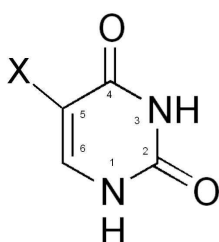


Ionization and fragmentation of radiosensibilizing molecules upon 100 keV protons collisions: evidence for keto \rightarrow enol tautomerism for Uracil and halogenated derivatives.

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We have experimentally studied the fragmentation following ionization upon 100 keV protons collisions of Uracil and its halogenated derivatives 5-X-Uracil (X=F, Cl, Br, I) as well as of Thymine. By means of a coincidence detection scheme, we can distinguish between fragments originating from singly or doubly ionized parent molecules.



Molecules under investigations in their keto form.

X = CH₃ (Thymine), H (Uracil), F, Cl, Br, I (halogenated derivatives)

In the case of fragmentation following single ionization of the 5-X-Uracil molecules, one of the major fragmentation channels is the loss of a mass 70 neutral moiety which can be obtained only after transferring a proton from the nitrogen atom in position 3 to its neighboring oxygen atom in position 4 as in the keto \rightarrow enol tautomerism reaction. This fragmentation channel has not been observed in the case of Thymine where the major channel corresponds to the loss of a mass 71.

The doubly ionized molecules also lead to the creation of a mass 70. The analysis of the correlation islands of each dissociation channel allows discriminating between instantaneous and sequential dissociations and, in the later case, establishing the sequence under which the dissociation occurs.

The fact that fragments produced after proton transfer are observed only for the radiosensibilizing molecules 5-X-Uracil but not for Thymine, is of particular interest. Indeed, in a Uracil molecule paired with an Adenine basis, the proton transfer could trigger a breakdown in the hydrogen bonds networks of the ensemble, yielding to mispairing which, in turn can lead to mutation and cells death.