ENG

english version

CHEMISTRY OLYMPIAD OF THE BALTIC STATES

PRACTICAL EXAMINATION

29 April 2006

Rīga

Student's name, surname: [ ] Country: [ ]

DIRECTIONS

- All the time you are in the laboratory you must wear safety spectacles or optical spectacles, in case the latter are needed. Pipettes have to be filled with a pipette bulb. Eating in the laboratory is strictly prohibited.
- Participants have to follow the safety rules, to be kind to each other and to keep their labware and working place in order. Do not be shy to ask the laboratory assistant about the safety rules.
- You may begin working only after the "START" signal. You have 5 hours to complete the practical examination and to fill in the answer sheets. 15 minutes before the end of this period you will be warned. Working has to be stopped right after the "STOP" signal. Being 5 minutes late will result in receiving 0 points for the practical examination.
- Write your name and code (indicated in the working place) in the corresponding boxes on the answer sheets.
- All results have to be written in the corresponding boxes on the answer sheets. Results written elsewhere will not be graded. If you need some paper for calculations or an additional answer sheet, ask the laboratory assistant.
- When you have finished working, place all answer sheets into the provided envelope. Only the sheets in the envelope will be graded.
- Do not leave the room prior to receiving permission.
- You have to use only the provided labware.
- The number of significant figures in the numerical answers has to correspond to the laws of experimental errors and rounding up. Failing to do the calculations correctly will result in penalties, even if your technique is impeccable.

Collection of used and spilt chemicals and broken glassware

- Organic filtrates, washings and any other waste have to be put into the corresponding vessels or bottles.
- For disposing of waste and chemical waste use the corresponding containers.
- Broken glassware and split glass has to be disposed of in the waste basket. For breaking glassware or asking an additional sample you receive a 2 point penalty.

Periodic Table of Elements

Atomic weights based on $^{12}C = 12$
(Numbers) = most stable isotope

s block | d block: Transition Metals | p block: Metals, Non-metals

I	II											III	IV	V	VI	VII	VIII
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 105.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 **Ac 227.03	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (?)											

f block

*Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
**Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

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Problem 1 ORGANIC CHEMISTRY

HANTSCH DIHYDROPYRIDINE SINTHESIS

15 points

Labware:

technical balance	1
50 mL round bottom flask	1
heating plate	1
reflux condenser	1
boiling stones	2-3
Bunsen flask	1
Buchner funnel	1
Petri dish	1
spatula	1
50 mL cylinder	1
10 mL measuring pipette	1
laboratory stand	1

In the free area to the right draw schematically the reaction assembly.

Reaction assembly

Reagents:

Ethanol

Safety information:

R11	Highly flammable
S7	Keep container tightly closed
S16	Keep away from sources of ignition - No smoking

Ethyl acetoacetate

Safety information:

R36/37/38	Irritating to eyes, respiratory system and skin
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S37/39	Wear suitable gloves and eye/face protection

Ammonium acetate

Safety information:

S24/25	Avoid contact with skin and eyes

Urotropine

Safety information:

R11	Highly flammable
R42/43	May cause sensitization by inhalation and skin contact
S16	Keep away from sources of ignition - No smoking
S22	Do not breathe dust
S24	Avoid contact with skin
S37	Wear suitable gloves

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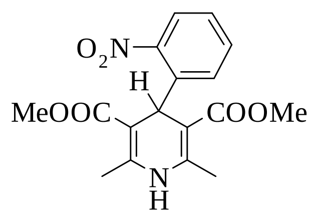
Objective:

Synthesize diethyl 2,6-dimethyl-1,4-dihydropiridine-3,5-dicarboxylate from the provided starting compounds.

Introduction:

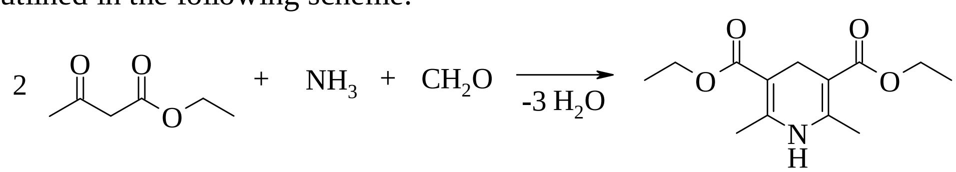
The reaction of 1,3-dicarbonyl compounds with aldehydes and ammonia that gives 1,4-dihydropyridines was described by Hantsch more than a hundred years ago. This method is widely used for the synthesis of symmetrically substituted 1,4-dihydropyridines. Lately this method has acquired a special popularity because some compounds obtained this way have valuable properties. For example, medication nifedipine (Adalat®, produced by Bayer-AG) is a calcium antagonist *in vivo* and is used as a hypertensive.



