Selectivity in bond cleavage in amines and thiols by dissociative electron attachment

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Abstract. A study on the dissociative electron attachment to amines and thiols is presented. The previous observations made for oxygen containing compounds, namely the use of methyl as a protective group, the dependence of the energy for the observed DEA band on which alkyl group is lost and the non-dissociative nature of the (^2n, $3s^2$) Feshbach resonances with respect to the Y$-$C bond (Y=N or O), are extended to amines. Amendments to these trends are provided by the study of primary and secondary amines. For thiols the selectivity in bond cleavage is reflected in the fact that S$-$H bonds are broken in the 0-3 eV range by shape resonances, while Feshbach resonances lead to the preferential breaking of the S$-$C bonds in the 7-15 eV range.

1. Introduction

Dissociative electron attachment (DEA) represents one of the many processes that can occur when a molecule collides with an electron in the gas phase. The interest in this process has increased due to emerging applications in technology [1] and the need to understand radiation-induced damage to living tissue [2]. An important role in biology and technology is played by heteroatom-containing compounds, primarily alcohols and ethers, but also amines and thioalcohols.

For saturated compounds DEA fragmentations are observed at electron energies in the 6-15 eV range, sometimes with substantial cross sections, but very little is generally known about the assignment of the resonances responsible for the corresponding bands in the DEA spectrum, and even less is known about the mechanisms of the dissociation. These DEA bands are generally assigned to Feshbach resonances, with two excited electrons, but only rarely has a specific assignment been given for large polyatomic molecules. At the same time DEA bands in the 6-15 eV range are often responsible for a significant fraction of the electron-induced chemistry. Bands in this energy range have been reported in the context of electron-induced damage in DNA [2, 3], suggesting that Feshbach-type resonances may be responsible even for electron-induced chemistry in condensed-phase biomolecules.

Previously we discovered that the presence of lone pairs of electrons in saturated compounds with heteroatoms leads to Feshbach resonances with interesting properties [4, 5, 6]. In the 6-15 eV region the spectra of alcohols [4, 7, 8] show the presence of three types of Feshbach resonances with a hole in either the oxygen 'nonbonding' orbitals n_O or $\bar{n}_O$, or in the σ orbitals manifold. They were designated as n-, $\bar{n}$- and σ-Feshbach resonances. In ethers and alcohols the resonances

localized on the heteroatom are not dissociative with respect to the $O-C$ and they do not lead to any observable DEA signal, indicating the presence of an activation barrier on their potential energy surface. Additionally, the energy of the detected σ-Feshbach resonance depends on the size of alkyl group, being 9 eV for ethyl and 8 eV for butyl.

Little experimental data is available concerning DEA to thiols. H_2S has received the most attention and low energy electron collisions with H_2S have been treated both experimentally [9, 10, 11] and theoretically [12, 13, 14], suggesting several resonant states.

The current paper extends the observations previously made for saturated compounds with oxygen to two different classes of compounds with biological relevance – amines and thiols. In amines, just as in the case of ethers the bond breaking occurs only at specific energies, dependent on the alkyl fragment that is lost irrespective of the target molecule and many of the empirical rules observed for oxygen containing compounds can be easily extended to these compounds. In thiols a different case of site selectivity is observed. The 0-3 eV region is dominated by shape resonances that break predominantly the $S-H$ bond, while the $C-S$ bond is cleft predominantly by Feshbach resonances in the 7-15 eV region.

2. Experimental and Theoretical Methods

The dissociative electron attachment spectrometer used to measure the yield of mass-selected stable anions as a function of electron energy has been described previously [15, 16]. It employs a magnetically collimated trochoidal electron monochromator [17] to prepare a beam of quasi-monoenergetic electrons, which is directed into a target chamber filled with a quasi-static sample gas. Fragment anions are extracted at 90° by a three-cylinder lens and directed into a quadrupole mass spectrometer. The energy scale was calibrated on the onset of the O^-/CO_2 signal at 4.0 eV. The electron current was around 100 nA and the resolution about 150 meV. All the spectra were recorded at a temperature of 353-363 K.

