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Low Energy (0-12 eV) Electron Interaction with Gas Phase Building Blocks of DNA/RNA

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Abstract. We review recent results on dissociative electron attachment (DEA) to gas phase D-ribose, tetraacetyl-D-ribose (TAR) and dibutyl phosphate (DBP), which serve as model compounds for the DNA or RNA backbone. New results are presented on negative ion formation in D-ribose probed by matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectrometry. The two methods reveal that the transient D-ribose anion \( R^{-} \) decomposes in the same way like the deprotonated D-ribose molecule \([R-H]^{-}\), i.e. by abstraction of different numbers of water and formaldehyde units. In DEA the TNI \( R^{-} \) is generated at very low energies close to 0 eV most likely through a vibrational feshbach resonance. The fragmentation pattern and the characteristic resonances of D-ribose are preserved in TAR, where a furanose is bound to four acetyl groups. The presence of an acetyl group leads additionally to fragmentation through a shape resonance. Shape resonances were also observed in DBP, followed by C-O and P-O bond breaking.

1. Introduction
We present recent results on the interaction of low energy electrons (LEEs) with the components of the DNA backbone in an effort to unravel the molecular mechanism how low energy electrons (LEEs) damage DNA. We consider biomolecular systems that may serve as appropriate models to probe the response of the sugar and the phosphate moiety in DNA towards the attack of LEEs. It appears that in order to assess the role of a particular DNA component it is not sufficient to study the isolated molecule. Instead one has to find appropriate molecular systems that mimic its coupling within DNA. The interaction of high energy radiation (\(\alpha, \beta, \gamma\)) abundantly generates secondary electrons along the ionisation track [1]. In the meantime it is well recognised that reactions induced by these LEEs with the vital components of a cell (DNA, proteins, water) is an important contribut or in radiation damage of living cells. Within this context, reactions directly induced in DNA are referred to as direct damage. With regard to the molecular mechanisms behind direct radiation damage a great number of experimental and theoretical works has been performed within the last few years [2], and the state of the art can briefly be summarised as follows:

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Exposure of plasmid DNA to free electrons at energies already below the ionisation threshold leads to single strand breaks (SSBs) and double strand breaks (DSBs) [3]. These findings contrast the traditional notion which considered only electrons above the ionisation threshold to be involved in strand breaks. The number of strand breaks per incident electron flux shows a resonant behaviour with the electron energy. Both SSBs and DSBs are observed within a resonant feature in the energy range between 6-15 eV [3] while electron irradiation within a low energy resonance (in the range 0-4 eV) only induces SSBs [4]. These findings suggest that resonant capture of electrons at particular DNA sites may be the initial step towards SSBs and DSBs.

The interaction of LEEs with the isolated gas phase DNA bases thymine (T), cytosine (Cy), adenine (A) and guanine (G) studied in crossed electron- molecular beam experiments [5-10] showed that all the DNA bases undergo dissociative electron attachment (DEA) via two resonant features located between 0-4 eV and 6-12 eV, similar to the energy dependence of strand breaks in plasmid DNA. While processes within the high energy feature lead to the loss of H- and larger fragment ions [6], partly associated with the deterioration of the cyclic structure, DEA via the low energy feature exclusively abstracts a neutral hydrogen atom from the N sites thereby generating the closed shell DNA base anion [7,8]. This hydrogen loss is subjected to a remarkable site selectivity as (in T) electrons of 1 eV energy exclusively induce loss of H from the N1 site while at 1.8 eV this occurs preferentially from the N3 site [8].

Experiments on self assembled monolayers of short oligonucleotides [11] and oligonucleotides immobilised on microarrays [12] revealed that the DNA bases act as antennas for electrons at subexcitation energies thereby also inducing damage of the oligonucleotide [12].

Based on these findings an electron transfer mechanism for DNA strand breaks was proposed by theoretical studies [13,14] modelling a section of DNA composed of cytosine, sugar and the phosphate group. These calculations predict a low-lying anionic potential energy surface which connects the initial \( \pi^* \) anion state of the base to a \( \sigma^* \) state in the backbone. An electron captured by a DNA base may thereby be transferred to the backbone leading to rupture of the C-O bond between the phosphate and the sugar.

