

Formation of Reactive Species under Electron Irradiation

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Electron-induced chemistry is relevant to many processes that occur when ionizing radiation interacts with matter. This includes radiation damage, curing of polymers, and nanofabrication processes but also the formation of complex molecules in molecular ices grown on dust particles in space. High-energy radiation liberates from such materials an abundance of secondary electrons of which most have energies below 20 eV. These electrons efficiently trigger reactions when they attach to molecules or induce electronic excitation and further ionization.

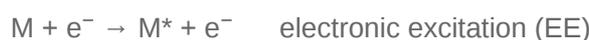
Electron Irradiation

Reactive Species

electron-induced reactions

1. Basics of Electron Molecule Interactions

Upon interaction with a free electron, a molecule can be promoted to different states that are often more reactive than the molecular ground state. In electron ionization (EI), the impinging electron liberates another electron from the target to leave a radical cation behind. Electronic excitation (EE) leads to a neutral excited state while electron attachment (EA) to the molecule yields a radical anion:



The dependence of the three processes on electron energy is different, with EE and EI showing a threshold-type behavior. When the energy of the impinging electron exceeds the threshold for electronic excitation (EE) or the ionization threshold (EI), the cross section for interaction steadily increases until it reaches a plateau between 30 to 70 eV (for EE) and 50 to 100 eV (for EI) ^[1]. After this plateau, the cross section decreases due to ever shorter interaction times owing to the increasing speed of the electron. In contrast, electrons can attach to a molecule only if there is an anion state available for the energy of the incoming electron. This leads to EA in well-defined energy ranges called resonances. At energies typically below 5 eV, this happens in so-called single particle resonances, where the incoming electron occupies a previously unoccupied orbital. At higher energies, electron attachment is usually accompanied by electronic excitation leading to core-excited resonances.

The three states that a molecule M can occupy after the encounter with the electron (radical cation, radical anion, excited neutral) can be more chemically reactive than the ground state molecule M. If these reactive species are in contact with other molecules or atoms, further chemical synthesis can be triggered.

The described processes assume that the molecule itself stays intact. Yet, molecules do in fact often dissociate after interaction with an electron, if the energy of the electron is sufficiently high to overcome the dissociation energy of a chemical bond in the molecule. This energy can be offset to some degree by the formation of new chemical bonds ^[1]. There are thus a number of further processes that can lead to the formation of reactive species:



For DI, the thresholds are the same as for EI increased by the required bond dissociation energy. The same can hold for ND as compared to EE. Often, however, the presence of dissociation is not governed by additional energy but by whether the primary excited state M* is dissociative or not. This also applies to anion states M*⁻ formed by EA but here dissociation competes with autodetachment of the electron ^[2]. Furthermore, anion states M*⁻ are preferentially formed at near-thermal electron energies where excess energy can be removed from a particular bond by redistribution of energy to different internal degrees of freedom of the molecule ^[3]. There is also an additional dissociative process following electronic excitation, namely dipolar dissociation (DD) of the excited state into a cation and an anion.

2. Reactive Intermediates Formed by EI/DI

The energy of the impinging electrons typically ranges up to around 20 eV. This energy range spans the lower part of the typical energy distribution of LESEs and includes their maximum yield for diverse materials ^{[3][4][5]}. The reactive species discussed here thus do not include ions and radicals with an appearance energy above ~20 eV.

Evidence for EI/DI as initiating step of electron-induced reactions in mixed ices has been obtained for the prototypical reactants C₂H₄, CO, NH₃, H₂O, CH₃OH and CH₄. Researchers omit for simplicity propene and amines because the reactions identified in this case were analogous to those of the shorter analogues C₂H₄ and NH₃ ^[6]. With the exception of CH₃OH, where significant fragmentation in the gas phase sets in almost at the ionization threshold, evidence was not found that dissociation following EI contributes to the electron-induced reactions. While EI fragments with appearance energies below 20 eV are known ^[7], apparently their formation cross sections are too low to play a significant role. People thus refer to the conditions present in the experiments as “soft ionization”.

