Combined Electron Magnetic Resonance and Density Functional Theory Study of Thermally Induced Free Radical Reactions in Fructose and Trehalose Single Crystals, M. A. Tarpan, H. De Cooman, H. Vrielinck, E. Pauwels, M. Waroquier, E. Sagstuen, F. Callens, *European conference on the spectroscopy of biological molecules*, Palermo, Italy, **August 28 - September 2, 2009**

Both as models for studying the effects of radiation on the DNA sugar unit and for applications in dosimetry, radiation-induced defects in sugars have in the past few decades been intensively studied with electron magnetic resonance (EMR) techniques, often with considerable success. However, irradiation generally gives rise to a large variety of free radicals, resulting in strongly composite Electron Paramagnetic Resonance (EPR) spectra. This complexity makes studying them quite a challenge. Despite considerable efforts, little is still known about the identity of the radicals and even less about the radical formation and transformation processes and mechanisms. At room temperature (RT) the primary radiation products, which may be stabilized upon low temperature (LT) irradiation, transform into stable radicals via multistep reaction mechanisms. While the species formed at LT are expected to be formed by simple processes, the molecular structure and geometry of the stable radicals may differ considerably from that of the intact molecule even in the solid state (crystals). Studying the intermediate radicals in the reactions occurring after LT irradiation helps elucidating the formation and identity of the stable radicals. The structural identification of these radicals is in most cases the result of a combination of EPR, Electron Nuclear Double Resonance (ENDOR) and ENDOR Induced EPR (EIE) experiments and advanced quantum chemistry calculations based on Density Functional Theory (DFT). In the present study a summary is given of the experimental EMR results obtained so far on radiation-induced radicals at different temperatures in fructose and trehalose single crystals and powders. "In situ" X-irradiation at LT (10 K) without annealing, leads to spectra strongly different from those observed after RT irradiation and offers the possibility to study and characterize the primary radiation products [1]. Performing EMR measurements on samples irradiated and/or annealed at various temperatures between LT (10 K or 77 K) and RT allows us to study the intermediate products, and such studies therefore have the potential to devise mechanistic links between the primary radicals and the stable radicals. In the present work, our own measurements are compared with results reported in the EMR literature. An outline at future experimental (EMR) and theoretical (DFT) research will also be given.

References

[1] M.A. Tarpan, E. Sagstuen, E. Pauwels, H. Vrielinck, M. Waroquier, F. Callens, *J. Phys. Chem* .A **112**, 3898-3905 (2008).