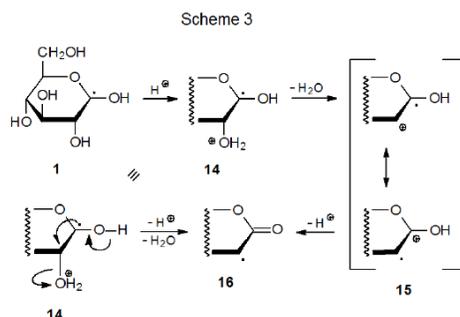
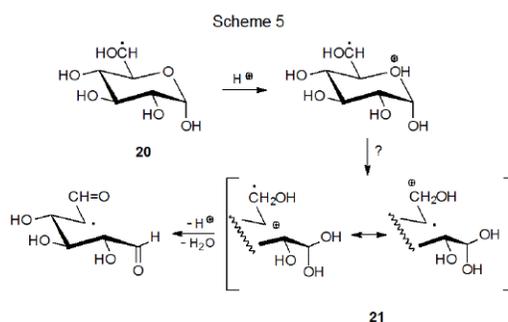
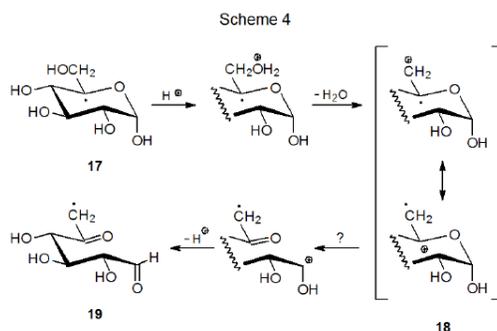


B. Acid-Catalyzed Reactions

Under strongly acidic conditions ($\text{pH} = 1$) four of the first-formed radicals generated from D-glucose eliminate the elements of water to give in each case a carbonyl-conjugated radical.^{6,26} A proposed mechanism for this reaction, shown in Scheme 3, involves protonation of the hydroxyl group adjacent to a radical center in the first-formed radical **1** to produce an intermediate (**14**) with an excellent leaving group that departs to form a radical cation (**15**). This radical cation then deprotonates to give the carbonyl-conjugated radical **16**. Another mechanistic possibility for forming **16** is a concerted reaction beginning with the protonated radical **14** (Scheme 3). Forming carbonyl-conjugated radicals by acid-catalyzed reaction also has been studied in noncarbohydrate systems.^{5,27,28}

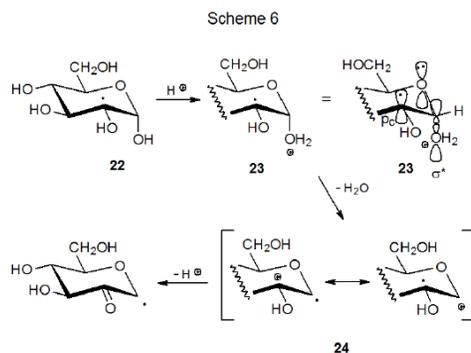


The acid-catalyzed reactions of three first-formed radicals produced from D-glucose deserve further comment. Two of these radicals, **17** (Scheme 4) and **20** (Scheme 5), do not undergo the carbonyl-group-forming reaction characteristic of the other first-formed radicals (Scheme 3).⁶ Although **17** could start along this pathway by producing the radical cation **18**, deprotonation of **18** to give a carbon-centered radical with an adjacent carbonyl group cannot take place. Formation of a carbonyl-conjugated radical from **18** would require opening of the pyranoid ring (Scheme 4). Evidence against such reaction is that **17** is less reactive than other first-formed radicals, and when it does react, no carbonyl-conjugated radical can be detected. The first-formed radical **20** also must undergo ring opening if a carbonyl-conjugated radical is to be produced; in fact, ring opening in this case is necessary to form the radical-cation **21** (Scheme 5). The radical **20**, which is the least reactive of the first-formed radicals derived from D-glucose, also gives no indication of forming a carbonyl-conjugated radical.⁶



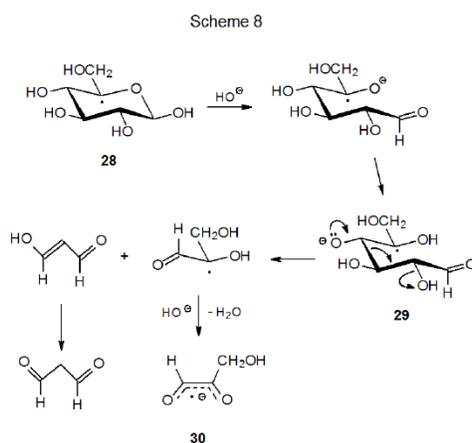
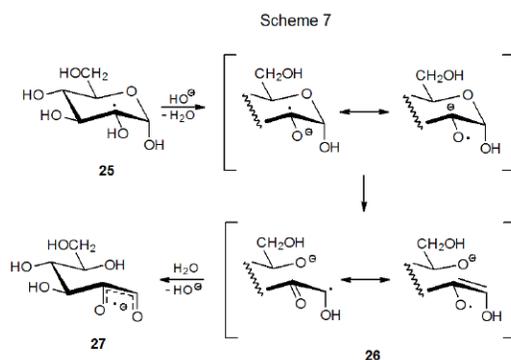
The radical **22** is the third, first-formed radical produced from D-glucose that deserves further comment. This radical is noteworthy because it is the most reactive of the first-formed radicals. Protonation of **22** gives the intermediate **23** in which the leaving group

has an axial orientation and, therefore, the *p*-type orbitals on C-2 and the ring oxygen atom in **23** begin stabilizing the radical cation **24** as it starts to develop (Scheme 6).⁶



C. Base-Catalyzed Reaction

Proton abstraction from O-2 in the first-formed radical **25** begins a process that generates the ring-open radical anion **26** (Scheme 7). (Since an α -hydroxy radical is far more acidic than its parent alcohol,² the proton attached to O-2 should be removed much more readily than any other proton in **25**.) The radical anion **26** rapidly undergoes a proton transfer to produce the semidione **27**, one of two semidiones formed from base-catalyzed reaction of a first-formed, D-glucopyranosyl radical.^{11,29} The second of these two (**30**) is proposed to arise from the radical **28** according to the mechanism outlined in Scheme 8.¹¹ (Semidiones **27** and **30** are readily detected because for each of them the negative charge slows the rates of dimerization and reduction and thus leads to more prominent ESR spectra.¹¹)



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