

Article

Electron-Induced Chemistry in the Condensed Phase

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Abstract: Electron–molecule interactions have been studied for a long time. Most of these studies have in the past been limited to the gas phase. In the condensed-phase processes that have recently attracted attention from academia as well as industry, a theoretical understanding is mostly based on electron–molecule interaction data from these gas phase experiments. When transferring this knowledge to condensed-phase problems, where number densities are much higher and multi-body interactions are common, care must be taken to critically interpret data, in the light of this chemical environment. The paper presented here highlights three typical challenges, namely the shift of ionization energies, the difference in absolute cross-sections and branching ratios, and the occurrence of multi-body processes that can stabilize otherwise unstable intermediates. Examples from recent research in astrochemistry, where radiation driven chemistry is imminently important are used to illustrate these challenges.

Keywords: low-energy electrons; electron–molecule interactions; astrochemistry

1. Introduction

In many physical processes that involve ionizing radiation, chemical reactions take place, sometimes unbeknownst to the experimenter. Ionizing radiation is any form of electromagnetic or particulate radiation that has sufficient energy to overcome a substance's ionization potential, thus knocking out an electron from an atomic or molecular orbital and forming a cation. Often, some care is taken to make sure that the formed cations do not interfere with the intended outcome of a process, but the electron is just as often neglected. In dilute gas phase or vacuum, where mean free paths are long, this treatment is certainly warranted, but when number densities are higher, like in cold plasmas or in solid-state processes, the reactions caused by these secondary electrons can no longer be neglected. Especially so, since estimates put the number of secondary electrons generated per MeV of energy lost at around 50,000 [1]. The energy of all these electrons is typically some few eV, which makes them extremely potent at triggering chemical reactions. Depending on the exact energy of the electron, its interaction with a molecule can trigger three main principal processes, which produce reactive species that can go on to form bigger and more complex chemical structures:

Above the ionization threshold, the impinging electron will knock out one other electron from the molecule in a process called electron impact ionization (EI). This forms a molecular cation. If the original molecule was in a singlet or triplet state, the formed cation will be a duplet (a radical). The energy dependence of this process sees a steady rise from onset at the ionization threshold to a plateau between roughly 50 to 100 eV and a slow decrease towards higher energies. This decrease is caused by the ever shorter interaction times between the molecule and increasingly faster electrons. At energies well above the ionization threshold, the formed cation often breaks up into smaller fragments. This happens in a characteristic way depending on energy and molecular structure. This effect is utilized in mass spectrometry, where the characteristic fragmentation patterns of molecules at a standardized ionization energy of 70 eV are widely available in databases. Data on the ionization

potential can likewise be found for a huge range of compounds. Data on the energy dependence of both fragmentation (appearance energies) and total ionization cross-sections are also available, but to a much smaller extent.

At energies below the ionization threshold, the formation of cationic species is usually not possible. There are however two other mechanisms that play a role here. The first one is neutral dissociation (ND), where inelastic scattering of the impinging electron leads to excitation of the targeted molecule and its subsequent breakup into smaller uncharged fragments. This process is believed to follow a similar energy dependence as EI, albeit with lower total cross-sections and an onset energy that is lower than the ionization threshold. There is however very little data on the fragmentation pathways or energy dependence of ND processes, since the formed species carry no charge and are thus very hard to collect, detect and identify experimentally.

The third primary interaction process of electrons and molecules that can be used to drive chemical reactions is electron attachment (EA). EA can happen at specific energies, where the molecule can capture the impinging electron into either an unoccupied molecular orbital or into a dipole-bound state. These energies are called resonances and are specific to the targeted molecule. The formed radical anion state is much less stable than the cations formed by EI, since the simple detachment of the electron leads back to the original molecule. If the electron affinity of the molecule is positive, it is possible that the hyperpotential surface of the newly formed state is dissociative, which leads to bond cleavage. This process is called dissociative electron attachment (DEA). Usually one of the fragments retains the extra electron, while the other part remains with the radical site. The bond cleavage is specific to the resonance, which provides a tool for selective bond cleavage in larger molecules [2]. Some data on the energy dependence of EA/DEA cross-sections are available, at least for small and simple molecules.

