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Electron-Induced Ethanol Synthesis

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Electron-Induced Hydration of an Alkene: Alternative Reaction Pathways**

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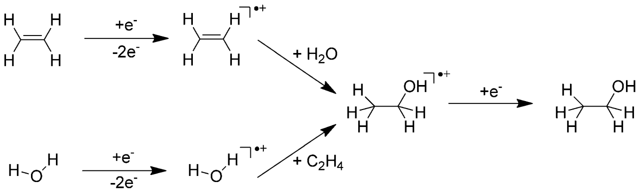
Abstract: *Electron-induced reactions in condensed mixtures of ethylene and water lead to the synthesis of ethanol, as shown by post-irradiation thermal desorption spectrometry (TDS). Interestingly, this synthesis is not only induced by soft electron impact ionization similar to a previously observed electron-induced hydroamination but also, at low electron energy, by electron attachment to ethylene and a subsequent acid/base reaction with water.*

Chemical transformations induced by electron irradiation are mostly associated with destructive effects such as radiation damage in biological systems (e.g. DNA)[1] or the decomposition of volatile precursors in focused electron beam induced processing (FEBIP).[2] Depending on the electron energy (E_0), bonds can be selectively cleaved.[3] However, irradiation of condensed matter also leads to the formation of new bonds.[4] As an example, NH_3, RNH_2, and R_2NH add to the double bond of alkenes following electron irradiation of frozen layers of the reactants.[5,6] These hydroamination reactions are induced by using E_0 values near the ionization threshold of the reactants to achieve a soft, that is, nondissociative, electron impact ionization. While the electron-rich double bond of the alkene and the lone electron pair of the nitrogen atom in the neutral reactants repel each other and prevent a reaction, ionization of one reactant turns this barrier into an attractive force. This leads to bond formation between the reactants. Neutralization of the resulting adduct by a thermalized electron then yields the neutral product which contains all the atoms of the reactants. Electron irradiation thus induces chemical synthesis through an atom-efficient reaction mechanism. We show here that this principle is transferable to other reactants. In fact, post-irradiation thermal desorption spectrometry (TDS) reveals that ethanol is produced in condensed mixtures of ethylene (C_2H_4) and H_2O. However, we also present evidence that ethanol is not only formed by ionization (oxidation) of C_2H_4 (Scheme 1) but also following electron attachment (reduction).



Scheme 1. Proposed reaction mechanism for the hydration of ethylene induced by soft electron impact ionization. After ionization of water or ethylene, the attractive interaction between the radical cation and the electron-rich double bond or free electron pair drives the reaction.

Details of the experimental procedures can be found in Ref. [7] and in the Supporting Information. Figure 1 shows TDS data for multilayer films formed by depositing equal quantities of C_2H_4 and H_2O vapor on a gold surface held at 38 K. Prior to exposure, desorption signals of C_2H_4 ($m/z = 28$) at 80 K and H_2O ($m/z = 18$) at 150 K are observed. After electron exposure of 500 $\mu C\,cm^{-2}$ at $E_0 = 15$ eV, new desorption signals with an intensity ratio of 2:1 appear at 160 K in

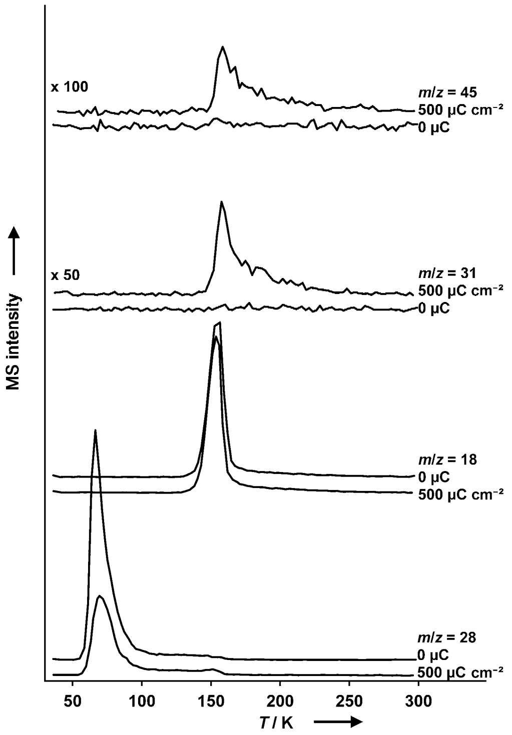


Figure 1. Thermal desorption spectra obtained from 20 monolayer (ML) films of a 1:1 mixture of C_2H_4 ($m/z = 28$) and H_2O ($m/z = 18$) before (0 μC) and after electron exposure of 500 $\mu C\,cm^{-2}$ at $E_0 = 15$ eV. The signals at $m/z = 31$ and $m/z = 45$ with an intensity ratio of 2:1 illustrate the formation of ethanol.

