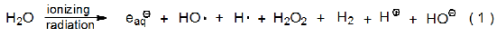
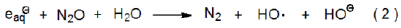
II. Radicals That Abstract Hydrogen Atoms from Unprotected Carbohydrates

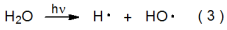
A. Hydroxyl Radicals

1. Ionizing Radiation and Ultraviolet Light

γ-Radiolysis of water produces hydroxyl radicals along with the compounds, ions, and other radicals shown in eq 1.[1–4] The yield of hydroxyl radicals in this reaction can be increased by adding N_2O to the reaction mixture because hydrated electrons react with N_2O to form hydroxyl radicals (eq 2).[2–4] In N_2O-containing solutions 85% of the radicals are HO· and 15% are H·.[4] Both HO· and H· abstract hydrogen atoms from carbon–hydrogen bonds.[4] Hydroxyl radicals (and hydrogen atoms) also can be produced by photolysis of water with ultraviolet light of wavelength less than 185 nm (eq 3).[1]

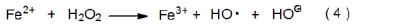


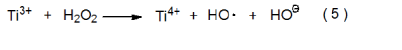


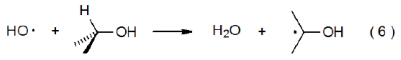


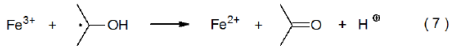
2. Reaction of H_2O_2 with Fe^{2+} and Ti^{3+}

Reaction of H_2O_2 with Fe^{2+} (eq 4) or Ti^{3+} (eq 5) produces hydroxyl radicals.[5–8] (These reagent combinations are sometimes described as radiomimetic, that is, imitating radiation.) Each hydroxyl radical produced is capable of abstracting a hydrogen atom from a carbon–hydrogen bond present in a molecule of substrate (eq 6). The Ti^{4+} generated by the reaction shown in eq 5 does not react further with the carbon-centered radical produced, but the Fe^{3+} formed in the reaction shown in eq 4 does;[8] Fe^{3+} oxidizes an α-hydroxy radical to a carbonyl group while itself being reduced to Fe^{2+}. Regeneration of Fe^{2+} from Fe^{3+} by the reaction shown in eq 7 means that when this reaction occurs, only a catalytic amount of Fe^{2+} may be necessary for complete decomposition of H_2O_2 (eq 4). (The combination of H_2O_2 and Fe^{2+} is known as Fenton's reagent,[9] and that of H_2O_2 and Te^{3+} as a Fenton-type reagent.[8])









B. Sulfate Radical Anions

The sulfate radical anion ($SO_4^{\cdot -}$) forms when the peroxydisulfate dianion ($S_2O_8^{2-}$) reacts with Ti^{3+} (eq 8).[10] A low concentration of Cu^{2+} present in the reaction mixture enhances the rate of generation of $SO_4^{\cdot -}$ via the reactions shown in equations 9 and 10. The sulfate radical anion also forms from direct photolysis of $S_2O_8^{2-}$ (eq 11).[10]