3. Results and Discussion

3.1. Cleavage of the $N-C$ bond in saturated amines

Fig. 1(a) shows in solid line the DEA spectra of diethylamine (DE), diethylmethylamine (DEMA), triethylamine (TEA) and ethylbutylamine (EBA), amines that lose an ethyl radical upon electron collision. Additionally DE and EBA can also lose an H-atom forming the $(M-1)^-$ anion, shown in dotted line in Fig. 1(a). DEA of DE has been previously studied by Skalický and Allan [7] and our spectrum is in agreement with theirs. They have observed two distinct bands, at 4.7 eV and 8.4 eV. These bands were assigned to Feshbach resonances, with the lower energy band assigned to the $^2(n_N, 3s^2)$ Feshbach resonance where n_N is the a' nonbonding lone pair orbital, while the higher energy band assigned to the $^2(\pi_{CH_3}, 3s^2)$ Feshbach resonance, where π_{CH_3} is the a'' pseudo π orbital.

Fig 1(a) shows that the loss of an ethyl radical occurs at 8.3 eV irrespective of the target molecule. Similar to the above case encountered in DE, in EBA the ethyl radical can also be lost through a resonance at 5.0 eV albeit significantly less than the other resonance detected at 8.3 eV. As in DE, we assign the resonances at 5.0 eV to $^2(n_N, 3s^2)$ Feshbach resonance localized on the heteroatom. In all 4 amines we assign the 8.3 eV resonance as being a Feshbach resonance where the hole is predominately localized on the ethyl fragment.

Loss of butyl radical offers similar insight as the loss of the ethyl fragment. Fig. 1(b) shows the DEA spectra of dimetylbutylamine (DMBA), tributylamine (TBA) and EBA. The DEA spectra show that loss of butyl radical occurs mainly through a resonance located at 7.7 eV irrespective of the target molecule. As in the previous cases we assign this band to a Feshbach resonance, where a pair of electrons are in a $3s$ Rydberg type orbital and a hole is in an orbital mainly localized on the butyl chain.
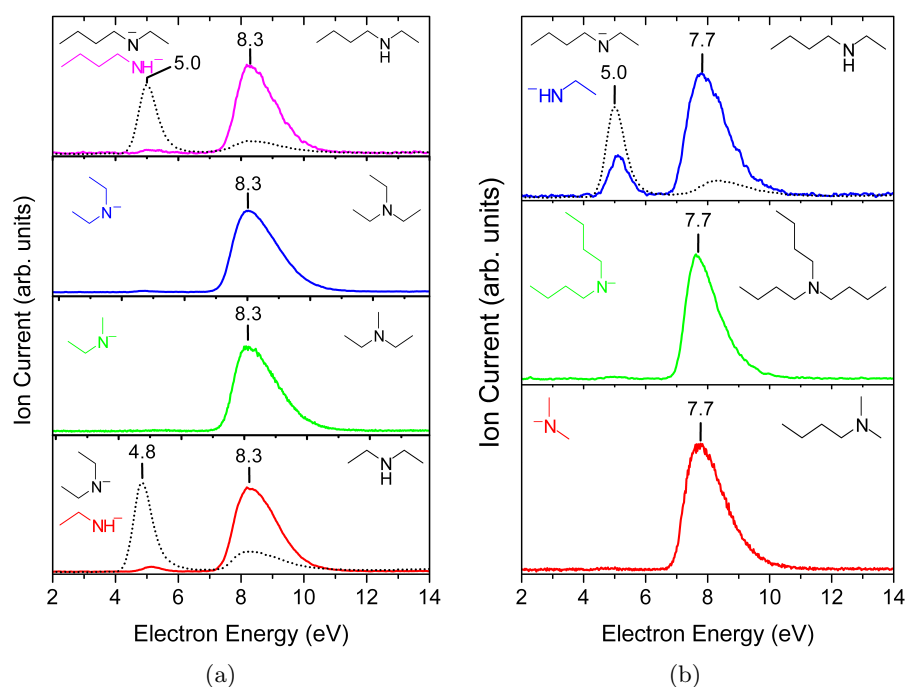
Figure 1. Loss of an ethyl radical (a) or butyl radical (b) from various amines. The resulting anion is shown in the left corner of each spectrum, while in the right corner the initial molecule is shown. For comparison loss of an H-atom is included as dotted lines.