On the other hand, gas phase studies on thymidine (a thymine coupled to a deoxyribose molecule by the glycosidic N1-C1 bond) [15] did not show any electron transfer from thymine to the sugar moiety via the low energy resonance, at least no electron transfer associated with DEA. The low energy resonance only resulted in the H loss from the N3 position. These findings do not necessarily contradict the above electron transfer mechanism as the presence of the phosphate group may modify the electron transfer behaviour of the system. It demonstrates, however, that coupling of the molecule in the DNA network significantly modifies its properties with respect to DEA. While in T the loss of neutral hydrogen from the N1 position is the dominant DEA reaction in the free molecule, DEA is completely suppressed once the deoxyribose is coupled at N1 [15]. This observation is corroborated by methylation experiments indicating that the loss of H is completely blocked, once the corresponding hydrogen atoms are replaced by the methyl group [8]. These results clearly demonstrate that in order to study the role of individual DNA components it is not sufficient to probe the isolate molecule but one has to find appropriate molecular systems that mimic its coupling in DNA.

An alternative mechanism for DNA strand breaks is based on proton transfer triggered by an excess electron [16]. DFT calculations on the nucleotide of cytosine predict that Cy hydrogenated at the C6 position (Cy+H) can strongly bind an excess electron to form the closed shell moiety (Cy+H) with the excess charge localized at the C-6 position of (Cy+H). A proton transfer process then induces a barrier free sugar-phosphate C-O bond cleavage. It should be noted that these calculations refer to the electronic ground state of the system, while the electron transfer model from above [13] treats the system initially as a resonant state, i.e. the DNA base captures a free ballistic electron to form a transient negative ion state which is embedded in the detachment continuum.

On the background of the present experimental material and the different theoretical models the evolution of an excess charge initially localised on a DNA base is hence not resolved. The question then arises on the sensitivity of the sugar and the phosphate unit towards low energy electrons. A DFT
treatment of the thymine nucleotide [17] in fact predicts low lying resonant states localised directly on the phosphate moiety. An exploration of the adiabatic and vertical (C-O) potential energy surfaces (including solvation by water molecules and the presence of a Na+ counter ion at the phosphate) supports the picture that LEEs transiently captured at the phosphate can induce SSBs via rupture of the sugar-phosphate (C-O) bond.

Here we review recent results on DEA to ribose [18], tetraacetyl-D-ribose (TAR) [19] and dibutylphosphate (DPB) [20]. The latter two systems can be considered as reasonable surrogates to probe the behaviour of the deoxyribose and phosphate moiety in DNA towards the interaction of low energy electrons. In combination with new experiments on negative ions generated through matrix assisted laser desorption and ionisation (MALDI) a more comprehensive picture of negative ion formation and decomposition in D-ribose is obtained.

2. Experiments

Dissociative electron attachment (DEA) is studied using a crossed electron molecular beams arrangement [21], which is housed in a high-vacuum chamber. The electron beam is generated with a trochoidal electron monochromator (TEM) [22] allowing an electron energy resolution of ≈ 100 meV at a current of 5-20 nA. The molecules of interest are evaporated from a small vessel inside the vacuum system by heating the whole chamber with two halogen bulbs to moderate temperatures not higher than 370 K. In the reaction volume the evaporative molecular beam crosses the electron beam, and the generated anions are extracted by ion optics and mass analysed and detected with a quadrupole mass spectrometer. The energy scale is calibrated using the formation of metastable SF6- from SF6 at 0 eV. The flow of SF6 gas was switched off prior to each measurement.

MALDI-TOF experiments have been performed in the Reykjavik laboratory with a REFLEX IV (Bruker Daltonics) instrument that is equipped with a time-of-flight (TOF) Reflectron type mass spectrometer and a pulsed N2 laser (337 nm, 10 Hz, 400 μJ/pulse) [23]. Ion extraction is pulsed with 400 ns delay time. For each spectrum the samples were irradiated at different spots to compensate for inhomogeneities of the sample. In-source decay (ISD) spectra were measured in reflectron mode using 300 laser shots. For post-source decay (PSD) the deprotonated D-ribose was selected at a gate and its fragmentation was measured in six mass segments. For each segment the reflection voltage is stepped down to ensure for collection and detection of all fragment masses, and 500 laser shots per segment were collected. Samples were prepared by deposition of 0.5 μL of a 3.5 mM solution of matrix (Bis-benzimide (C_{25}H_{24}N_{6}O)) in methanol on a polished stainless steel sample carrier and allowed to dry in air. Afterwards 0.5 μL of 0.13 M D-ribose solution in methanol was spotted on the matrix and allowed to dry.

