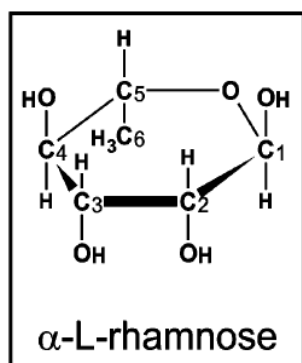


DFT and TDDFT studies of deprotonation from oxygen in rhamnose cations.

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When carbohydrates in the condensed phase are oxidized by ionizing radiation, cationic radicals and free electrons are generated. These products then partake in subsequent chemical reactions. To restore charge balance, the cations can deprotonate from a hydroxyl position, giving rise to an alkoxy radical. The carbohydrate α -L-rhamnose (see Figure) has four possible positions for such deprotonation reactions. The radiation-induced radicals in this sugar have been examined by means of electron paramagnetic resonance (EPR) spectroscopy [1,2] but only one alkoxy radical was found, indicating that deprotonation selectively occurs from *one* of the four hydroxyl groups. Theoretical quantum chemistry calculations based on density functional theory (DFT) later [3] confirmed that the rhamnose alkoxy radical is deprotonated at O4 (see Figure), yet no explanation was found for the observed selectivity.



In the present work, the electronic ground-state energy profiles for deprotonation of hydroxyl groups in rhamnose are examined theoretically by means of DFT calculations, using both periodic boundary conditions and a multi-layer cluster approach (ONIOM). The profiles clearly indicate that deprotonation from O4 is both thermodynamically and kinetically preferred. Although these calculations would explain the observed preference for the O4-centered alkoxy radical, the calculated energy barrier for the deprotonation reaction is still much higher than the thermal energy available at the typically low temperatures of the experiment (4 K or 77 K). Hence, in the electronic ground state, the deprotonation reaction would not be likely to occur.

One possible explanation is that excited states are involved in the alkoxy radical formation. The solid-state carbohydrate cation is extremely unstable and deprotonation may well occur before the molecules relax back to the electronic ground state after the initial ionization event. In order to investigate the possible role of excited electronic states of the cation, we will use time-dependent DFT (TDDFT) methods. At first instance, we will focus on excited states with strong oscillator strengths or conical intersections with the ground-state potential energy surface.

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