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the TDS spectra at $m/z = 31$ and 45. This ratio is characteristic of ethanol, as verified by leaking the pure compound into the chamber. The desorption temperature agrees with that of pure ethanol (see Figure SI1 in the Supporting Information). Together, this supports that ethanol is in fact produced.

Low-energy electrons can thus drive the formation of ethanol in mixed films of C_2H_4 and H_2O at cryogenic temperature. As for the electron-induced hydroamination,[5,6] ionization of one of the reactants removes the activation barrier for the reaction. The formation of ethanol thus proceeds under conditions that are fundamentally different from those of technical processes for the production of ethanol by hydration of C_2H_4. These processes require high temperatures, high partial pressures, and a catalyst.[8] This suggests that the described approach to control adduct formation may also allow for an atom-efficient synthesis of other carbon structures containing heteroatoms.

In the case of ethylamine,[5,6] the reaction occurred only at E_0 values above the ionization threshold of C_2H_4 and NH_3. To confirm that electron impact ionization also drives the formation of ethanol, we have measured the dependence of ethanol yield on the E_0 value. The ionization thresholds of H_2O and C_2H_4 in the gas phase are 12.6 eV and 10.5 eV, respectively.[9] In the condensed phase, polarization forces can lower such thresholds by up to 2 eV.[10] The continuous increase in product yield with E_0 above about 8 eV confirms an ionization-driven reaction. Surprisingly, however, the yields of ethanol also increase considerably as the E_0 values decrease below 6 eV (Figure 2).

At E_0 values well below the ionization threshold, electron attachment (EA) to molecules can occur. In the gas phase, the resulting molecular radical anions usually decay into an anion and a radical, a process named dissociative electron attachment (DEA).[3,4] However, in condensed phase where polarization forces stabilize the charge, the radical anion may also survive.[3,4] As neutral excitation processes are absent below roughly 4 eV in both C_2H_4 and H_2O,[11] such anionic processes must be responsible for the ethanol yield at low E_0 values.

DEA processes for H_2O in the gas phase occur around 7 eV, 9 eV, and 11 eV[12] and thus above the range of E_0 values concerned here. No production of $OH^\bullet$ radicals occurs below 5 eV.[13] In clusters, EA is observed at slightly different energies, but again not below about 6 eV.[14] However, nondissociative EA to C_2H_4 proceeds around 1.5 eV.[15] Therefore, EA to C_2H_4 to yield a radical anion $C_2H_4^{\bullet -}$ must trigger the formation of ethanol at low E_0 values. This provides, at the same time, the first example of an electron-induced synthesis controlled by a nondissociative EA process. The range of E_0 values observed for this process compares well with the broadening of a similar EA process in condensed N_2,[16,17] thus supporting our conclusion.

