Dissociative Electron Attachment

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Influence of Functional Groups on the Site-Selective Dissociation of Adenine upon Low-Energy Electron Attachment**

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Recently an increasing number of dissociative electron attachment (DEA) studies have been performed with isolated biomolecules in the gas phase.[1] Interest in these molecules rose from the discovery that electrons with energies below 15 eV can induce substantial yields of single- and double-strand breaks in plasmid DNA.[2] This damage of DNA was attributed to the fast decay of transient negative resonances localized on the DNA base constituents.[1] For nucleobases the most abundant anion formed is the closed-shell dehydrogenated molecular anion [Eq. (1)]. Here, $M^{-}*$ is the transient

$$e^- + M \rightarrow M^{-}* \rightarrow (M{-}H)^- + H \quad (1)$$

negative nucleobase ion formed by resonant electron capture. For all nucleobases reaction (1) is mainly operative at electron energies below 3 eV. The plot of the ion signal versus the applied electron energy shows a characteristic structure with a few narrow overlapping peaks followed by one or two broad resonances.[3–6] DEA experiments with partially deuterated thymine[6] showed that for thymine (T) reaction (1) leads exclusively to the loss of a hydrogen atom from one of the two nitrogen sites. Subsequent measurements with partially methylated pyrimidine bases[7,8] showed that all of the narrow vibrational progressions in the ion yield result from hydrogen loss from the N1 site. Thus these previous DEA experiments with T and uracil (U) showed bond and site selectivity which in the meantime has also been observed in the H^- channel in DEA to T,[9,10] for U,[9,10] and for simple organic molecules like acetic acid[11] and D-Ribose.[12] These results demonstrate the possibility to control and induce selectively chemical reactions by using a specific electron energy in free DEA. Such a control has been achieved so far using inelastic tunneling of electrons in scanning tunneling microscopes[13] and in highly sophisticated laser experiments.[14]

The unanswered question is whether this steering of chemical reactions by DEA is also operative for other classes of (bio-) molecules. By using partially labeled derivatives of adenine (Ad) and by means of quantum chemical calculations, we have explored the origin of the various peaks in the ion yield of $(M{-}H)^-$ for purine derivatives. (The structures of the molecules investigated are included in Figure 1 and Figure 2.)

In the present collaborative study devices of two different laboratories (Innsbruck and Orsay) were used. The Orsay setup consists of an electron spectrometer equipped with two hemispherical energy analyzers in tandem, one in the monochromator (resolution from 25 to 60 meV) and one in the analyzer section in combination with a time-of-flight mass spectrometer.[16] In Innsbruck a hemispherical electron monochromator (resolution for the present work from 60 to 100 meV) and a quadrupole mass filter were used.[3,4] An effusive beam of molecules was generated by vaporizing commercial products in ovens heated to temperatures between 115 and 190 °C depending on the sample. The energy scale was calibrated with the SF_6^- and Cl^- anion signals formed upon electron attachment to SF_6 and CCl_4, respectively, at 0 eV.

The ion yield of the dehydrogenated Ad anion $(M{-}H)^-$ is shown in the upper panel of Figure 1 measured with an electron energy resolution of about 60 meV (Orsay setup). There is good agreement with the previous measurement of $(M{-}H)^-$ of Ad carried out earlier in Innsbruck[17] which demonstrates the nearly identical performance of the two machines. The ion yield shows narrow peaks at 0.72, 0.84, and 1.07 eV (all values ± 0.07 eV), followed by two wide bumps at about 1.4 and 2.2 eV. Also shown in Figure 1 is the $(M{-}H)^-$ signal of adenine deuterated at the C2 position ([2-D]Ad) recorded with an energy resolution of 80 meV. The measured ion yield of $(M{-}H)^-$ is virtually identical for both molecules. The less resolved peak structure in the case of [2-D]Ad can be attributed to the slightly worse energy resolution used for this molecule. Thus we can conclude that dehydrogenation of Ad does not occur at the C2 position, as this is blocked by D in the deuterated adenine and no $(M{-}D)^-$ signal is observed.

The purines studied have all negative electron affinities (EAs). The bond dissociation energies (BDEs) of the hydrogen atoms of Ad and the energies required for reaction (1) have been calculated with the G2(MP2) quantum chemical extrapolation method[18] (Table 1; estimated accuracy:

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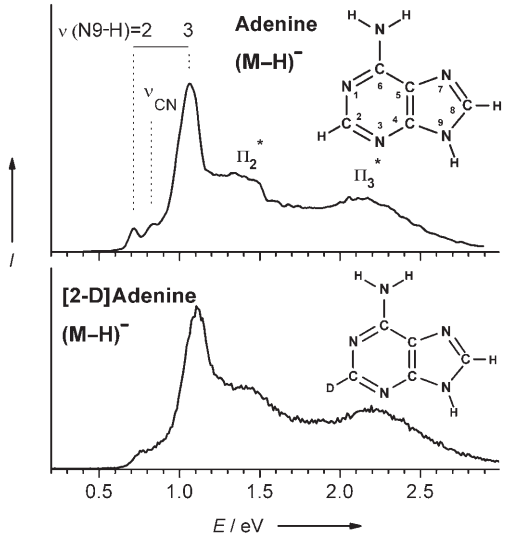