Fig. 1 shows DEA spectra of tertiary amines able either to lose an ethyl or a butyl radical. An inspection of these spectra reveals that the breaking of the N−C bond occurs only at 8.3 eV for the loss of an ethyl and at 7.7 eV for loss of butyl. In all cases these bands have been assigned to a resonance localized on the respective alkyl group. There is no doubt that there must be a resonance at a lower energy, around 4.5-5 eV, localized on the nitrogen atom, similar to the secondary amines presented in Fig. 1. But the fact that no DEA band has been detected at these energies for tertiary amines is an indication for the presence of an activation barrier on the potential energy surface for the $^2(n_N, 3s^2)$ resonance.

A dependence on the alkyl chain can be noticed for the observed Feshbach resonance in the 7-14 eV energy range. The energy of this resonance is 7.7 eV when it is localized on a butyl chain and 8.3 eV for an ethyl chain. This energy dependence is particularly visible for EBA, an amine that can lose both ethyl and butyl radical, with the two processes proceeding independently of each other, even though both Feshbach resonances are present in the molecule.

This situation is very similar to that previously observed for ethers [6] where the energy of Feshbach resonance dropped from 9 eV when it was localized on an ethyl chain to 8 eV when it was localized on the butyl chain. Fig. 2 shows a comparison of the loss of cyclopentyl radical (top) and *tert*-butyl radical (bottom) from alcohols, ethers and amines. In all the presented compounds the bond dissociation is mediated by Feshbach resonances, but the loss of the radical (*tert*-butyl or cyclopentyl) occurs at the same energy independent on the heteroatom to which the group is linked. Cyclopentylamine (CPA) is a special case because the N−C bond breaking also occurs at 5.7 eV, suggesting a lowering of the barrier found in other amines and ethers.

For linear alkyl chains, like ethyl or butyl, we observe that the energy of the resonance depends on the heteroatom. When the heteroatom is oxygen then ethyl is lost at 9 eV while in the case of nitrogen it is lost at 8.3 eV. A similar shift is observed for butyl radical that is lost at 8.0 eV
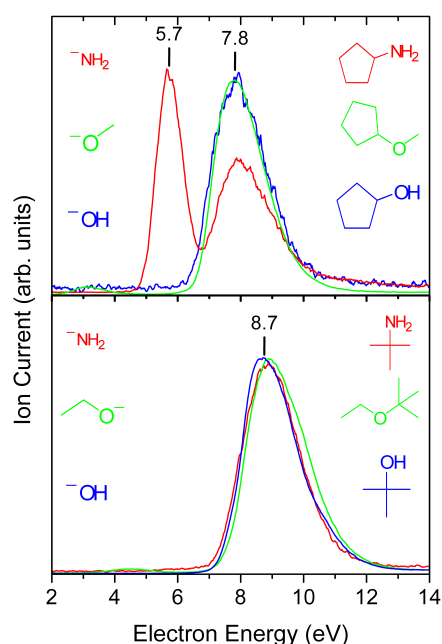
Figure 2. Comparison between loss of cyclopentyl radical (top) and *tert*-butyl radical (bottom) from various compounds. Amines are represented in red, ethers in green and alcohols in blue.