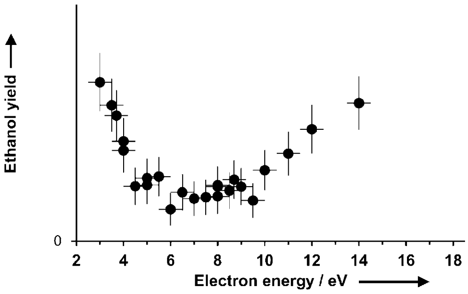


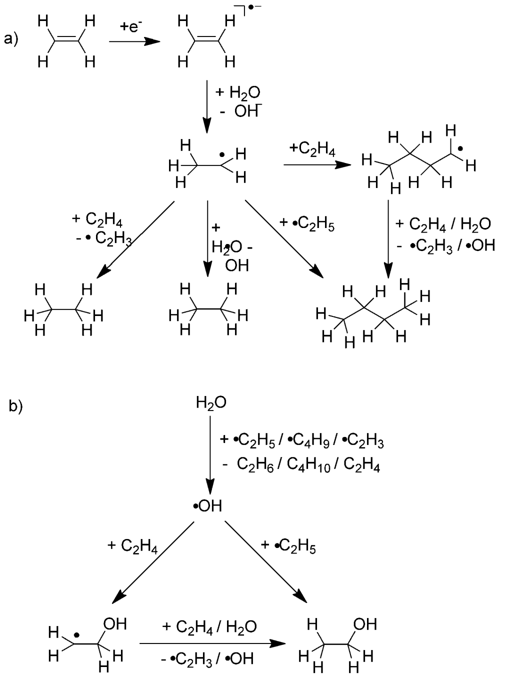
Figure 2. Dependence of ethanol yields on electron energy (E_0) as represented by the integrated TDS peak areas at $m/z = 31$ obtained from 30 monolayer (ML) films of a 1:1 mixture of C_2H_4 and H_2O after electron exposures of 600 $\mu C\,cm^{-2}$. The increase above 8 eV is attributed to a reaction initiated by electron impact ionization, while the ethanol formation below 6 eV is driven by an electron attachment process to C_2H_4.

Neither in films of pure C_2H_4, nor in mixtures of C_2H_4 and NH_3,[6] did we observe formation of any products at such low E_0 values. This observation points to a key role of H_2O in the reaction observed here, which can be explained by its acidic protons. Radical anions are typically basic species.[18] The transient radical anion $C_2H_4^{\bullet -}$ formed by EA to C_2H_4 can accept a proton donated by H_2O to form an ethyl radical ($C_2H_5^\bullet$). In contrast, in aprotic media the radical anion can only relax through autodetachment of the captured electron, which is a relaxation channel in all EA processes.[3] We propose that this proton transfer triggers the complete sequence of reactions shown in Scheme 2.

Support for the proposed reaction mechanism can be derived from a thorough analysis of the side products. At E_0 values above the ionization threshold, electron irradiation of condensed C_2H_4 produces a variety of hydrocarbons, including ethane (C_2H_6), butane (C_4H_{10}), butene (C_4H_8), butadiene (C_4H_6),[6] and acetylene (C_2H_2, see Figure SI2). Among the C_4 hydrocarbons, the C_2H_4 dimer butene is the dominant product at $E_0 = 15$ eV.[6] This, together with electron-stimulated desorption (see Figure SI2), contributes to the loss of C_2H_4 during irradiation, as seen in Figure 1. In contrast, ethane and butane are the predominant products in the EA regime. Significant contributions of butene and butadiene can be excluded based on the mass peaks seen by TDS (see Figure SI3). Furthermore, butane is only formed in the presence of H_2O (see Figure SI4). Together, these findings strongly support the scenario depicted in Scheme 2.

The intermediate reactive species proposed in Schemes 1 and 2 cannot be monitored directly, although their contribution to the reactions can be inferred from the product yields as a function of sample thickness (Figure 3). Anions resulting from EA are short-lived species that can decay by loss of the excess electron.[3] This process is enhanced in the vicinity of a metal surface to which the electron can be transferred.[19] The opposite process, namely transfer of an electron from the surface can neutralize cationic intermediates. The probability of such quenching processes depends on the distance between the ions and the surface.[19]

At E_0 values above but near the ionization threshold, a radical cation initiates product formation. In very thin layers, quenching of this species by the nearby metal surface inhibits product formation, as shown here for ethanol, ethane, and butane (Figure 3, top). At $E_0 = 3$ eV, the formation of ethane and butane follows the same trend (Figure 3, bottom), thereby pointing again to quenching by the metal surface. In both cases, neutralization by quenching occurs before the intermediate radical ion can react with an adjacent molecule. However, the production of ethanol at low E_0 values only



Scheme 2. Proposed reaction pathways for the formation of ethanol by electron irradiation in the EA regime. The first step (a) is initiated by the formation of a radical anion $C_2H_4^{\bullet-}$, which is a basic species and reacts with a proton to form the main reactive intermediate species in the reaction sequence, the ethyl radical $C_2H_5^{\bullet}$. The resulting radical may react with another $C_2H_5^{\bullet}$ radical to form butane (C_4H_{10}), H_2O to afford ethane (C_2H_6) and an $OH^{\bullet}$ radical, or C_2H_4, which would ultimately result in either C_4H_{10} or C_2H_6 and another $OH^{\bullet}$ radical. The formation of ethanol (b) is the result of a multistep mechanism with these $OH^{\bullet}$ radicals as key intermediates and may proceed in an autocatalytic reaction. The $OH^{\bullet}$ radicals can add to C_2H_4, and after abstraction of a hydrogen atom from a neighboring molecule yield ethanol. The direct reaction by a combination of $OH^{\bullet}$ and $C_2H_5^{\bullet}$ radicals is in our opinion far less likely, since radical densities in the film are presumably low.

