

Chemistry 41c Quiz 4 Review Sheet – Spring Quarter 2013

Projected Quiz 4 point allocation/tips:

'Think Deeply' topic, **Structures of the Monosaccharides** (Loudon, pages 1173-1182), 10 pts

Assigned Chapter 24 problems, 10 pts

Other problems relating to Chapter 24 topics, 10 pts

Bonus questions, 5 pts

Additional information: model kits can be used during the quiz, and D-glucose/D-glyceraldehyde are the only structures you need to know.

Chapter 24 Goals:

1. Classification of carbohydrates, D and L designation- historical aspects and use of glyceraldehyde as a reference compound, Bijvoet's contribution to this use of stereochemical descriptors. Review the R/S system and be able to correlate this system with the D/L & d/l systems for glyceraldehyde and the optically active tartaric acids.
2. Structural formulas for monosaccharides: be able to translate a Fischer projection into a pyranose, furanose, or lactone, depending upon the C.1 oxidation state. Use your model kit if necessary. Be able to do this translation in the opposite direction as well. Definition of α and β pyranose/furanose and pyranoside/furanoside. Use D-glucose as your practice molecule in these transformations.
3. Mutarotation for carbohydrate-based hemiacetals--mechanism of this process.
4. Glycoside formation- know the mechanism of this process forwards (glycoside formation) and backwards (glycoside hydrolysis).
5. Origin of the stereoelectronic effect (the anomeric effect) used to explain axial preference of glycosides, and the enhanced axial preference seen in six-membered hemiacetals (e.g., glucose). Relevance of substituted cyclohexanes (OH) in these discussions.
6. Base-catalyzed isomerization of glucose to mannose and fructose—mechanism of reaction.
7. Reactions of sugars: methylation, benzylation, esterification, cyclic acetals and ketals (rules for formation-- 1,3 diols can also undergo this reaction); nature of Tollen's and Benedict's solutions: def. of reducing or nonreducing sugars; Bromine water oxidation of aldoses- outcome of reaction and potential lactone formation; nitric acid oxidation of aldoses--outcome of reaction and potential lactone formation; periodate oxidations- mechanism and outcome (glycerol, glyceraldehyde, and dihydroxyacetone) of reaction and utility in structure elucidation; reductions of aldoses and ketoses with NaBH_4 or H_2/Pt .
8. Fischer's proof of the relative configuration of glucose: no need to memorize the structures involved, but be familiar with the reactions and general strategy used to eliminate the possible structures (know how to predict the maximum number of stereoisomeric structures for a given sugar (e.g., 4 carbon, 5 carbon, 6 carbon, 7 carbon). The Ruff degradation and how it added to the proof. Could you, for example, use the tools that Fischer had and propose the relative configuration of an aldopentose, given ample experimental data?
9. The structure of sucrose-- every organic chemist should know it, but according to the 41c ground rules, **you** only need to know the structure of the glucose moiety. But wait—glucose can be isomerized under

basic conditions to fructose, so you do know the structure of the fructose component. Link them together at their anomeric centers and put a fork in the structure—you are done. But seriously, review the evidence for the structure of sucrose. Keep raffinose, a trisaccharide with an embedded sucrose unit, in mind for gas-based party or family/friend-based humor. The Ben Franklin-Beano™ connection, discussed in class, is optional.

10. The structure of the disaccharides maltose and cellobiose—no need to commit to memory, but these are easy to remember because they are both glucose-based, 1,4-linked, and differ only at the glycoside linkage. Review the structural evidence for maltose and check the method used to determine the nature (α/β) of the glycosidic linkage in each.
11. Oligomerize maltose to cyclodextrins (Febreze™) or polymerize maltose to starch and do the same for cellobiose to cellulose. Examine the resulting structures and recognize the dramatic differences in secondary structure-- a direct consequence of different primary structure. Explore the structural similarities of chitin and cellulose.