

## ADVANCED ORGANIC CHEMISTRY – a.a. 2024/2025

### *Part A – Prof. Paolo Tecilla*

Chemical reactivity: temperature dependence of reaction rate. Rate constant. Transition state theory. Hammond postulate. Molecular structure and chemical reactivity: Reaction maps.

Kinetic methods for mechanistic investigation: 1° and 2° order reactions. Reversible reactions. Parallel reactions: kinetic and thermodynamic control. Consecutive reactions. Pre-equilibrium. Reactive intermediates and steady-state approximation. Curtin-Hammet principle.

Non-kinetic methods for mechanistic investigation: isolation of intermediates. Spectroscopic identification of intermediates. Isotopes labelling. Stereochemical tools. Isotope effects upon chemical reaction (KIE): the vibrational origin of KIE. Primary, secondary and solvent KIEs.

The Hammett equation. The Taft equation. Steric and electronic effects of substituents.

### *Part B – Prof. Paolo Pengo*

Nucleophilic substitution at saturated carbon: SN1 and SN2 limiting mechanisms, stereoelectronic effects.

Salt and common ion effects, ion pairs and their kinetic implications; stability of carbenium ions. Solvent effects, Winstein-Grunwald equation. Nucleophilicity and leaving group effect. Vinylic nucleophilic substitutions.

### **Libri:**

- Howard Maskill, Structure and Reactivity in Organic Chemistry, OUP Oxford.
- Neil Isaacs, Physical Organic Chemistry, Longman Sc & Tech
- F.A. Carey and R. J. Sundberg, Advanced Organic Chemistry. Part A: Structure and Mechanisms; Part B: Reactions and Synthesis, Springer
- E. Anslyn, D. Dougherty, Modern Physical Organic Chemistry, University Science Books.