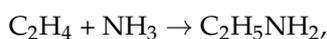
In all three cases, highly reactive (intermediate) species are formed, which can then react with a neighboring molecule, to form larger and more complex species from simple starting materials. These electron-induced reactions have increasingly attracted academic attention in recent years, be it in the context of technical applications like Focused Electron Beam Induced Deposition (FEBID) [3] and curing of polymers [4], as well as the driving force for reactions in astrochemical settings [5,6]. The transfer of the available gas phase data to processes in the condensed phase, however, is not always quite as straightforward as one might hope. In the following paragraphs, I will present a few recent examples of astrochemical research from my lab that highlight the typical challenges faced by experimenters, when trying to apply gas-phase data to condensed-phase problems.

2. Results and Discussion

2.1. The Ionization Potential

The most important parameter for electron-induced chemistry is very often the ionization potential, IE , of a substance. Values for most chemical compounds can be found in the literature or in databases such as the NIST Chemistry Webbook [7]. There exist a number of theoretical approximations that describe the energy dependence of the ionization cross-section, starting from IE . The most commonly used one is the Binary Encounter-Bethe (BEB) model [8,9], which takes a number of molecular parameters as input, all of which are quite easily accessible by quantum chemical calculations. Together, the IE as onset and σ_{BEB} as the energy dependence, give an accurate prediction of the ionization probability by electron impact. For energies that are not greater than IE by more than a few eV, no significant fragmentation of the molecular compound is observed. This is referred to as 'soft ionization'. If the formed cation undergoes a chemical reaction, IE and σ_{BEB} should give an accurate prediction of the energy dependence of product yields.

Figure 1 depicts the calculated formation cross-section of ethylamine from the net reaction



which is triggered by electron impact ionization of either ethylene (C_2H_4) or ammonia (NH_3), as well as experimentally obtained data of the amount of ethylamine actually produced. Upon inspection of the data, two things are very clear: (1) There is considerable product formation at energies below the predicted threshold; and (2) product formation reaches saturation between 10 and 12 eV, even though there is a predicted increase at higher energies.

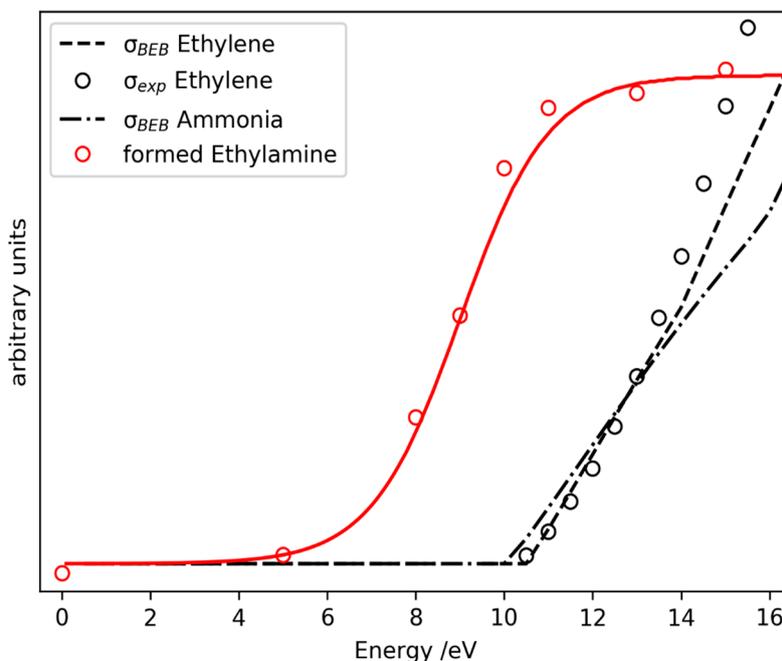


Figure 1. Predicted (black lines) electron impact cross-sections for ethylene and ammonia. Experimental cross-sections for ethylene (black open circles) are taken from Rapp and Englander-Golden [10]. The amount of ethylamine actually formed by electron irradiation of a 1:1 mixture of ammonia and ethylene is shown in red circles. The red line only serves as guide to the eye. Experimental data taken from Böhler et al. [11].