5-13C-D-ribose and C,1-D-D-ribose were obtained from Cambridge Isotopes Laboratories, Inc., and all other samples were purchased from Sigma Aldrich. All substances were used as delivered.

3. Results and Discussion

All investigated compounds serve as models for the DNA or RNA backbone. The isolated monosaccharide D-ribose (C_{5}H_{10}O_{5}) is a rough model for the sugar unit in RNA (and DNA), tetraacetyl-D-ribose is used as an improved model for a furanose sugar coupled within a more complex molecular environment, and dibutylphosphate mimics a neutral phosphate group bound to two aliphatic carbon chains. Our findings indicate that all compounds are sensitive towards low energy electron attachment and show characteristic ion yield curves. The anion formation and fragmentation is ascribed to the dissociative electron attachment (DEA) mechanism [21], viz.:

\[ \text{ABC} + e^- \rightarrow \text{ABC}^\text{-} \rightarrow \text{AB} + \text{C}^- \quad (1) \]

An electron of defined energy is resonantly captured by the neutral molecule to form a transient negative ion (TNI). The TNI ABC^\text{-} is basically unstable towards autodetachment of the extra electron, however, if the lifetime exceeds one vibrational period it may dissociate into a stable anion and neutral fragment. The resonant character of the process is determined in the ion yield curve of a given
fragment ion, for instance $C^-$. The production of a fragment ion may proceed either directly within the lifetime of the resonance, i.e. usually $10^{-15} - 10^{-12}$ s, or indirectly via the formation of metastable intermediates. The DEA experiment does not allow distinguishing these processes whereas some details of the fragmentation dynamics are revealed by MALDI experiments.

DFT calculations (section 3.1.1.) on stable anionic products generated through DEA to D-ribose and MALDI mass spectra of D-ribose (section 3.1.2.) reveal slightly different reaction pathways and structures of product anions than previously suggested in [18].

3.1. D-ribose

3.1.1. DEA spectra. D-ribose captures electrons already at very low energies close to 0 eV and decomposes subsequently into various fragment anions [18]. The most effective dissociation channel is loss of one or two water molecules leading to formation of $C_5H_8O_4^-$ (132 amu) and $C_5H_6O_3^-$ (114 amu), respectively [18]. But also the carbon ring is decomposed resulting mainly in generation of $C_4H_5O_3^-$ (101 amu), $C_3H_4O_2^-$ (72 amu) and $C_2H_3O_2^-$ (59 amu).

Unambiguous assignment of decomposition products is achieved using the isotope labelled analogues 5-13C-D-ribose, 1-13C-D-ribose and C,1-D-D-ribose (figure 1). For instance, the 101 amu fragment can also be assigned to $C_5H_9O_2^-$ that contains all five carbon atoms. However, the DEA spectra in figure 1 show that in 5-13C-D-ribose the signal remains at 101 amu, whereas it vanishes completely in 1-13C-D-ribose and C,1-D-D-ribose, respectively, and shifts to 102 amu (left column of figure 1). Moreover, it follows that production of $C_4H_5O_3^-$ proceeds via selective excision of C-5. The experiment does not deliver information on the neutral decomposition products, but the most likely composition is $CH_2O + H_2O + H$, since all products can be formed with low bond-breaking barriers from the sugar. However, the thermodynamics are more favorable for other channels (sum of heats of formation of neutral products is $\Sigma_{\text{neut.prod.}} \Delta H^0 = -140 \text{ kJmol}^{-1}$ [24]) like $CO_2 + 2H_2 + H$ ($\Sigma_{\text{neut.prod.}} \Delta H^0 = -176 \text{ kJmol}^{-1}$ [24,18]). Nevertheless the latter reaction is unlikely due to large activation barriers. Consequently the carbon atom of the generated formaldehyde molecule, $CH_2O$, is C-5 (figure 2).
Basically the molecular structure of the 101 amu fragment may be a 5-ring structure containing one oxygen atom. However, DFT calculations on different stable anionic structures for C$_5$H$_{10}$O$_5^-$ reveal that only an open chain anion, that is stabilized by a hydrogen bond (as is shown in figure 2) can be formed at threshold [25].