in oxygen containing compounds and at 7.7 eV in the case of amines. The shift to lower energies when the heteroatom in the molecule is changed from oxygen to nitrogen depends on the size of the alkyl chain involved. For relatively small chains, such as ethyl the shift is 0.7-0.8 eV and, as the chain size is increased, it drops to 0.3 eV for butyl chains and, finally for very bulky chains such as *tert*-butyl or cyclopentyl, it is not observable. A similar situation has been observed by Robin when he studied term energies and band shapes in VUV spectra [18]. He has observed that the term value that links the positive core observed in photoelectron spectroscopy and the Rydberg states observed in VUV spectra decreases as the volume of the group is increased from ethyl to *tert*-butyl [18]. At this point we can only speculate about the possible reasons such as the size of the positive core from the Feshbach resonance that could affect the interaction with the electronic cloud.

3.2. Dissociation patterns in ethanethiol

Little experimental data is available concerning dissociative electron attachment to thiols, with H_2S receiving the most attention. In this molecule the DEA process gives rise to HS^-, S^- and H^- ions. The recent work of Abouaf *et al.* [11] reveals marked differences between the DEA processes in H_2S and H_2Se on the one hand and H_2O on the other hand. They observed the presence of three separated bands in the S^- spectrum and suggested the occurrence of at least three resonant states. The lowest resonance at 2.2 eV was attributed to a shape resonance, involving an attractive resonance state. The higher resonances are most likely Feshbach resonances, but the corresponding parent states were not identified.

As a model compound for thiols we have measured the DEA spectra of ethanethiol that are presented in Fig. 3. The DEA band of $CH_3CH_2S^-$ reveals the presence of only one band at 1.8 eV. This band is too low to be assigned to a Feshbach resonance and, most likely, is due to a shape resonance. The thermodynamical threshold energy (1.74 eV) calculated with the method developed for alcohols [4] indicates that the band occurs as soon as the process becomes thermodynamically available.

Another ion formed in the dissociation of the ethanethiol is CH_3CHS^-. The DEA spectrum of the anion reveals two bands at 0.61 eV and 1.66 eV. The lowest band is very close to the
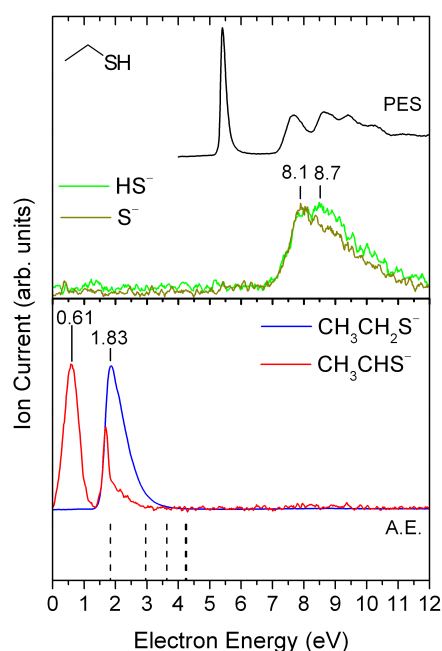
Figure 3. DEA spectra of ethanethiol. The HeI photoelectron spectrum is displayed on the top (shifted by -4.0 eV). The attachment energies are calculated using the empirical formula of Chen and Gallup [19] and are diplayed on the bottom.

calculated thermodynamical threshold (0.44 eV) for formation of this ion. Also, it is too low in energy to be considered as a Feshbach resonance. All these, and the similarity to the band in the spectrum of the previously discussed ion indicate that the band is a shape resonance occurring at the thermodynamic threshold.

