

Electron transfer processes in potassium collision with nitroimidazoles: the role of methylation at N1 site

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Synopsis We present site selectivity studies by electron transfer induced dissociation experiments in potassium collisions with nitroimidazoles and methylnitroimidazoles. In this contribution we report on H loss leading to the dehydrogenated parent anion formation in such experiments.

The nitroimidazoles are a family of molecules that have been used as radiosensitizers in radiation treatments to enhance the effect of ionizing radiation in radioresistant hypoxic tumours [1]. These compounds are electroaffinic structures that react with free radicals as oxygen producing DNA lesions. However detailed knowledge of the underlying molecular mechanisms of the radiosensitization process is still unclear. It is well-known that low-energy electrons (<30 eV) are the most abundant secondary species produced by primary radiation along the ionization track. The interaction of these electrons with biological tissues and molecules, like DNA, water represents a key issue for radiation damage studies, but also for the performance of radiosensitizers used in cancer therapy. These secondary electrons interact with the bio-environment creating large quantities of reactive species, like radicals, anions and cations, which will cause a series of chemical damages in biological tissues leading to double and single strand breaks, mutations and cluster lesions [2].

A literature survey reveals some studies on the formation of radical ions from radiosensitizers using different spectroscopic techniques [3][4]. It has been shown that low-energy electrons (0-8 eV) effectively decompose 4-nitroimidazole and two methylated isomers via a dissociative electron attachment (DEA) process. Moreover, these studies also demonstrated that the fragmentation pattern of 4NI is completely inhibited after methylation at the N1 site.

The importance of controlling chemical reactions in electron induced collisions with molecules has been one of the most challenging key

aspects of the physical chemistry community over the last decades. This has been achieved using several different experimental techniques where mode-selective excitation, stereodynamic and orbital alignment control in molecular collisions. In atom-molecule collisions, the electron donor projectile interacts with a given molecule transferring an electron to a specific molecular orbital creating instability to the molecule. In the collision energy regime where formation of a transient negative anion (TNI) occurs, leads to several pathways including fragmentation into stable anionic species and access to parent molecular states which are not accessible in free electron attachment experiments [5].

Here we show novel results on time-of-flight (TOF) negative ion formation in potassium (electron donor) and nitroimidazoles collisions in the energy range between 8 and 1000 eV, exploring site and bond selective excision of H leading to the dehydrogenated parent anion formation. Negative ion mass spectra were obtained at several collision energies for different molecular targets as 4-nitromidazole, its methylated analogue in the N1 site and 1-methyl-5-nitromidazole.

References

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