The second observation is explained more easily. The very simple kinetic model used here is based on the assumption of initial rates, i.e., that use of starting materials is negligible. It also neglects any product degradation by the electron beam. The first observation, the shift in energy, however, is not explained by such omissions in the modeling. The data used for the prediction was obtained in the gas phase, where produced cations do not feel any influence of other molecules. In the condensed phase, the energy of the cation is lowered by the polarization of the surrounding medium, which leads to a lowered ionization potential. This is an effect universally observed in experiments with ions in the condensed phase. The shift is usually around 2 eV [12–14].

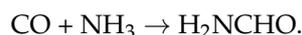
The gas phase data for ionization potentials, although widely available, is not directly applicable to condensed-phase chemistry, because of the energy shift that ensues when ions are stabilized by polarization of a matrix.

2.2. DEA Cross-Sections

When dealing with electrons with an energy below the ionization threshold of a substance (gas phase IE minus approximately 2 eV), the most discussed process that leads to chemical reactions is DEA. The formed radical anions are highly reactive and the specificity with which bonds can be cleaved allows for very precise reaction control. This makes DEA a powerful tool in a chemist's toolbox. Fortunately, there is some data available on EA and subsequent fragmentation channels, at least for small molecules like water [15], ammonia [16], carbon monoxide [17], and carbon dioxide [18]. Here, the same caveats as in IE data apply: The process forms an ionic species, which is stabilized by

polarization and thus the energy at which these processes are observed is lowered with respect to the gas phase. The predictions of fragmentation patterns and especially about where the charge and the radical site end up, nevertheless are very valuable when trying to untangle a reaction mechanism.

Rawat et al. [19] measured absolute DEA cross-sections in ammonia and found two energies at which DEA occurs. At the lower of the resonances, centered around 5.5 eV, cross-sections for the formation of NH_2^- (and by extension H^*) were determined to around $1.6 \times 10^{-18} \text{ cm}^2$, while the formation of H^- and NH_2^* was observed with a cross-section of $2.3 \times 10^{-18} \text{ cm}^2$. At the higher resonance, centered around 10.5 eV, the cross-sections were $1 \times 10^{-19} \text{ cm}^2$ for NH_2^- and $5 \times 10^{-19} \text{ cm}^2$ for H^- . This data helped a lot in understanding the formation of formamide (H_2NCHO) from the electron irradiation of mixed $\text{CO}:\text{NH}_3$ ices in a reaction like,



The energy dependence of formamide production shows a resonance with a maximum between 8 and 9 eV (Figure 2). This resonant shape and product formation observed at energies as low as 6 eV pointed to DEA as the initial electron–molecule interaction process.