Figure 1. Ion yield of the dehydrogenated molecular anion $(M-H)^-$ formed by DEA to adenine (top; measured in Orsay) and [2-D]adenine (bottom; measured in Innsbruck). Also indicated are energy levels of the vibrational modes ascribed to the N9–H stretch and C–N ring stretch (see text). The canonical form of Ad shown represents the most stable tautomer in the gas phase.[15]

Table 1: Bond dissociation energies (BDEs) of hydrogen atoms in neutral adenine and energies (E_{DEA}) required for the DEA process $Ad + e \rightarrow (Ad-H)^- + H$.[a]

H abstraction from	BDE	E_{DEA}
C2	4.74	3.63
N6	4.69	1.72
C8	5.06	2.53
N9	4.38	0.94

[a] From G2(MP2) calculations; the values are given in eV and include electronic energy and zero-point vibration energy.

± 0.2 eV). The present values are very similar to those from DFT studies reported by Evangelista et al.[19] (within 0.02 eV) and in fair agreement with those of Zierhut et al.[20] (within 0.35 eV). It follows from the data in Table 1 that the H atom at the N9 site has the smallest BDE. For the DEA this energy is about half of that required to dissociate the next strongest bond which is N6–H. The difference between the two values is equal to the EA of (M–H). Thus one obtains an EA of 3.44 eV for (M–H) of Ad (H loss from N9).

According to these calculations one can assume that the narrow peaks at low energies (below about 1.07 eV) in Figure 1 should originate solely from H loss from the N9 position. This prediction can be easily verified by measurements with 9-methyladenine (9-mAd), in which the N9 position is blocked with a CH_3 group. Indeed, the corresponding ion yield (shown in Figure 2, upper panel) starts only above 1.4 eV. Taking into account the data from Table 1 this weakly observed signal could be ascribed to H loss from the NH_2 group attached to the C6 position. For a conclusive check on this latter conjecture we performed an additional experiment with 6-dimethyladenine (6-dimAd), thus blocking the H positions at the amino group with CH_3, in which the

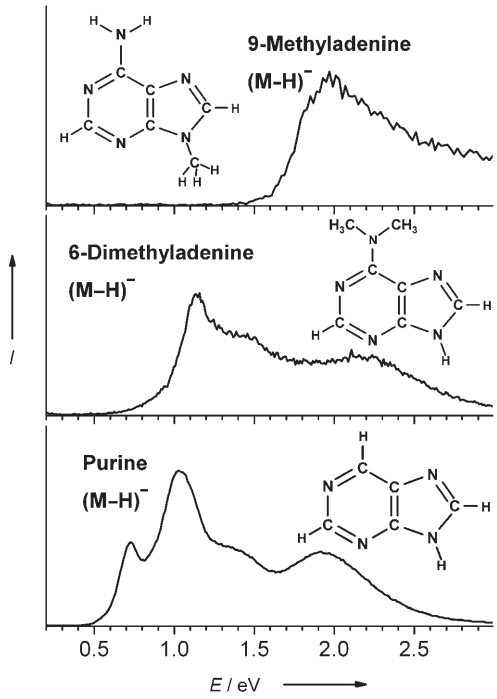

Figure 2. Ion yield of the dehydrogenated molecular anion $(M-H)^-$ formed by DEA to 9-methyladenine (top), 6-dimethyladenine (middle), and purine (bottom), respectively (recorded in Innsbruck).

NH_2 group is replaced with an $N(CH_3)_2$ group Surprisingly the corresponding ion yield of $(M-H)^-$ (see Figure 2, middle panel) shows not only a peak structure at low energies (presumably due to H loss from the "open" N9 position), but also one at the higher energies, which for 9-mAd corresponds to hydrogen loss from the amino group. However, analogous to the case of 3-methyluracil[7,8] Feshbach resonances with additional quantum modes may contribute to the resonances above 1.07 eV for 6-dimAd (see below).

Moreover, it is worthy to note, that when comparing the curves for Ad (Figure 1) and for 6-dimAd (Figure 2), the first two sharp peaks at about 0.7 and 0.8 eV present in Ad are not present for 6-dimAd. In addition, the relative height of the resonance at 1.07 eV is substantially reduced (as compared to the high-energy humps). In passing we note that the resonances below 1 eV are also quite different for purine (Pu) (Figure 2). For this compound also the positions of the resonance features above 1 eV are different than for Ad.

