

direct-effect radiation chemistry of solid-state carbohydrates using emr and dft

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To contribute to a mechanistic understanding of radical reaction pathways in the sugar-phosphate backbone of DNA, we are investigating primary radicals induced by X-rays, as well as their transformation into stable radicals or diamagnetic products, in crystalline sugar and sugar derivatives. Radicals are identified and characterized mainly via the hyperfine interactions of the electron spin with protons in the molecular environment. These interactions are determined experimentally with electron magnetic resonance (EMR) techniques and compared to theoretical *ab initio* calculations based on density functional theory in a periodic approach. Different stages of the radiation-induced processes are investigated by irradiating *in situ* at various temperatures and controlled annealing experiments.

Here, results obtained in single crystals of the dipotassium salt of glucose 1-phosphate (K₂G1P) and the disaccharides sucrose and trehalose are presented. The dominant radical in K₂G1P after irradiation at 77 K exhibits a broken phospho-ester bond and is chemically identical to one of the major stable sucrose radicals, the latter all being characterized by a broken glycosidic bond. This suggests that the ester bond is radiation sensitive and that the phosphate group is not essential for the reaction pathway leading to this scission. Surprisingly, however, no evidence for glycosidic bond scission has so far been observed in trehalose. Rather, a simple H-abstraction alkyl radical is remarkably stable in this system. In all three compounds, dominant radicals are formed with one or several concerted carbonyl group formations. Extended studies are necessary to establish how and to which extent structural or geometrical factors determine the radiation chemistry, but certain general principles are starting to emerge.