electron from the π orbital of C₂H₄ (Scheme 1a). The cation interacts attractively with the lone pair of NH₃ that is either leaked into the vacuum chamber during electron exposure or initially admixed to the C₂H₄ deposit. Alternatively ionization can also occur from the lone pair of NH₃ (Scheme 1b), and the resulting cation is attracted towards the electron-rich double bond of C₂H₄. Intramolec-

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[**] P.S. thanks Sven Doye for an inspiring GDCh lecture on hydroamination. This work was funded by the DFG and has profited from exchange within COST action ECCL. ular hydrogen migration and subsequent neutralization of the resulting adduct by thermalized electrons within the film then produces aminoethane ($C_2H_5NH_2$), which can be detected by post-irradiation thermal desorption spectrometry (TDS).

Figure 1 shows the TDS data for multilayer films formed by condensing a mixture of equal quantities of C₂H₄ and NH₃ vapor at 32 K. Without exposure, the characteristic desorption peaks of C₂H₄ at 67 K and NH₃ at 96 K are observed in the 28 amu and 17 amu curves, whereas the data recorded at 30 amu, 44 amu, and 45 amu show a flat baseline. After electron exposure of 4000 μ C at $E_0 = 15 \text{ eV}$ new desorption signals appear at 71 K and 138 K in the 30 amu curve and at 138 K in both the 44 amu and 45 amu curves. In addition, a new signal is observed at 40 K in the 28 amu curve. This latter signal is ascribed to N₂ formed from NH₃ upon electron exposure. In multilayer films of NH₃ this reaction proceeds without thermal activation^[7] and is ascribed to the disproportionation of NH2 radicals formed upon electron exposure.^[8] Taking into account that ions in the condensed phase are stabilized by typically 1 to 2 eV relative to the gas



Scheme 1. Proposed mechanism of the electron-induced reaction producing aminoethane in mixed condensed films of ethylene and ammonia for electron incident energies above the ionization threshold of ethylene and ammonia.

phase, NH₂ radicals can be produced here by the dissociative ionization of NH₃ yielding NH₂⁺ (gas-phase threshold: 15– 16 eV^[6]) followed by neutralization by thermalized electrons during exposure. In the present experiment, the H atoms thus released reduce C₂H₄ to ethane (C₂H₆) as evidenced by a new 30 amu desorption signal at 71 K after electron exposure. DEA probably does not contribute to this reaction as it has been reported to be efficient only at lower E_0 .^[9,10]

The relative intensities of the desorption peaks at 138 K for 45 amu, 44 amu, and 30 amu of 20:20:100 (Figure 1) reproduce well the mass spectrum of $C_2H_3NH_2$ obtained also with electron impact (EI) ionization at 70 eV.^[6] This shows that electron exposure at $E_0 = 15$ eV also drives formation of a stable addition product of NH₃ and C_2H_4 , namely $C_2H_5NH_2$. Formation of its isomer dimethylamine ((CH₃)₂NH) is excluded because the mass spectrum of this compound shows only a very small signal at 30 amu.^[6] The absolute

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Communications



Figure 1. Thermal desorption spectra of multilayer films of a 1:1 mixture of ethylene and ammonia without electron exposure (0 μ C) and after an exposure of 4000 μ C. The films were deposited from the gas phase at a thickness corresponding to 15–20 monolayers and exposed at 32 K. The electron incident energy was 15 eV. Signals above 200 K are attributed to desorption from the sample holder.

quantity of $C_2H_5NH_2$ can not be determined from the present data because the absolute ionization cross section for $C_2H_5NH_2$ is not available. An ongoing study will address this question by comparison with samples of known composition as described earlier.^[11]

The same reaction is observed when NH₃ is dosed onto a condensed film of C_2H_4 during electron exposure but leads to a smaller quantity of products (Figure 2). Mixing of this layered film during desorption thus does not efficiently counterbalance the smaller degree of direct contact between NH₃ and C_2H_4 during electron exposure as compared to a film produced from deposition of a gas mixture. This suggests that the actual reaction occurs mainly on a short time scale during electron step.

