

**Problem 1 – KINETICS – Hydrolysis of pyrophosphate**

Let us take a look at the hydrolysis of pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ) by the enzyme. It is assumed that the concentration of pyrophosphate is much lower than the Michaelis constant; thus, the reaction is formally supposed to be first-order. At pH = 7 at 25 °C, the apparent first-order rate constant (relative to pyrophosphate total concentration) is  $k_7^* = 0.0010 \text{ s}^{-1}$ . The mechanism of the hydrolysis is as follows:  $\text{H}_2\text{P}_2\text{O}_7^{2-} \rightleftharpoons \text{HP}_2\text{O}_7^{3-} \rightleftharpoons \text{P}_2\text{O}_7^{4-} \rightarrow 2\text{HPO}_4^{2-}$  where  $\text{p}K_{\text{a}1} = 6.12$  and  $\text{p}K_{\text{a}2} = 8.95$  (1<sup>st</sup> and 2<sup>nd</sup> stages), and  $k$  is the true rate constant that does not depend on pH (3<sup>rd</sup> stage). It is assumed that acid dissociations are faster compared to hydrolysis.

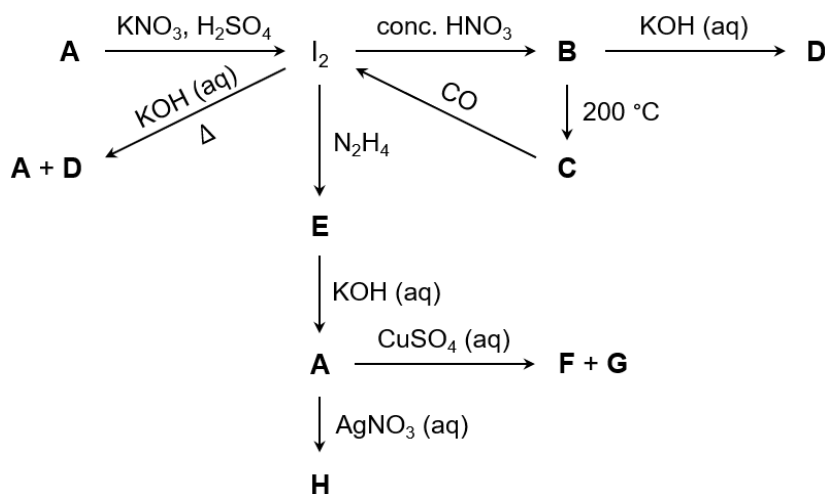
- Calculate the value of true rate constant  $k$  relative to  $[\text{P}_2\text{O}_7^{4-}]$ .
- Calculate the values of apparent rate constants  $k_6^*$  and  $k_8^*$  at pH = 6 and 8.

**Problem 2 – ABC, CALC – Iodine and polyiodides**

Iodine was discovered in 1811 by the French chemist Courtois during the process of manufacturing potassium nitrate, with which he supplied Napoleon's armies. While washing seaweed ashes with sulfuric acid, he noticed violet fumes that condensed on his copper equipment and caused corrosion. Below, you see a diagram that represents some iodine chemistry. Only iodine-containing substances A to H are indicated in this diagram. In some cases, it might be more reaction products.

- Write chemical formulas of compounds A–H.

- Write chemical equations from the scheme:



One of the remarkable features of iodine is the possibility of forming so-called polyiodide ions. One of the simplest polyiodide ions is present in the tincture of iodine. This tincture is prepared by dissolving iodine in a KI solution. In this mixture, triiodide ions  $\text{I}_3^-$  are present. Until now, anions of the form  $\text{I}_2^-$  to  $\text{I}_{29}^{3-}$  have been established.

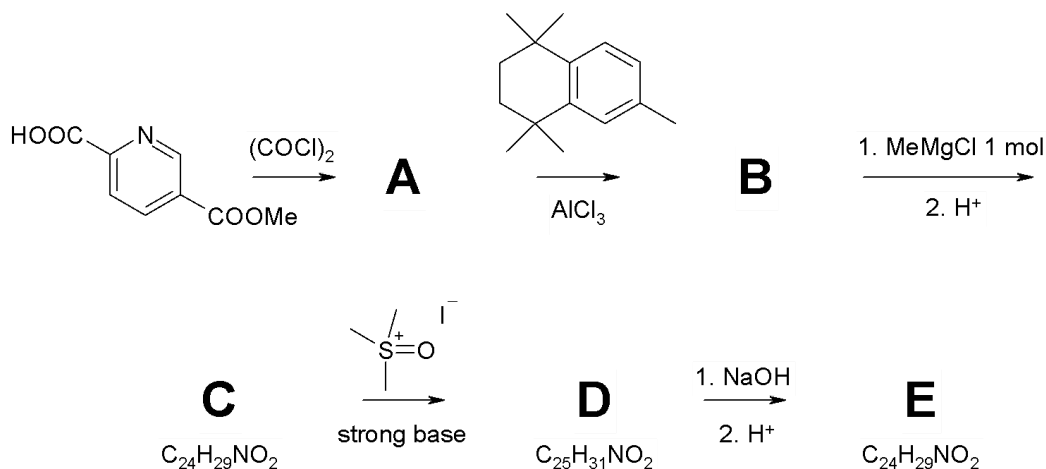
- Write Lewis structures of  $\text{I}_3^-$  and  $\text{I}_5^-$  ions with correct geometry.