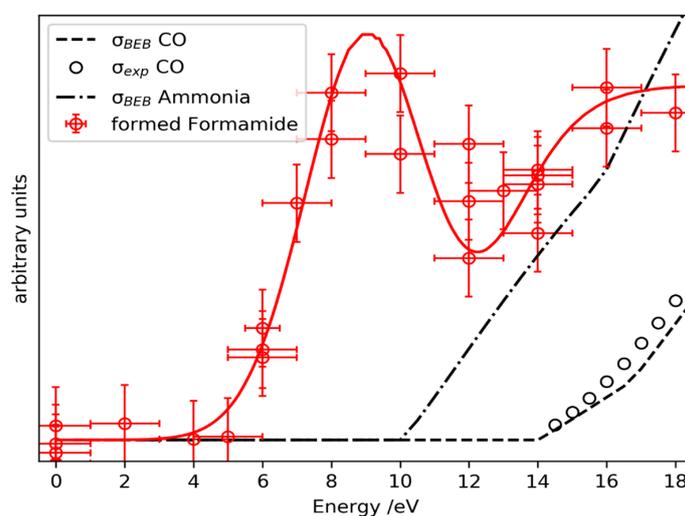


Figure 2. Predicted (black lines) electron impact cross-sections for carbon monoxide and ammonia. Experimental cross-sections for carbon monoxide (black open circles) are taken from Rapp and Englander-Golden [10]. The amount of formamide actually formed by electron irradiation of a 1:1 mixture of ammonia and carbon monoxide is shown in red circles. The red line only serves as a guide to the eye. Experimental data taken from Bredehöft et al. [20].

The reaction could proceed via either the NH_2^* radical or the H^* radical attaching to carbon monoxide. The formed intermediate radicals $^*\text{H}_2\text{NCO}$ or $^*\text{HCO}$ could then go on to form formamide after reaction with another molecule of ammonia. However, neither of the two radicals could be observed experimentally, since both are very short-lived species thanks to their extremely high reactivity. In cases like this, the reaction mechanism can often be inferred by looking at the side-products of the reaction. If the reaction proceeds via the $^*\text{H}_2\text{NCO}$ radical, one side-product would be formed by addition of another amino-group ($-\text{NH}_2$) rather than an $-\text{H}$. This would form the molecule urea ($(\text{H}_2\text{N})_2\text{CO}$). If the reaction proceeds via the $^*\text{HCO}$ radical, the corresponding side-product would form by addition of $-\text{H}$ rather than $-\text{NH}_2$, leading to formaldehyde (H_2CO) (see Figure 3). The gas phase data by Rawat et al. [19] predicts a ratio of 5:1 urea:formaldehyde. The experiment, however, shows absolutely no trace of urea at all, while formaldehyde is formed in about the same quantity as formamide. This is a very strong indication that the reaction proceeds via the channel that is less favorable in the gas phase. This could be due to a perturbation of the electron structure with respect to the gas phase, which is caused by close proximity to other molecules. In the

case of water ice, it has been shown that DEA energies can shift with film thickness and temperature and thus film structure, and can even be higher than in the gas phase [21]. These changes to electronic structure can very well have an influence on electron affinity of the fragments and thus on branching ratios for anion formation.

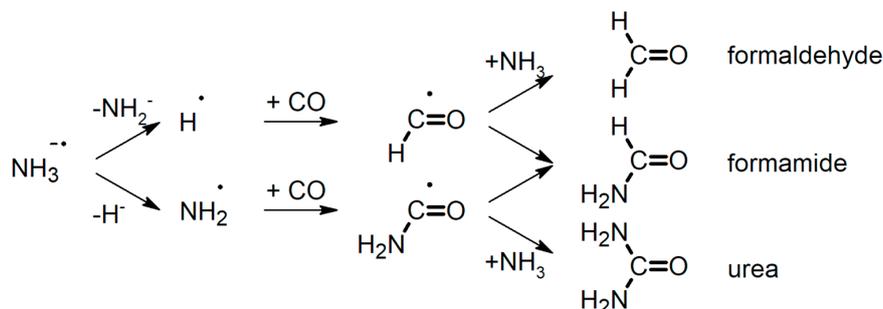
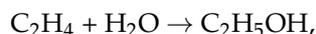


Figure 3. Possible reaction pathways from ammonia to formamide as well as the two expected side-products formaldehyde and urea.

Data on DEA in the gas phase can thus predict which reaction channels are possibly open in condensed-phase chemistry. They need to be corrected in terms of energy due to stabilization of ions and absolute cross-sections seem to be no reliable indication of which channels are actually most active in condensed-phase chemistry, but they do give a prediction of what possible reaction products could look like.