The fragment anion at 72 amu (shown in the right panel of figure 1) is ascribed to the following reaction: e$^-$ ($\approx$ 0 eV) + C$_5$H$_{10}$O$_5$ $\rightarrow$ C$_5$H$_{10}$O$_5^-$ + 2 CH$_2$O + H$_2$O. The site selectivity is similar to the 101 amu fragment since the m/Z 72 signal is almost completely shifted in 1-$^{13}$C-D-ribose and C$_1$-$^{13}$C-D-ribose to 73 amu but almost no signal is observed at 73 amu in 5-$^{15}$C-D-ribose. Consequently the only difference to the 101 amu fragment anion is presumably the generation of an additional formaldehyde molecule that is most likely formed from C-4 (figure 2). However, from thermodynamics the production of neutral CO$_2$, methanol (CH$_3$OH) and H$_2$ is more favourable ($\Sigma_{\text{neutr.prod.}} \Delta H^0 = -595$ kJmol$^{-1}$ [24]) compared to $\Sigma_{\text{neutr.prod.}} \Delta H^0 = -518$ kJmol$^{-1}$ for production of formaldehyde and water.

**Figure 2.** Formation of the 101 amu and 72 amu fragment ions from the D-ribose transient anion. According to recent DFT calculations [25] the reaction pathways shown here are exothermic; they differ slightly from the reaction products originally proposed in [18].

### 3.1.2. MALDI-TOF spectra

Figure 3 displays MALDI-TOF mass spectra of anions produced from D-ribose. In ISD (upper panel of figure 3) the main fragmentation reactions are:

- C$_5$H$_{10}$O$_5$ $\rightarrow$ (R-H)$^-$ (149 amu) + H (2)
- C$_5$H$_5$O$_4^-$ (129 amu) + H$_2$O + H$_2$ + H (3)
- C$_4$H$_4$O$_1^-$ (100 amu) + H$_2$O + CH$_2$O + H$_2$ (4)
- C$_3$H$_2$O$_2^-$ (71 amu) + 2 CH$_2$O + H$_2$O + H (5)
- C$_2$H$_2$O$_2^-$ (58 amu) + H$_2$O + C$_3$H$_4$O$_2$ + H (6)

The ISD spectrum is due to ionization and fragmentation inside the ion source, i.e. prompt decay in the plume up to early metastable decay within the 400 ns before ion extraction. Unlike the DEA experiments described above the conditions in the MALDI plume are far from single collision conditions [26], that is multiple collisions are likely and the observed product ions have a chance to relax through collisions. The ionization mechanism in MALDI is not fully understood to date, but deprotonation of the analyte molecules leading to a closed shell anion is considered to be the most important process. Additionally electron capture processes may be involved [26,27]. The presence of low energy photoelectrons was shown previously through the production of SF$_6^-$ from SF$_6$ [27], which was introduced into the vacuum system of a MALDI source combined with a FT-ICR mass spectrometer. A similarity of the fragmentation patterns in MALDI ISD and DEA processes is obvious, i.e. release of neutral water and formaldehyde molecules from the parent anion.
In most cases the signals in MALDI ISD are shifted by one mass unit (100, 71, 58 amu) compared to DEA spectra (mainly 101, 71, 72 and 59 amu). One exception is the signal at 129 amu, which is accompanied by small contributions of 130 and 131 amu. The deprotonated parent ion [R-H] at 149 amu was not observed at all in DEA.