Polyiodides are not very stable compounds, but large cations with high symmetry can be used to obtain thermally stable polyiodides. In the laboratory, polyiodide  $\text{R}_4\text{NI}_{2x+1}$  ( $x = 1, 2, 3, 4, \dots$ ) large cations were investigated. R is a radical of alkane. For titration of 0.219 g of  $\text{R}_4\text{NI}_{2x+1}$ ,  $10.23 \text{ cm}^3$  of 0.112 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution was consumed.

- Determine the molecular formula of  $\text{R}_4\text{NI}_{2x+1}$ . Show your calculations.

### Problem 3 – MECH, SYNTH – Small rings fighting diabetes

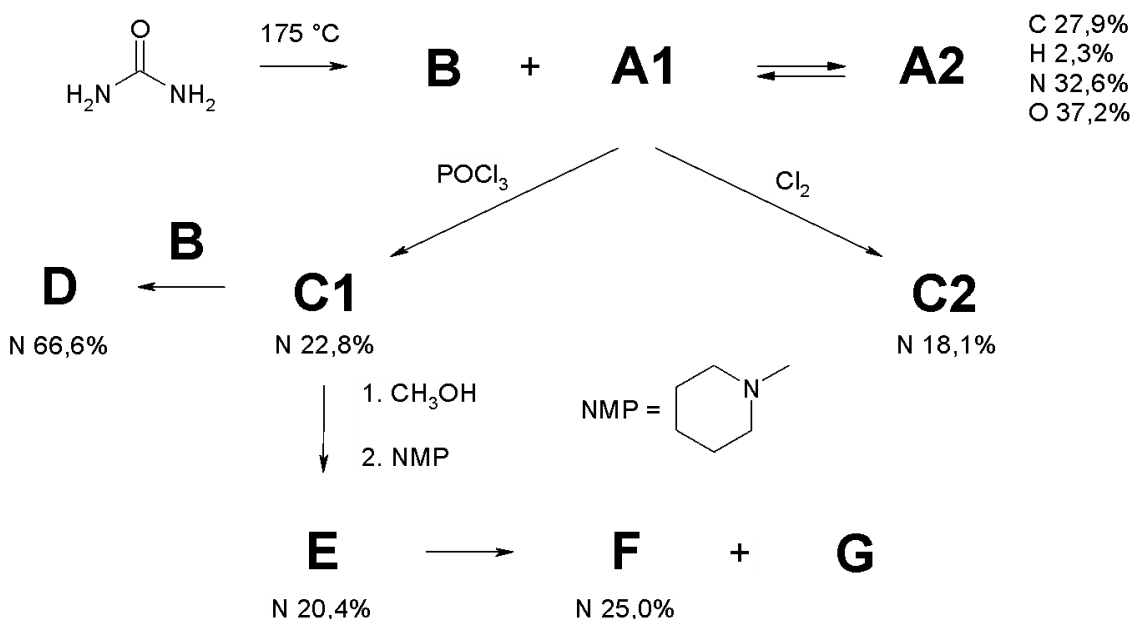
The scheme shown below represents the industrial synthesis of a new class of drugs for the treatment of type 2 diabetes. The synthesis, remarkable in its simplicity and especially in the effortless purification of products, is used to produce the target molecule in kilogram quantities for clinical development.



- Draw structural formulas of compounds A-E.
- Draw the mechanism for the formation of **D** from **C**. Consider this reaction as a three-step process. Formation of the active reagent from sulfur compound and strong base, its addition to **C** and elimination of side product to give **D**.

### Problem 4 – ABC, INORG – Uses and misuses of nitrogen compounds

The thermal decomposition of urea at 175 °C affords the highly symmetrical, acidic ( $\text{p}K_{\text{a}1} = 7$ ) compound **A** ( $\text{C}_n\text{H}_n\text{N}_n\text{O}_n$ ) along with colorless gas **B**. Compound **A** exists in solution as a mixture of isomers **A1** and **A2**, where aromatic isomer **A1** is the predominant form. **A** can be converted into two different chlorides, **C1** ( $w_{\text{N}} = 22,8\%$ ) and **C2** ( $w_{\text{N}} = 18,1\%$ ). **C1** is well suited for multiple functionalizations with nucleophiles and is commonly used as a precursor in the production of pesticides and fluorescent dyes, while **C2** found its widespread use as a water disinfectant and bleaching agent. Although it is not commercially viable, compound **D**, in principle, could be obtained from **C1** and gas **B**. **D** has a very high nitrogen content ( $w_{\text{N}} = 66,6\%$ ). The use of **D** in dairy products to artificially boost protein content was at the core of the scandal in China in 2008. **C1** is also widely utilized in organic synthesis. The wide range of reagents based on **C1** allows a simple one-step transformation of a carboxylic acid into amide, ester and even alcohol. Sequentially treating **C1** with methanol and then *N*-methylpiperidine (NMP) affords coupling agent **E** ( $w_{\text{N}} = 20,4\%$ ) in the form of chloride salt. Coupling reagent **E** is primarily used in the synthesis of various amides. Although **E** is cheap and easy to use, which allows the synthesis even on a multikilogram scale, it has one significant drawback. The reaction solvent choice is limited to tetrahydrofuran. In other solvents, like chloroform or acetonitrile, **E** undergoes rapid degradation with the formation of neutral compound **F** ( $w_{\text{N}} = 25,0\%$ ) and gas **G**.