Taking into account the data in Figures 1 and 2 (demonstrating that the small peaks at low energy are predominantly due to H loss from the N9 position) the DEA to Ad producing $(M-H)^-$ may be viewed to be very similar to the case of T and U. We therefore propose an interpretation similar to that given by Burrow et al.[8] for T and U in terms of vibrational Feshbach resonances due to an avoided crossing between the potential curves of the lowest σ* state and the dipole-bound state (according to our calculations the dipole moment of Ad is 2.36 D). Thus the peaks at 0.72 and 1.07 eV would then be due to Feshbach resonances associated with the $\nu = 2$ and $\nu = 3$ levels of the N9–H stretching mode (see Figure 1). Of course the dissociation is not purely diatomic, and the peak at

0.84 eV is assigned to a Feshbach resonance associated with a combination mode N–H ($\nu = 2$) plus an additional quantum of the C–N stretch mode of the ring atoms (about 0.13 eV) as assigned in Figure 1. Moreover, the energy locations of the π_2^* and π_3^* resonances observed at 1.36 and 2.17 eV, respectively, by electron transmission spectroscopy[21] seem to perfectly match the locations of the two wide humps observed at about 1.4 and 2.2 eV. It is then likely that a predissociation process of these π^* resonances by higher σ^* resonances occurs through vibronic coupling leading to the appearance of these features.

Finally, we turn to the intriguing question why the C6–H, C6–NH_2, and C6–$N(CH_3)_2$ groups, which differentiate the purine derivatives from each other (Pu, Ad, and 6-dimAd, respectively), and are rather far away from the N9 site, cause remarkably different spectra, in particular at the low energies where H loss from the N9 position is the solely operative channel for DEA to Ad. It is interesting to note that when going from Pu to Ad to 6-dimAd the dipole moment vector moves out of the direction of the N9–H bond and its magnitude decreases from 3.66 to 2.19 D. This obviously causes a considerably different electrical field at the N9–H bond for the three molecules. More detail on this can be provided, for example, by looking at the electrostatic potentials (ESP) of the molecules. Whereas for Pu the only region of strongly positive ESP is around the N9–H site (and the neighboring C8–H site), in case of Ad and also for 6-dimAd a second positive ESP region appears around the NH_2 and $N(CH_3)_2$ groups (Figure 3). Since regions of positive ESP attract an electron, the various functional groups leading to different ESPs should therefore influence the DEA spectrum. Indeed the lowest virtual σ^* molecular orbital (MO) of the neutral molecule (which could be occupied in the metastable anion) show the expected differences. In Figure 3 we plotted these virtual σ^* MOs (calculated with the B3LYP/aug-cc-pVTZ method and basis set) at the equilibrium geometry of the neutral molecules. It can be clearly seen that there is no wave-function density in the C6–H region for Pu, whereas there is one in the C6–NH_2 and C6–$N(CH_3)_2$ regions of Ad and 6-dimAd, respectively. It is remarkable that indeed the lowest pair of virtual σ^* MOs for each molecule (the second one is related to the first by symmetry breaking and a changed sign of the wave function and is not shown) have node surfaces intersecting the N9–H bond since this is a second indication, independent of the energy criteria, of the dissociation site. The next higher virtual σ^* MOs have additional density at the C8–H site, also in accordance with the ESP. We further checked whether 9-mAd is indeed similar to Ad by comparing their ESP, the lowest σ^* MO, and the dipole moments. Both the ESP and the shape of the lowest virtual σ^* MO of Ad and of 9-mAd are very similar. The approximate energy of the MOs differs by 0.05 eV. Since also the calculated dipole moments of Ad and 9-mAd are similar (2.37 and 2.55 D, respectively) we believe this basic assumption to be justified.

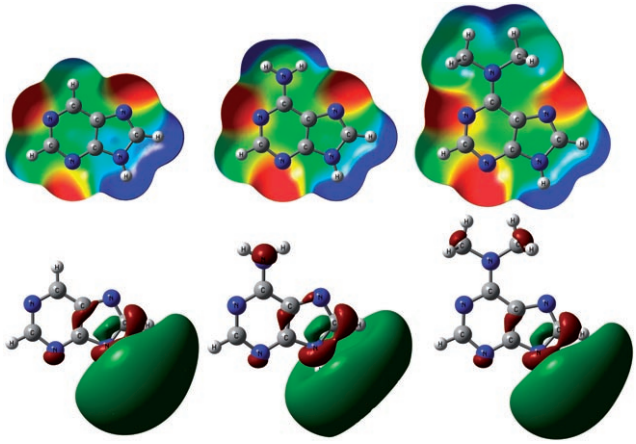

Figure 3. Electrostatic potential maps (top) of purine (left), adenine (middle), and 6-dimethyladenine (right). Regions with positive ESP are blue, those with negative ESP are red. The bottom row shows isodensity maps of the lowest virtual σ^* molecular orbitals (B3LYP/aug-cc-pVTZ calculations).

In conclusion, we performed a detailed study of site-selective DEA to adenine and partially labeled derivatives. A change of the substituent at the C6 site leads to a strong modification of the peak structure of $(M-H)^-$ below 1.4 eV although the hydrogen loss can be ascribed exclusively to the N9 position. Even if we cannot provide a quantitative simulation of the processes, calculations show the influence of the functional groups on the electrostatic moments. This changes the bond-weakening σ^* molecular orbitals at N9–H which finally leads to the difference in the observed DEA spectra.

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