The contour of the 1.66 eV band is distinct from those of the bands encountered so far. It has an onset at 1.37 eV with a maximum at 1.66 eV. But there are several distinctive features: the onset of the band corresponds to that of the band at 1.81 eV in the $CH_3CH_2S^-$ spectrum. Additionally, at 1.82 eV it shows a dramatic change in the slope corresponding to the maximum in the $(M-1)^-$ spectrum. The coincidence in the onset of the band indicates that the same process is responsible for both bands. But the change in the slope at 1.82 eV is indicative for another process becoming dominant. These processes are not pressure dependent and thus not the result of ion-molecule reactions. We conclude that, initially, the electron is trapped in a shape resonance. The newly formed temporary negative ion dissociates initially through the CH_3CHS^- channel. But as soon as a new channel ($CH_3CH_2S^-$) becomes available the dissociation in the old channel decreases significantly, indicative of interchannel coupling.

Fig. 3 shows the spectra of two more fragments: S^- and HS^-. They are the result of breaking of the C−S bond either alone or accompanied by the breaking of the S−H bond. In both situations this process shows a remarkable energy selectivity since it occurs at energies above 7 eV. This suggests that the primary process for the formation of both ions is cleavage of the C−S bond *via* a Feshbach resonance, in contrast to the breaking of the S−H bond which in ethanethiol occurs through a shape resonance.

The DEA spectrum of S^- shows the presence of a single asymmetric band with a maximum at 8.1 eV. The energy of this band can be associated with the second band in the PE spectrum shifted by -4.0 eV. This is an indication that the resonance associated with the band could be a Feshbach resonance with a hole in the in-plane sp lone pair of the S-atom. It is unclear why there is no band associated with the p lone pair from the S-atom, but most likely an activation barrier on the potential surface of the Feshbach resonances could inhibit dissociation during the lifetime of the resonance.

The DEA spectrum of HS^- ion consists of two resonances as indicated by the additional

signal observed when the spectrum of HS$^-$ is compared to that of S$^-$. As explained above, the 8.1 eV is most likely a Feshbach resonance where the hole is localized in the in-plane sp lone pair of the S-atom, while the 8.7 eV resonance could be another Feshbach resonance that could be associated with the third band in the PE spectrum.

4. Conclusions

The dissociation of amines upon electron collision occurs mainly through the breaking of either N$-$H, with the loss of an H-atom, or N$-$C bond, with the loss of an alkyl radical. In all cases the bond breaking is mediated by Feshbach resonances.

Two Feshbach resonances have been detected in the DEA spectra of amines. The first resonance is at 4.8-5.0 eV and has been identified as a $^2(n_N, 3s^2)$ Feshbach resonance (as shown by the energy relation with the grandparent cation [7]), while the second one is placed at energies higher than 7 eV. The latter resonance shows a particular dependence on the alkyl chain which is lost as neutral fragment, being at 7.7 eV for butyl and at 8.3 eV for ethyl chains, even in molecules where these chains are both present such as EBA.

In secondary amines the Feshbach resonances at 4.8-5 eV breaks also the N$-$C bond, similar to the case of C$-$O bond encountered in monoethers of ethyleneglycol [6], a result of the lowering of the activation barrier otherwise present on the potential surface of the resonance. In monoethers of ethylene glycol this is the result of an hydrogen bond between the two oxygen atoms, situation not applicable to amines for which the lowering of the activation barrier is most likely due to the pyramidal geometry of the primary molecule allowing for more energy to be stored in the structure of the molecule. This energy can be used to surpass the barrier as the molecule changes from pyramidal geometry of the initial molecule to the planar geometry of the final anion.

Thiols present a different case of site selectivity. The DEA spectra for the loss of H-atom and H$_2$ from ethanethiol seem to be dominated by shape resonances in the 0-3 eV region. Even if the capture mechanism of the electron to form the shape resonance is unclear for the moment, these resonances are responsible for breaking of the S$-$H bond. In the case of the C$-$S bond the main mechanism of dissociation most likely involves Feshbach resonances and they are found above 8 eV. This leads to a clear separation of the type of dissociation, with the S$-$H bond being broken preferentially in the 0-3 eV range and C$-$S bond in the 7-15 eV region. Unfortunately the selectivity is not restricted to the formation of one ion, but rather to the bond that is broken in the dissociation.

5. Bibliography

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