- Draw structural formulas of compounds **A1**, **A2**, **B**, **C1**, **C2**, **D**, **E**, **F** and **G**.
- Suggest a solution to avoid degradation of activating agent **E**.
- Draw the mechanism for the conversion of  $\text{RCOOH}$  into  $\text{RCONHR}$  using activating agent **E**.

### Problem 5 – EQUILIB, KINETICS – Kinetics and equilibrium

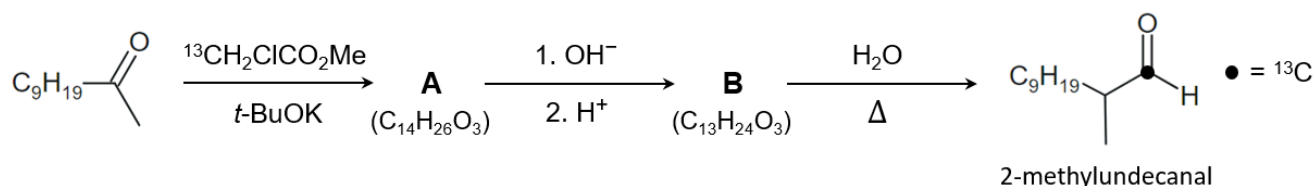
The rate constant for the reaction  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$  at 273 K is  $0.0375\text{ s}^{-1}$  and at 298 K –  $0.0021\text{ s}^{-1}$ . Under standard condition  $\Delta H_r^\circ = 4730\text{ J mol}^{-1}$ ,  $\Delta S_r^\circ = -33,5\text{ J mol}^{-1}\text{ K}^{-1}$ . Assume that  $\Delta H_r^\circ$  and  $\Delta S_r^\circ$  have the same values under normal conditions.

- Calculate the equilibrium constants of the reaction at 0 °C and 25 °C.
- Calculate the activation energy for the backward reaction.

### Problem 6 – SYNTH – Chanel №5

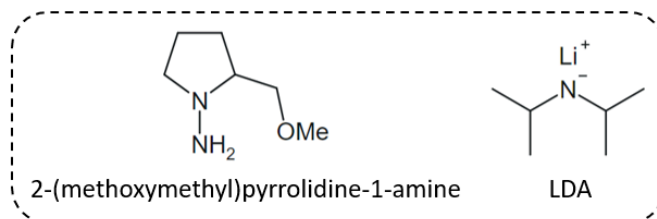
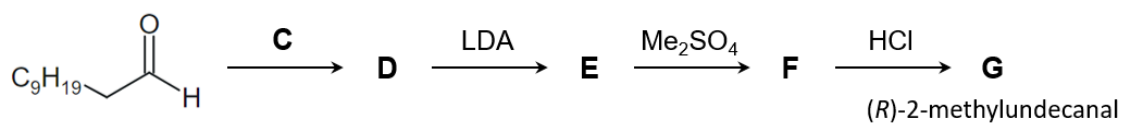
The legendary fragrance Chanel No. 5 was created in 1921 and retains its popularity nowadays. It was Marilyn Monroe's favorite perfume. She noted she only slept wearing a few drops of Chanel No. 5. One of the stories tells that this scent was accidentally made by the assistant adding too much 2-methylundecanal to the mixture. Like the majority of all the perfumes' components, 2-methylundecanal is a purely synthetic artificial substance, so a convenient synthesis was proposed.  $^{13}\text{C}$  carbon isotope was used to make the investigation of the reaction mechanism easier.

- Draw the structural formulas of compounds **A** and **B**.



- Draw the mechanisms of the first and the third reaction.

A stereoselective synthesis of (*R*)-2-methylundecanal **G** was also suggested to find out which of the two enantiomers has the required odor for the perfume. The asymmetric center was introduced using a chiral 2-(methoxymethyl)-pyrrolidin-1-amine **C**.



- c)** Draw the structural formula of *(R)*-2-methylundecanal **G**.
- d)** Which 2-(methoxymethyl)pyrrolidine-1-amine **C** enantiomer is used in the synthesis?
- e)** Draw the structural formula of compounds **D–F**.

After completing the synthesis, it was discovered that both the isomers have very similar smells.