CNO^- formation through selective bond cleavage

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CNO^- formation through selective bond cleavage

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Synopsis H^- and CNO^- site and bond selectivity formation is shown in the context of atom-molecule collisions.

The importance of radiation-induced low energy electron damage to DNA has recently become a source of great attention regarding the underlying processes. Low energy electrons, formed by incident radiation in living tissue, have been shown to have a tremendous impact on the indirect damage capability of the primary radiation [1]. As such, knowledge on the underlying molecular mechanisms of DNA damage is of critical importance. One such set of molecular mechanisms is site and bond selectivity, i.e. selective bond break through tuning the electron energy. This mechanism has been thoroughly studied in the context of dissociative electron attachment for a set of biologically relevant molecules, namely uracil [2, 3].

Herein we discuss site and bond selectivity in the context of atomic collisions with pyrimidine bases. We show that by tuning the kinetic energy of the neutral projectile (in our case potassium), we can effectively suppress the access to certain initial states, thereby not allowing for the formation of the resulting fragmentation products.

This study is achieved by means of a crossed molecular beam setup, where a neutral potassium beam of a chosen energy (from 15 to 300 eV) is made to collide with an effusive beam of the molecular target. This collision, owing to a non-adiabatic coupling between the ionic and covalent PESs, can result in a transfer of the valence electron of the potassium to form a transient negative ion, as in (Eq.1).

$$K + AB \rightarrow K^+ + \left(AB^-\right)^* \qquad \text{(Eq.1)}$$

This transient negative ion will eventually either re-eject the extra electron, or fragment. Through a TOF mass spectrometer, all the formed anionic fragments will be extracted and a mass spectrum will be obtained.

A recent study on site and bond selectivity of the formation of H- in pyrimidine bases showed that this molecular mechanisms indeed also occurs in atomic collisions [3] and paved the way for further similar studies into other fragments of these same molecules. Indeed, by using criterious methylations in the N-sites of uracil/thymine, we are able to determine from which site and bond breaks do the several CNO^- possibilities stem from [4].

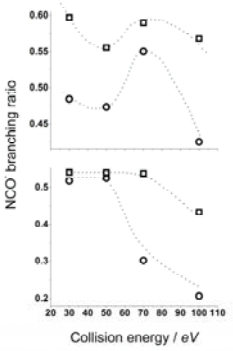

Figure 1. NCO^- branching ratios in collisions of potassium atoms with N-site methylated uracil and thymine molecules. Upper panel: □ 1-metU and ○ 3metU; Lower panel: □ 1-metT and ○ 3metT. The dotted lines are just to guide the eye.

References

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