

17th Chemistry Olympiad of the Baltic States

Riga, Latvia, 2009

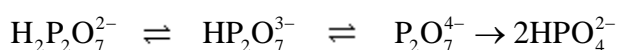
Theoretical examination

Problem set



Problem 1. Hydrolysis of pyrophosphate (10 pts).

Let's 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 is $k_7^* = 0,0010 \text{ s}^{-1}$. The mechanism of the hydrolysis is as follows:



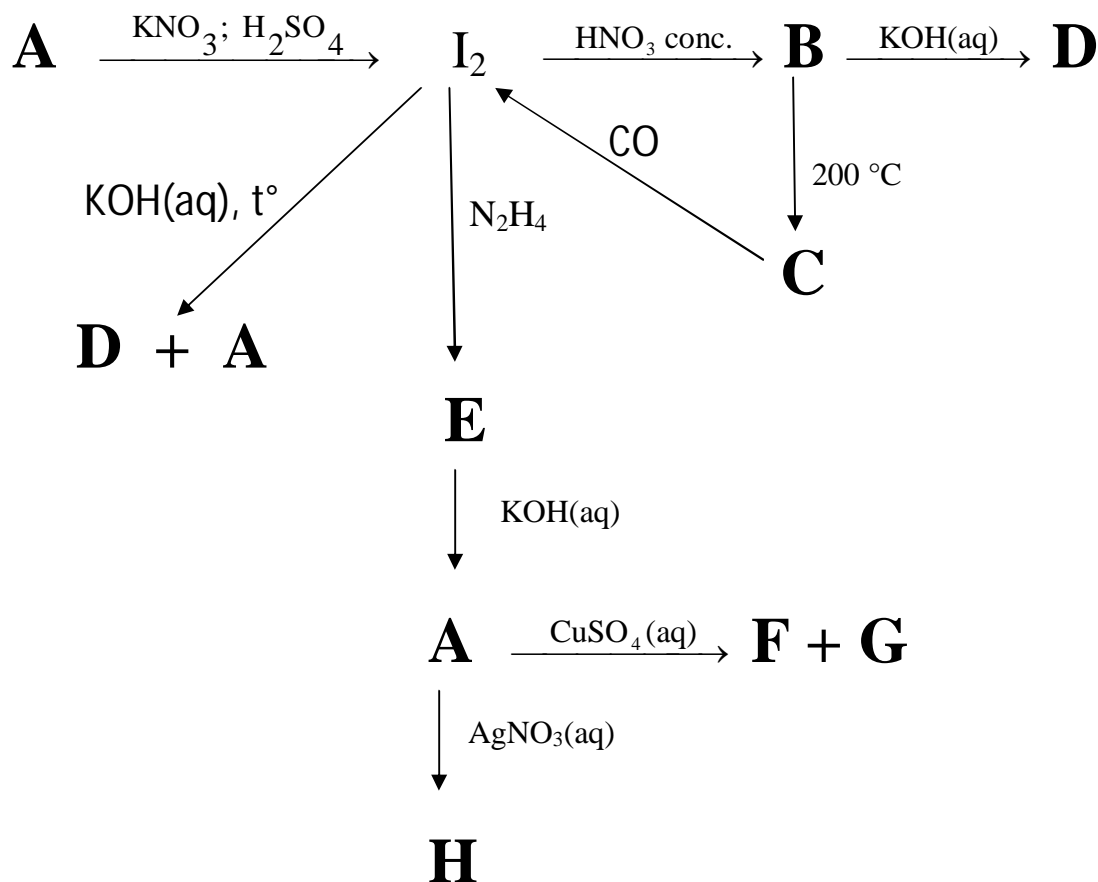
where $\text{p}K_1 = 6.12$ and $\text{p}K_2 = 8.95$ are the acid dissociation constants (1st and 2nd stages), and k is the true rate constant which does not depend on pH (3rd stage). It is assumed that acid dissociations are fast compared with the hydrolysis.

- Write down the equations for the acid dissociation constants K_1 and K_2 , and derive an expression of pyrophosphate total concentration.
- Calculate the value of true rate constant k .
- Calculate the values of apparent rate constants k_6^* and k_8^* at pH = 6 and pH = 8.

Problem 2. Iodine and polyiodides (12 pts).

Iodine was discovered in 1811 by the French chemist Curtois during the process of manufacturing potassium nitrate, with which he supplied the Napoleon armies. While washing seaweed ashes with sulphuric acid, he noticed violet fumes that condensed on his copper equipment and caused corrosion. Below you see 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.

- Identify substances **A** to **H** and write appropriate balanced molecular chemical equations:



One of remarkable features of iodine is possibility to form so called polyiodide ions. One of the simplest polyiodide ion present in tincture of iodine. This tincture is prepared by dissolution of iodine I_2 in a solution of KI. In this mixture triiodide ions I_3^- present. Until now anions from I_2^- to I_{29}^{3-} have been established.