2.3. Prediction of Possible Reaction Routes

In the last example of this paper, the reaction of ethylene and water to form ethanol,



shall be described. It is the analogous reaction to the formation of ethylamine from Section 2.1, and above the ionization threshold, the reaction indeed proceeds in much the same way, with only the NH_3 replaced by H_2O . Below the ionization threshold, however, there is also some formation of ethanol, especially at energies below 4 eV. Figure 4 depicts the experimental data as well as some σ_{BEB} -based predictions for the formation via EI above the ionization threshold.

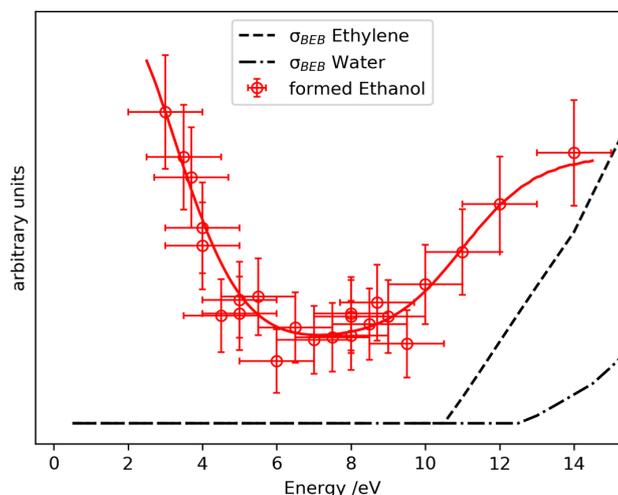


Figure 4. Predicted (black lines) electron impact cross-sections for ethylene and water. The amount of ethanol actually formed by electron irradiation of a 1:1 mixture of ethylene and water is shown in red circles. The red line only serves as a guide to the eye. Experimental data taken from Warneke et al. [22].

There is obviously some significant process at work at very low energies. Since this was not observed in the case of ethylene + ammonia, but is observed in ethylene + water, ostensibly DEA to water must be responsible. DEA cross-sections of water were reported by Curtis et al. [23]. Their data, unfortunately, shows the lowest resonance centered around 6.5 eV, with absolutely nothing happening below 5 eV. While this needs to be corrected for stabilization of the ion, a shift of around 4 eV cannot be explained in this way, ruling out DEA to water as the initiating step in the reaction. DEA cross-sections to C₂H₄ have also been reported, by Szymańska et al. [24], but in much the same way as in water, no anion formation was observed below 6 eV. The only process that is known to occur is a non-dissociative electron attachment to water at around 1.5 eV. It produces the short-lived C₂H₄^{-*} radical anion, which quickly decays by auto-detachment (loss of the electron). It is not readily apparent why this process should lead to product formation in the case of ethanol, but not in the case of ethylamine. This conundrum was resolved by looking at the chemistry of the C₂H₄^{-*} radical anion. It is a strong base and will quickly abstract a proton from a nearby water molecule when embedded in a water ice matrix. The formed ethyl radical *C₂H₅ cannot decay back and is thus available for driving the reaction to ethanol. This is not possible with the much less acidic ammonia. This type of process can of course not be captured by gas phase experiments, where great care is taken to eliminate contaminants such as water, and where molecular beams are tuned so as to exclude interactions between molecules.

3. Conclusions

When endeavoring to investigate condensed-phase chemistry triggered by electron–molecules interactions, often the only help in interpreting experimental data is found in data gathered on electron–molecule interactions in the gas phase. Some data, like ionization potentials are easily available, while others, like data on neutral dissociation cross-sections are pretty much non-existent. While being of great help, these gas phase data:

1. must be corrected for the energy shift due to stabilization of ions in a matrix,
2. should be taken with a great deal of caution with regards to absolute cross-sections and thus branching ratios, and
3. are utterly unable to predict the formation of reactive species that relies on interaction between molecules as well as with electrons.

Nevertheless, data that is of limited use is still much better than no data at all.

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