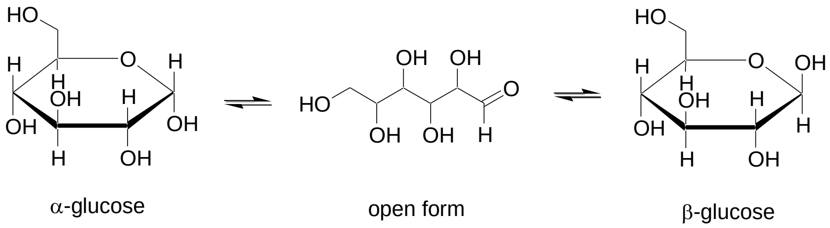
Answer on Question #44417 -Chemistry - Organic Chemistry

Question:

1. In aqueous solutions there are three forms of glucose: the a-form of glucose (36%), the b-form (64%) and a trace amount of the open chain form. Explain (a) why the cyclic forms exist predominately in solutions, and the (b) why the b-form is more abundant than the a-form?

Answer:

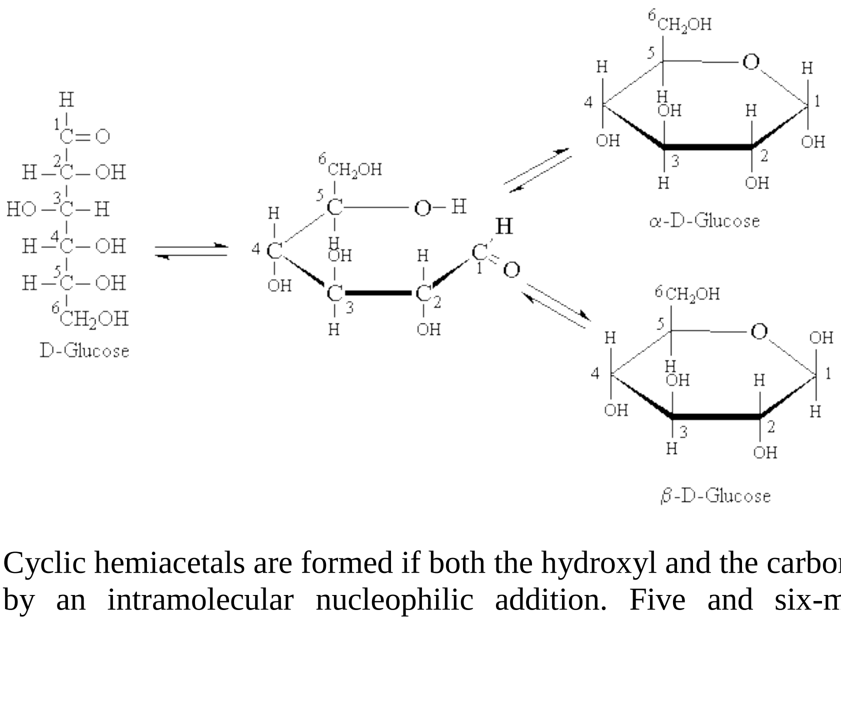
a. In aqueous solution, glucose exists as three forms in dynamic equilibrium:



The two cyclic forms of glucose differ only in the orientation of the OH group at C-1, upward in β-glucose and downward in α-glucose. At equilibrium, the proportions in solution are 36% α-glucose, 0.02% open-chain glucose, and 64% β-glucose.

In actuality the open-chain form of glucose is present in very small concentrations in aqueous solutions or in living cells. It exists predominantly in either of the two cyclic forms of a-D-glucose or b-D-glucose. The hydroxyl group at C-5 reacts with the carbonyl group at C-1 to produce either of the two cyclic forms via the formation of a cyclic intramolecular hemiacetal.

These cyclic forms are enantiomeric pairs due to the fact that a new chiral carbon is created at C-1 in the cyclization process.



Cyclic hemiacetals are formed if both the hydroxyl and the carbonyl group are in the same molecule by an intramolecular nucleophilic addition. Five and six-membered cyclic hemiacetals are particularly stable and many carbohydrates therefore exist in equilibrium between open-chain and cyclic forms.

Glucose exists in aqueous solution primarily as the six-membered pyranose form resulting from intramolecular nucleophilic addition of the -OH group at C5 to the C1 carbonyl group.

Thus, the existence of the cyclic forms in solutions has to do with sterics. In organic chemistry, we learn that substituents on six-membered rings are most stable in equatorial positions than in axial positions because this minimizes 1,3-diaxial interactions and other unfavorable repulsive interactions in the molecule.

b. When glucose forms a ring (Haworth conformation), carbon one can have its hydroxyl group in one of two conformations: axial (pointing straight down) or equatorial (pointing slightly up). When it is axial, the glucose is alpha. When it is equatorial, it is beta. This doesn't have as much impact on free, monomeric glucose because it can switch back and forth rapidly (though beta is preferred because it is more stable). When glucose is polymerized into polysaccharides, it matters a lot.

In the beta form of glucose, all of the substituents on the ring are equatorial. But in the alpha form, one of the hydroxyl groups will necessarily be axial, making the molecule higher in energy. Consequently, the beta form will be favored at equilibrium.