The DEA experiments are controlled by single-collision conditions, i.e. the reactive transient negative ion is an open shell radical anion that decays into one (neutral or anionic) radical species. In other words the whole system always contains an excess electron and relaxes into a thermodynamically stable system with respect to the TNI. In contrast to that the deprotonated D-ribose is a closed shell anion and the fragmentation is controlled by the neutral products leading finally to closed shell fragment anions having one hydrogen less than the ions observed in DEA. If we additionally consider electron capture processes that may take place in ISD, it has to be noted that the in-plume conditions in MALDI allow generation of thermodynamically more stable products, i.e. closed shell anions. For instance abstraction of two formaldehyde molecules and one water molecule from the TNI R’ve generates the radical anion C3H4O2- (72 amu) that presumably possesses two conjugated double bonds with the extra electron residing in a $\pi^*$ orbital. The radical anion may still be reactive if it is allowed to collide, and may thus lose a hydrogen atom in the course of collisions with surrounding molecules - for instance matrix molecules - resulting in the anion C3H3O2- with mass 71 amu as it is observed in ISD and PSD.

The same considerations are valid for the PSD spectrum of the closed shell deprotonated D-ribose molecular anion [R-H] (lower panel of figure 3). [R-H] decays into the following products:

\[
\begin{align*}
\text{C}_5\text{H}_9\text{O}_5^- \quad &\rightarrow \quad \text{C}_4\text{H}_7\text{O}_4^- + \text{H}_2\text{O} \\
&\rightarrow \quad \text{C}_3\text{H}_5\text{O}_3^- + 2 \text{CH}_2\text{O} + \text{H}_2\text{O}
\end{align*}
\]

All these anions occur in DEA as well, but with one hydrogen atom more and in different intensity ratios. Thus the neutral decomposition products are identical in DEA and MALDI-PSD.

The comparison with free electron attachment shows that the TNI of D-ribose R’ve as well as the deprotonated D-ribose [R-H] decompose in a characteristic manner, i.e. by abstraction of different numbers of neutral water and formaldehyde molecules. The abstraction of one and two formaldehyde molecules (in addition to one H2O molecule; resulting in 101/100 amu and 72/71 amu, respectively) proceeds site selectively from C-5 and C-4 (figure 2).

3.1.3. Mechanism of ion generation in DEA. The DEA reactions discussed above occur with electrons having essentially no energy. The usual mechanism of electron attachment at low energies is described...
via the formation of shape resonances, i.e. the electron occupies a virtual orbital of the neutral molecule without changing the initial electronic configuration. However, the energy of $\sigma^*$ orbitals of the saturated sugar molecule is too high to be accessible by electrons with energies close to zero eV. In fact recent calculations on electron scattering on D-ribose [28] showed that no shape resonances occur at low energies, but higher energy signals in the ion yield curves of the 72 amu and 59 amu fragments (not shown here) may be explained by the presence of shape resonances [28].

A possible explanation of the threshold signals is the initial formation of a vibrational feshbach resonance [29], which is supported by the large dipole moment of the sugar molecules. For such a doorway mechanism certain conditions need to be fulfilled [30,31]: (1) A dipole bound state must exist, where the excess electron occupies a very diffuse Rydberg-like orbital, (2) a valence anionic state with a positive electron affinity must be present, (3) the coupling of the dipole bound and the valence anionic states must be efficient, and (4) the valence state has to dissociate into more stable products. A recent ab initio study on D-fructose [30] indeed showed that a dipole bound state having a binding energy of at least 5 meV as well as a stable valence state exist. The latter is an open-chain distonic radical anion, which is predicted to be the precursor for dissociation in D-fructose. The question if the coupling between these two states is strong was not fully answered in [30] due to the complexity of the sugar molecule, but it is expected that the presence of an additional electron lowers the bond-breaking barriers enough to enable electron transfer from the dipole bound state to the open-chain valence state.

3.2. Tetraacetyl-D-ribose (TAR)

The rich fragmentation of the transient D-ribose anion is remarkable; however, the structure of the sugar unit in DNA and RNA is considerably different from the isolated gas phase sugar. The question arises, which resonances and fragmentation reactions are preserved in a furanose sugar that is also bound to a more complex molecular network, in other words which does not possess free hydroxyl groups. Hence we investigated DEA of the furanose form of tetraacetyl-D-ribose [19] (TAR, figure 4a-c).