3. Reactive Intermediates from ND

In many of the studied systems, product formation was observed starting from energies well below the ionization threshold [8][9][10][11]. When the energy dependence reveals threshold-type processes and not resonances, the only primary interaction available in this energy range (usually between 6 and 10 eV) is ND. Contrary to EI thresholds, the exact thresholds for ND are often unknown, even in the gas phase [12]. This is in part due to the fact that ND as a source for reactive species under electron irradiation is difficult to assess due to the experimental difficulties in monitoring reactive neutral radical species [13]. The only recourse for the identification of ND processes in electron-driven chemistry is thus by exclusion of EI/DI processes on grounds of the lower observed threshold energy and exclusion of EA/DEA processes by their non-resonant energy dependence. If an observed process starts near the minimum energy for electronic excitation, it is attributed to ND. It has been observed product formation triggered by ND in systems containing NH_3 , H_2O , CH_4 , and especially CH_3OH , which produces a number of very important radical species. Note that in the case of CO and C_2H_4 , the formation of products could be rationalized without having to resort to ND. While it has not been observed the formation of butadiene in the latter case, this was at energies that also allow DI processes [14][6].

4. Reactive Intermediates from (D)EA

Resonant structures in the energy dependence pointing to the formation of products via EA/DEA processes was observed for ices containing C_2H_4 , CO , H_2O , CH_3OH and CH_3CN . In contrast, no true evidence for product formation that starts with EA to NH_3 and CH_4 was found. While researchers have invoked DEA to NH_3 as explanation for the resonant formation of formamide from NH_3 and CO at around 10 eV [15], recent preliminary results led to question this assignment, as people now see it as much more likely that the process is instead triggered by (D)EA to CO , as observed in the formation of other compounds from CO at that energy [8][10][16].

5. Effect of Condensed Phase

Most studies on the fundamental electron-molecule interactions are conducted in the gas phase. These crossed beam experiments typically have an energy resolution in the meV range and very low detection limits of charged particles [3][2]. For the interpretation of condensed phase experiments, these data are very helpful, but need to be treated with a bit of caution [17]. In particular, the threshold energies needed to form a charged particle are often lowered by 1 to 2 eV in the condensed phase, because charged particles are stabilized by polarization of the matrix [18][19]. For the same reason, desorption of particles is often hindered and occurs at higher energies than expected from the gas phase, or might even be suppressed entirely [9][20].

On top of the changes in energy, additional effects come into play once an electron-molecule interaction occurs in a molecular matrix. The caging effect can suppress fragmentation, as particles quickly lose energy to the matrix and can then recombine. This was studied in detail for methanol, where it was shown that in clusters, DI fragmentation is almost entirely absent, compared to the gas phase [21][22]. This can also lead to DEA resonances disappearing in the condensed phase (see for instance Ref. [23]). EA resonances can also initiate fast reactions with the matrix [24]. The radical anions formed from EA to CO or C_2H_4 , $\text{CO}^{\bullet-}$ and $\text{C}_2\text{H}_4^{\bullet-}$, are very strong bases and

can quickly react with acidic protons from matrix molecules like H_2O , yielding HCO^\bullet and ethyl radicals $\text{C}_2\text{H}_5^\bullet$ respectively [8][14].

In a similar vein, the radical cations produced from EI can undergo acid-base reactions with neutral molecules [25] leading to proton transfer reactions [26] between $\text{H}_2\text{O}^{+\bullet}$ and H_2O to yield $\text{H}_3\text{O}^{+\bullet}$ and HO^\bullet radicals, or between $\text{NH}_3^{+\bullet}$ and NH_3 to yield NH_4^+ and NH_2^\bullet radicals. Such acid-base chemistry has also been observed for larger molecules like acetaldehyde [27][28], primary and secondary amines [6] and alcohols [11]. It is also important for H^- that is produced by DEA to numerous molecules. As a strong base, H^- abstracts a proton from many reactants. This yields species such as HO^- or CH_3O^- when reacting with H_2O or CH_3OH [29].

While radical recombination reactions are typically barrierless, the reaction between a radical and a closed-shell species usually comes with a (small) energy barrier [30]. In cryogenic ices, this energy might not be available, which would lead to the stabilization of radicals. Observation has, however, shown that in addition to anionic and cationic species, also neutral radicals can undergo further reactions in the condensed phase. For instance, the hydroxyl radical HO^\bullet , will react with CO from the matrix, yielding the radical species HOCO^\bullet [8]. This is mostly due to the fact that dissociative electron interactions usually impart some excess energy to fragments, which makes them hotter than their surroundings, enabling rapid diffusion as well as radical molecule interactions. When attempting to understand reaction mechanisms, not only HOCO^\bullet [8], but also other secondary radical species, such as HCO^\bullet [8][10][15], $\text{C}_2\text{H}_5^\bullet$ [14] or $\text{HOC}_2\text{H}_4^\bullet$ [14] need to be considered.

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