- Write Lewis structure for I_3^- ion. Don't forget to indicate lone pairs of electrons. Show geometrical arrangement of iodine atoms in this ion.
- Draw possible geometrical structures of I_5^- ion. In this case you might omit lone pairs of electrons.

Polyiodides are not very stable compounds, but large cations with a high symmetry can be used to obtain thermally stable polyiodides. In the laboratory polyiodide $\text{R}_4\text{NI}_{2x+1}$ ($x = 1, 2, 3, 4 \dots$) with

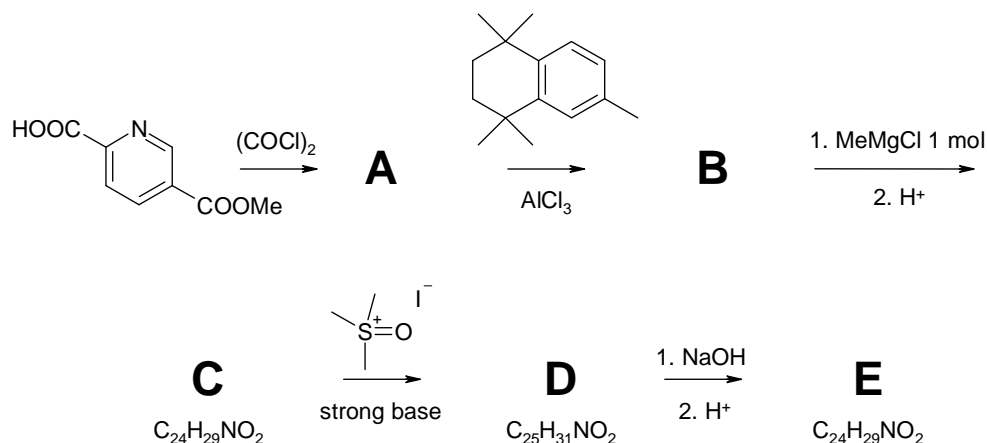


large cation was investigated. R is radical of alkane. For titration of 0.219 g of R_4NI_{2x+1} 10.23 mL of 0.112 mol/L $Na_2S_2O_3$ solution was consumed. In the course of titration $S_2O_3^{2-}$ is converted into $S_4O_6^{2-}$.

d) Determine molecular formula of R_4NI_{2x+1} . Clearly show your calculations.

Problem 3. Small rings fighting diabetes (10 pts).

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



1. Provide structures of compounds **A**, **B**, **C**, **D**, and **E**. (**B**, **C** are 2 pt each; **A**, **D**, **E** are 1 pt each)
2. Suggest 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**. (1 pt for each step, 3 pts total)



Problem 4. Uses and misuses of nitrogen compounds (10 pts).

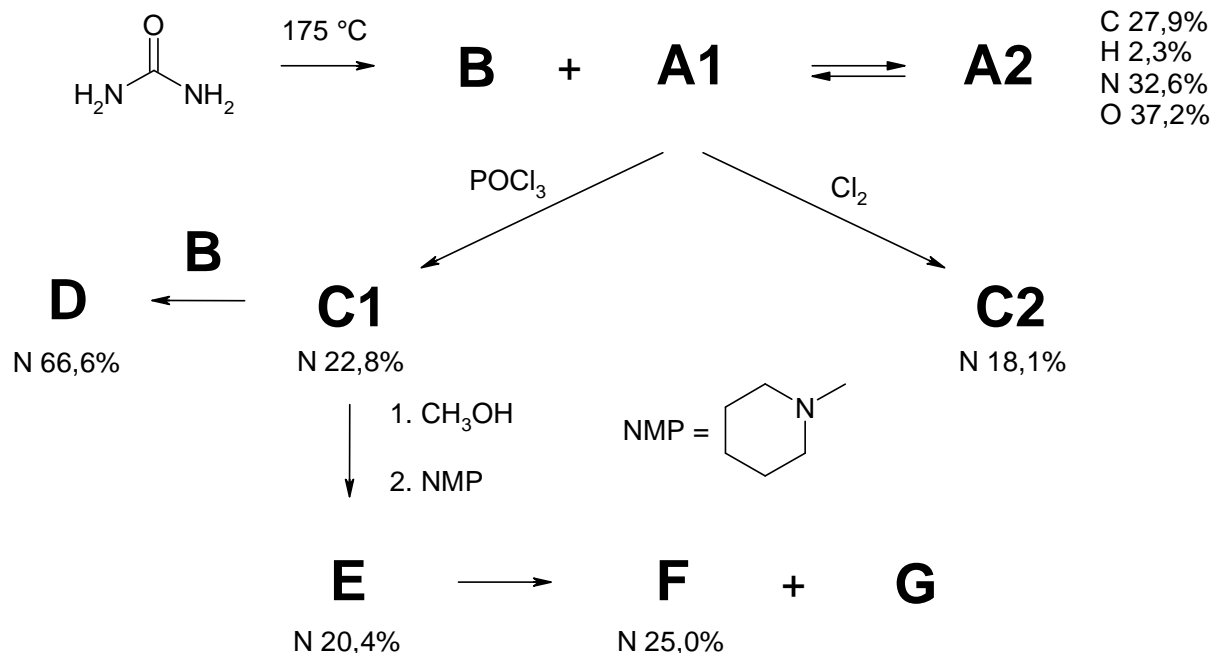
The thermal decomposition of urea at 175 °C affords the highly symmetrical, acidic ($pK_a=7$) compound **A** (composition: C 27,9%, H 2,3%, N 32,6%, O 37,2%) along with colorless gas **B**. Compound **A** exists in solution as a mixture of isomers **A1** and **A2**, where aromatic isomer **A1** is the predominant form.

