Chemistry 125 Fifth Examination Answers

Average Score 69.6

February 9, 2004

1/3 > 80 2/3 > 64

1. (3 minutes) How would you interpret a situation where quadrupling the amount of a reagent only doubles its reaction rate?

This means the reaction is 1/2 order, a situation that occurs when the dominant species in solution is a dimer of the reacting species.

Since the quotient $[\text{monomer}]^2/[\text{dimer}]$ is a constant (the equilibrium constant for dissociation of the dimer), quadrupling the concentration of dimer, will only require doubling the concentration of monomer to maintain the equilibrium.

[Note that this approximation requires that the material be predominantly dimeric at both concentrations, so that doubling the amount of reagent doubles the amount of dimer. If most of the material were monomer, doubling the amount of material would double monomer and increase dimer fourfold to maintain equilibrium.]

6. (5 min) Show **reagents** for accomplishing the following conversion in a practical manner. (No mechanisms are necessary, but do show the **isolable product from each reaction** in the required sequence).

$(CH_3)_3CH \rightarrow (CH_3)_3CD$

$(CH_3)_3CH + Br_2 \rightarrow (CH_3)_3CBr$ with light or initiator

[free radical chain reaction to create functional group in alkane]

$(CH_3)_3CBr + Li \rightarrow (CH_3)_3CLi$ (+ LiBr)

$(CH_3)_3CLi + D_3O^+ \rightarrow (CH_3)_3CD$

7. (5 min) Explain how the choice of reagents in the first step of the preparation in Question 6 might be influenced by familiarity with the Hammond Postulate.

The product of free-radical halogenation can be either primary (1-bromo-2-methylpropane) or tertiary (desired). Therefore one wants a reagent that will be selectrive in abstracting the single tertiary hydrogen atom rather than one of the nine primary hydrogen atoms of the three methyl groups. Bromination is more selective than chlorination, because the hydrogen abstraction by bromine atom is strongly endothermic (HBr bond 16 kcal/mole weaker than HCl bond). According to the Hammond Postulate this more endothermic reaction will have a transition state closer to the free-radical product of the abstraction step, and will thus profit more than abstraction by chlorine atom would from the extra stability of the tertiary over the primary radical intermediate. Thus one would choose bromination over chlorination.

8. (6 min) The following three alcohols have approximate pK_a values of 3, 10, and 16 (not necessarily in order). Under each formula write the appropriate pK_a., AND under the second and third list the factors that cause their acidity to differ from that of ethanol.

EtOH	$ClCH_2COOH$	C_6H_5OH ("carbolic acid")
$pK_a = 16$	$pK_a = 3$	$pK_a = 10$

Phenol (or "carbolic acid") is 10^6 times more acidic than generic alcohols because of resonance stabilization of the conjugate base. That is, the HOMO of the anion is stabilized by mixing with the LUMO of the π system of the benzene ring.

Chloroacetic acid is especially acidic for three reasons: resonance stabilization of the conjugate base (HOMO with π^* LUMO of C=O), inductive electron withdrawal by the oxygen atom on the carbon attached to the OH group, and inductive electron withdrawal by the chlorine atom on the carbon adjacent to the carbon attached to the OH group.

9. (6 min) The chloroacetic acid in Question 8 could was prepared in the 1830s by chlorination of acetic acid. Write a mechanism for this reaction AND explain whether you think this reaction could be used to prepare the corresponding bromo- and iodoacetic acids.

Reaction with Br_2 could probably be used to generate the bromoacid (although step 1, the H-abstraction, would be slower and thus the reaction would probably be less efficient.

Reaction with I2 would fail because the bonds formed (C-I and H-I, total 128 kcal/mole) would be weaker than the bonds broken (C-H and I–I, total 137 kcal/mole). Free radical iodination is thermodynamically forbidden.