

CHEM 331 – Review Material for Term Test #2 Substituent & Reaction Constants and Hydrolysis

Chapter 8 (Acid-Base & Substituents) and handouts on Hammett Eqn and Hammond Postulate
Chapter 12 (selections of Kinetics) and handout on Kinetics Review
Chapter 13 (Hydrolysis) and handout on Hydrolysis

Textbook Questions: 8.1 - 8.9, P8.1, P8.3 and handout *Example Problems Hammett Eqn*

Textbook Questions: 12.2, 12.5-12.8, 12.10, 12.11

Textbook Questions: 13.1-13.4, 13.6-13.9, 13.12, 13.13 and P13.2, P13.3, P13.5, P13.6 and handout *Example Problems Hydrolysis*

Electronic Substituent Effects on Equilibria and Kinetics

Electron withdrawing and donating ability by Induction and Resonance
Modified substituent constants

Hammett Equation and the reaction susceptibility constant

Mechanistic interpretation and transition state structure (Hammond postulate)

Predicting pKa's and rate constants (half-lives) from substituent and reaction constants

Hydrolysis Reactions of the following FGs

Alkyl halides (polyhalogenated aliphatics), Epoxides, Phosphoric acid esters

Carboxylic acid esters, Amides, Carbamates and Ureas

Kinetics of hydrolysis and the overall hydrolysis rate constant (k_h)

$$k_h = k_A [H^+] + k_N + k_B [OH^-]$$

$\log k_h$ versus pH

Hydrolysis Mechanisms: Substitutions versus Addition-Elimination

Substitutions (when LG is attached to sp^3 centre)

Alkyl halides: S_N1 and S_N2 , neutral and base enhanced

(also E1, E2 and $E_{cb}1$ for competing elimination reaction)

Epoxides: ' S_N1 – like' and ' S_N2 – like', acid, neutral and base enhanced

Phosphoric acid esters: S_N2 for 'soft' nucleophiles (i.e., H_2O) on alkyl carbon, neutral and S_N2 for 'hard' nucleophiles (i.e., OH^-) on central phosphorus, base enhanced.

Addition – Eliminations (when LG is attached to sp^2 centre)

Nucleophilic attack on acyl (carbonyl) carbon followed by elimination of LG

$B_{AC}2$ and $A_{AC}2$ for carboxylic acid esters and amides