A can be converted into two different chlorides **C1** (N 22,8%) and **C2** (N 18,1%). **C1** is well suited for multiple functionalizations with nucleophiles and is commonly used as a precursor in production of pesticides and fluorescent dyes, while **C2** found its widespread use as 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 very high nitrogen content (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 simple one step transformation of a carboxylic acid into amide, ester and even into alcohol. Sequentially treating **C1** with methanol then N-methylpiperidine (NMP) affords coupling agent **E** (N 20,4%) in a form of the 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 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 formation of neutral compound **F** (N 25,0%) and gas **G**.



- Provide structures of compounds **A1**, **A2**, **B**, **C1**, **C2**, **D**, **E**, **F** and **G**. (1 pt each, **B** is 0,5 pt)
- Suggest simple solution to avoid degradation of activating agent **E**. (0,75 pt)
- Draw the mechanism of conversion of carboxylic acid RCOOH into amide RCONHR', using activating agent **E**. (0,75 pt)

Problem 5. Kinetics and equilibrium (8 pts).

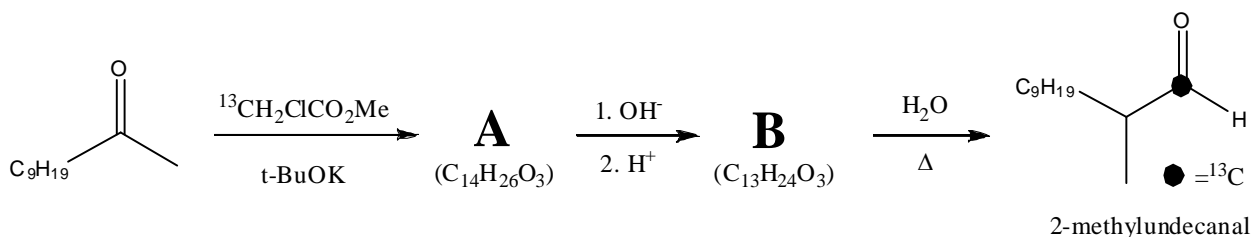
Under standard condition the rate constant for the reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ is 0.0375 s^{-1} and under normal condition — 0.0021 s^{-1} . Under standard condition $\Delta_r H^\circ = 4730\text{ J}\cdot\text{mol}^{-1}$, $\Delta_r S^\circ = -33,5\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Assume that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ under normal condition have the same values.

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

Problem 6. Chanel №5 (10 pts).

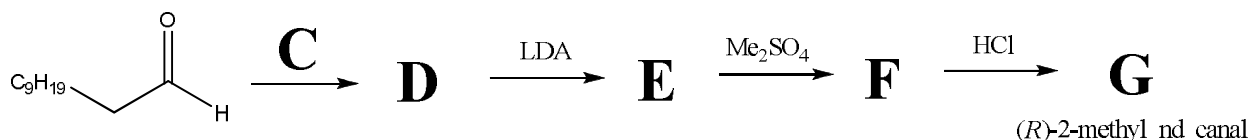
The legendary fragrance *Chanel No. 5* was created in 1921 and retains its popularity nowadays. It was the favorite Marilyn Monroe's perfume. She noted she only slept wearing a few drops of *Chanel No. 5*. One of the stories tell that this scent was accidentally made by the assistant adding too much of 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. ¹³C carbon isotope was used to make the investigation on the reaction mechanism easier.



- Draw the structures of compounds **A** and **B**.
- Write down the mechanisms of the first and the third reaction.

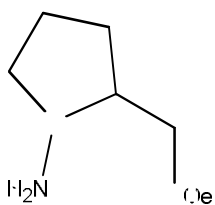
A stereoselective synthesis of (R)-2-methylundecanal **G** was suggested also to find out which one of the two enantiomers has the required odour for the perfume. The asymmetric center was introduced using a chiral 2-(methoxymethyl)-pyrrolidin-1-amine **C**.



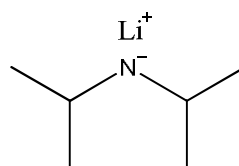


- c) Draw the structure of (R)-2-methylundecanal **G**.
- d) Which 2-(methoxymethyl)pyrrolidin-1-amine **C** enantiomer is used in the synthesis?
Why?
- e) Draw the structures of compounds **D** – **F**.

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



2-(methoxymethyl)pyrrolidin-1-amine



LDA