The most abundant fragment anion is the acetate anion at 59 amu. It is generated within three different energy regions: (1) Within a sharp peak close to zero eV, (2) between 1 and 3 eV from at least two overlapping resonances, (3) with lower intensity between 7 and 11 eV. A comparison with the free D-ribose molecule shows that only the 1-3 eV signal is a new feature in the spectra of TAR. It is due to $\pi^*$ shape resonances located at the exocyclic carboxyl groups [19], which are not present in the free sugar. Indeed a series of lower mass fragments (100 amu, 70 amu and 84 amu) that correspond to the

![Figure 4. DEA spectra of selected fragment anions of tetraacetyl-D-ribose (TAR, left column) and dibutylphosphate (DBP, right column). Adapted from [19] and [20].](image-url)
sugar ring are generated only at threshold and with lower cross sections between 7 and 11 eV. The $\pi^*$ shape resonance is also observed through generation of higher mass fragment ions (215 amu, 161 amu, 154 amu, 119 amu and 113 amu, not shown here, see [19]), which are produced exclusively at 1–3 eV.

These observations confirm that the threshold signals obtained in the free sugars are preserved also in a five-member ring sugar that is bound to other functional groups. A frequently used surrogate for the sugar in DNA is tetrahydrofuran (THF) [32]. DEA studies on gas phase THF showed that the pure carbon ring has much lower electron attachment cross sections and does not lead to fragmentation at energies below 7 eV [32]. Therefore the presence of several polar groups (hydroxyl or acetate) leads to threshold signals, most likely due to the higher dipole moment resulting in dipole supported states. However the doorway mechanism discussed above for the free D-ribose molecules requires an open chain parent ion as transition state [30]. In TAR C-1 is blocked with an acetate group, i.e. the formation of a chain-form is not possible. Thus the dissociation has to proceed via a cyclic valence state.

In comparison with free D-ribose the $\pi^*$ shape resonances at low energies in TAR from the exocyclic groups appear in addition to the threshold signals without suppressing them. This is also expected if a phosphate group is present (see next section), where $\pi^*$ shape resonances occur as well. The high energy signals between 7 and 11 eV correspond to the high energy shape resonance described above for D-ribose [28].

3.3. Dibutylphosphate (DBP)

To model the phosphate group that is bound to two sugar units in DNA and RNA we used dibutylphosphate [20] (figure 4d-f). The parent ion after loss of hydrogen is observed from different resonances between 0.5 eV and 4 eV with a maximum at 1 eV. These signals are assigned to $\pi^*$ shape resonances with temporary occupation of a $\pi^*$ orbital of the phosphate group.

An abstraction of the whole butyl group due to a C-O bond cleavage resulting in a fragment ion with mass 153 amu is observed from two broad resonances at 2-4 eV and 7-10 eV. This reaction corresponds directly to a strand break in DNA. The low energy feature is also assigned to a $\pi^*$ shape resonance located at the phosphate group, and the higher energy resonance is most likely due to a core excited resonance at the carbon chain.

[DBP-H]$^-$ and [DBP-C$_{4}$H$_{9}$]$^-$ arise from a single bond cleavage. Additionally OH$^-$ is easily generated by rupture of a single P-O bond (figure 4f). Multiple bond breaking was observed leading to fragment anions PO$^-$, PO$_3$$^-$, and H$_2$PO$_3$$^-$ (not shown here, see [20] for details).

3.4. Conclusions

The results on DEA of different model compounds for the DNA or RNA backbone indicate that the backbone itself is able to capture electrons leading to manifold fragmentation reactions with considerable cross sections. The fragmentation of D-ribose negative ions is mainly governed by the neutral decomposition channels as was shown in a comparative study of DEA and MALDI. Fragment anions observed in DEA correspond to the fragments detected in MALDI ISD indicating that fast fragmentation prevails in DEA rather than metastable decay processes. Consequently it is suggested that strand break formation by low energy electrons is also possible by direct electron attachment to the phosphate group or the sugar unit, especially at energies below 4 eV, where only single strand breaks have been observed [4]. To arrive at a global model that fully describes the interaction of LEEs with DNA the next step will be the experimental investigation of larger subunits containing the nucleobases, sugar and phosphate units. Gas phase studies are particularly valuable to reveal the intrinsic properties of these building blocks. This knowledge is vitally important for a proper interpretation of results from more complex systems in condensed phase.

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