The production of $C_2H_5NH_2$ was investigated at different E_0 to show that ionization in fact drives the reaction. TDS curves at 45 amu of multilayer films of a 1:1 mixture of C_2H_4 and NH_3 after an exposure of 4000 µC at different E_0 show that the amount of produced $C_2H_5NH_2$ is lower at $E_0 = 12$ eV than at 15 eV (Figure 3). At 9 eV and 5 eV, this product is not observed. These values of E_0 were chosen because they lie in the range of energies where DEA to NH_3 leading to dissociation of an NH bond was reported.^[9,10] We initially assumed that the reactive fragments formed in these processes could add to a hydrocarbon in a radical reaction similar to



Figure 2. Thermal desorption spectra of multilayer films of ethylene and ammonia without electron exposure (0 μ C) and after an exposure of 4000 μ C. The films were deposited from the gas phase at 32 K by first condensing ethylene and then an equal amount of ammonia. The exposure was performed simultaneously with the ammonia deposition. The overall thickness corresponds to 15–20 monolayers. The electron incident energy was 15 eV. Signals above 200 K are attributed to desorption from the sample holder.

that reported previously.^[5] This process is obviously not efficient enough to lead to a noticeable yield of $C_2H_3NH_2$. Only at E_0 above the ionization threshold reported as 10.07 eV and 10.50 eV for gaseous NH₃ and C_2H_4 ,^[6] respectively, does formation of $C_2H_5NH_2$ commence. Its rate increases with increasing E_0 , which is characteristic of an ionization-driven process.^[12] This finding supports the proposed reaction mechanism. Gas-phase cross sections for $E_0 =$ 15 eV^[12] further suggest that ionization of C_2H_4 (cross section of 0.661 Å²) is probably somewhat preferred over ionization of NH₃ (0.379 Å²).

A series of experiments aimed at inducing the formation of $C_2H_5NH_2$ in mixtures of C_2H_6 and NH_3 so far did not clearly yield the desired product. The ionization energy of C_2H_6 (11.52 eV in the gas phase^[6]) is also considerably lower than $E_0 = 15$ eV used in these experiments, and fragmentation to yield $C_2H_4^+$ occurs at about 0.5 eV above the ionization threshold.^[6] This would in principle yield the same intermediate as that assumed in the present reaction mechanism (Scheme 1). In ongoing experiments to be reported elsewhere we thus vary film thickness and electron exposure in order to give conclusive evidence for or against this reaction. It must be noted that cations with the stoichiometry $H^+(C_2H_5NH_2)$ -(NH_3)_n (n = 0-4) have been observed by electron-stimulated



Figure 3. Thermal desorption spectra of multilayer films of a 1:1 mixture of ethylene and ammonia recorded at 45 amu without electron exposure (0 μ C) and after an exposure of 4000 μ C at different E_0 . The films were deposited from the gas phase at 32 K at a thickness corresponding to 15–20 monolayers and exposed at the same temperature.

desorption at $E_0 = 1$ keV from condensed mixed films of C_2H_6 and NH_3 .^[13] However, this species was assigned to a $C_2H_5^+$ ion solvated with NH_3 rather than to protonated and solvated $C_2H_5NH_2$. In contrast, the present experiments produce a stable product that survives the thermally induced transition from the condensed phase to the gas phase suggesting that a true addition reaction has occurred.

In conclusion, we have demonstrated a new strategy to control chemical synthesis by exposure to low-energy electrons and used it to synthesize $C_2H_5NH_2$ from C_2H_4 and NH_3 . The direct reaction is exothermic according to standard thermodynamic data^[6] but hindered by the electrostatic repulsion between the neutral reaction partners. Our approach relies on the electrostatic attraction caused by the soft ionization of one of the reaction partners. It is thus complementary to the strategy of controlling chemical reactions by inducing DEA. So far, we have concentrated at irradiation using an electron energy roughly 4 to 5 eV above the ionization threshold of both reaction partners. This is sufficient to induce, to some extent, dissociation and thus concurrent reactions. Future work will aim at investigating whether further decrease of the energy can make the reaction more selective.

Experimental Section

The experiments were performed in an UHV setup^[14] with a base pressure of 10^{-10} Torr. Molecular films were deposited from the gas phase onto a polycrystalline gold substrate (area 2.8 cm²) held at 32 K by means of a closed-cycle helium cryostat. A commercial flood gun

delivering currents of the order of a few μ A cm⁻² to the sample with an estimated energy resolution of 0.5–1 eV was used for electron exposure at the same temperature. The film composition was monitored by TDS at a heating rate of 1 Ks⁻¹ using a Quadrupole Mass Spectrometer (QMS) residual gas analyzer (Stanford, 200 amu) with EI ionization at 70 eV. TDS curves were recorded simultaneously for five different masses.

For film deposition, the gas was leaked into the TDS chamber by means of a gas-handling manifold consisting of precision leak valves and a small calibrated volume where the absolute pressure was measured with a capacitance manometer. The pressure drop in the manifold was used to measure the gas quantity. The amount of gas required for monolayer formation was estimated from the thickness dependence of the TDS curves. Prior to each deposition, the substrate was cleaned by resistive heating of two thin tantalum ribbons spotwelded to the thicker gold substrate.

 $\rm C_2H_4,$ NH₃, and $\rm C_2H_6$ were purchased from Air Liquide at stated purities of 99.95 %, 99.98 %, and 99.95 %, respectively, and were used as received.

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