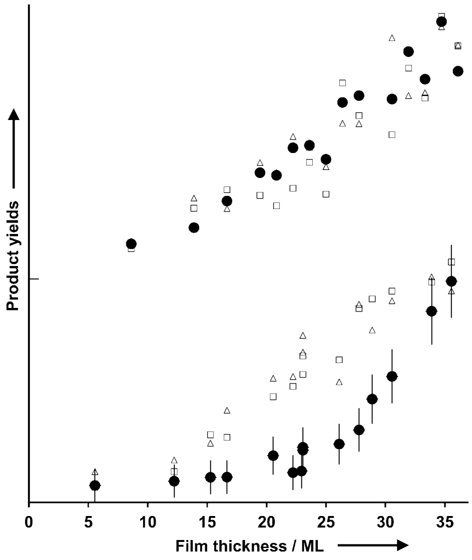


Figure 3. Dependence of product yields for ethanol (filled circles), C_2H_6 (open triangles), and butane (open squares) on film thickness as stated in monolayers (ML) for electron exposure of 600 $\mu C\,cm^{-2}$ at $E_0 = 15$ eV (top) and 3 eV (bottom). All product yields are scaled to the same height to facilitate comparison. All products follow the same trend except for ethanol produced at 3 eV. The latter is attributed to additional quenching of $OH^{\bullet}$ radicals by thermalized electrons, while formation of other products is impeded only by quenching of charged intermediates near the metal surface. Error bars are comparable over all sets of data, but omitted on all but one for better legibility.

occurs at strikingly larger film thickness (Figure 3, bottom) and is thus more visible in a thicker film (compare Figures 2 and SI5). $OH^{\bullet}$ radicals are required for the formation of ethanol in the EA regime (Scheme 2). As $OH^{\bullet}$ radicals possess a high electron affinity of about 1.8 eV[9] and energy is easily dissipated in a condensed phase, the capture of a thermalized electron to yield OH^- is thermodynamically favorable. We therefore propose that $OH^{\bullet}$ radicals only survive when they are formed at a depth where the electron current is attenuated enough to render encounter of a second electron with a given reaction site unlikely on the time scale of the reaction of $OH^{\bullet}$ radicals with adjacent molecules. Only then can the production of ethanol occur and trigger the chain reactions as proposed in Scheme 2. Similar radical quenching is unlikely for $C_2H_5^{\bullet}$ because of its negative electron affinity.[9]

Quenching of $OH^{\bullet}$ radicals is only overcome at a thickness far in the multilayer regime (Figure 3). This situation compares roughly with the electron penetration depth for mixed condensed layers of CH_4 and H_2O, as derived from saturation of product formation.[20] However, this comparison must be regarded with caution as our results show that the thickness dependence of the product yield depends critically on the reaction mechanism.

To conclude, the hydration of C_2H_4 in mixed condensed layers of C_2H_4 and H_2O proceeds through two different electron-induced reaction routes. At E_0 values above but near the ionization threshold (soft ionization), ethanol formation is driven by intact molecular radical cations, analogous to the electron-induced hydroamination described before.[5,6] On the other hand, we provide here the first evidence that synthesis of the same product can also be initiated at E_0 values below the ionization threshold through EA, a regime where degradation of the product ethanol is also considerably less efficient than above the ionization threshold (see Figure SI1). However, the acidity of water is essential for this newly discovered reaction pathway. This is, to the best of our knowledge, the first example of an electron-induced synthesis that proceeds through nondissociative EA. The reaction can be controlled by selecting between two different reaction mechanisms, an oxidative and a reductive process with regards to C_2H_4. Both mechanisms lead to the same product, but the formation of side products is more selective through the EA route. This finding is not only important from a mechanistic point of view, but might also have interesting applications in the field of electrosynthesis.

Keywords: alkenes · electron-induced reactions · radical ions · reaction mechanisms · water

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