Nifedipine

Nowadays various modifications of the classical Hantsch synthesis are known. For example, ammonium acetate is used as the source of ammonia and urotropine is used in place of formaldehyde. If ammonia is replaced by primary amines, *N*-substituted 1,4-dihydropyridines can be obtained. Other methods similar to Hantsch ester synthesis have also been developed that allow to obtain unsymmetrical 1,4-dihydropyridines.

You have to synthesize diethyl 2,6-dimethyl-1,4-dihydropiridine-3,5-dicarboxylate. The synthesis is outlined in the following scheme:



Procedure:

In a 50 mL round bottom flask dissolve 2.0 g of ammonium acetate and 0.80 g of urotropine in 22 mL of ethanol, add 7.8 mL of ethyl acetoacetate and reflux the solution for 1 hr in a boiling water bath, gently swirling the flask time to time (meanwhile you may start working with Problem 2 – determination of the percentage of hydrogen peroxide solution).

Cool the solution and filter off the precipitate using a Buchner funnel. Wash the precipitate on the filter with 2 mL of ethanol, 4 mL of water, and again 2 mL of ethanol. Recrystallize from ethanol. Dry in the air, covered with filter paper. A yellow crystalline compound is obtained.

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Questions:

Draw structure of the product that would form if phenylacetaldehyde were used in place of formaldehyde!

The synthesized 1,4-dihydropyridines can be easily oxidized to the corresponding pyridines. In classical methods nitric acid or nitrous acid are used as oxidants. Yet methods employing, for example, copper(II) acetate, manganese dioxide on a solid support or cerium(IV) ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ are more convenient.

Write reaction equation for the oxidation of diethyl 2,6-dimethyl-1,4-dihydropiridine-3,5-dicarboxylate with cerium(IV) ammonium nitrate.

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Problem 2 **PHYSICAL CHEMISTRY**

DETERMINATION OF THE CONCENTRATION OF HYDROGEN PEROXIDE SOLUTION AND KINETICS OF ITS DECOMPOSITION

25 points

Labware:

laboratory stand	3
clamps	4
30 mL burette	1
funnel	1
10 mL volumetric pipette	2/3
100 mL volumetric flask with H_2O_2 solution	1
250 mL Erlenmeyer flasks	3
50 mL conical flask	1
50 mL burette	1
separating funnel	1
magnetic stirrer	1
stopwatch	1
rubber tubing	2
5 mL measuring pipette	1
15 mL volumetric pipette	1

Reaction assembly for the study of kinetics of hydrogen peroxide decomposition

Reagents and safety information:

hydrogen peroxide, H_2O_2; approximately 3% solution

Safety information:

R22	Harmful if swallowed
R37/38	Irritating to respiratory system and skin
R41	Risks of serious damage to eyes
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S28A	After contact with skin, wash immediately with plenty of water
S36/37/38	Wear suitable protective clothing, gloves and eye/face protection
S45	In case of accident of if you feel unwell, seek medical advice immediately (show the label where possible)

potassium permanganate, $KMnO_4$; 0.020 M solution

Safety information:

R22	Harmful if swallowed
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R8	Contact with combustible material may cause fire
S60	This material and its container must be disposed of as hazardous waste
S61	Avoid release to the environment. Refer to special instructions / Safety data sheets

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sulfuric acid, H_2SO_4; 1 M solution + Mn^{2+} ions

Safety information:

R35	Causes severe burns
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S30	Never add water to this product
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)
S61	Avoid release to the environment. Refer to special instructions/safety data sheet

potassium iodide, KI; 0,25 M solution

Safety information:

S26	Avoid contact with skin and eyes

Objective:

By titration with permanganate determine the percentage of hydrogen peroxide solution. Determine reaction order of hydrogen peroxide decomposition and reaction activation energy.

Introduction:

Hydrogen peroxide is an interesting compound, because it is both an oxidizer and a reducing agent. In medicine hydrogen peroxide is used externally as an antiseptic. The antiseptic properties of hydrogen peroxide are based on its ability to liberate oxygen under influence of catalase (an enzyme), contained in blood. Catalase decomposes hydrogen peroxide, consequently, oxygen is liberated and foam is formed.

Hydrogen peroxide solution used in medicine is usually prepared by ten-fold dilution of the industrially produced solution, containing 27.0 – 31.0% hydrogen peroxide. The analysis is based upon a redox reaction that occurs during titration. This method provides good precision, and it can be successfully used for the analysis of both very dilute and more concentrated solutions.

The kinetics of hydrogen peroxide decomposition can be studied by measuring volume of the liberated oxygen as function of time. First, reaction order has to be determined. To do this, two solutions are prepared, as described below, with hydrogen peroxide concentration in one solution twice as high as in the other solution. The change of reaction rate is observed. In both cases the rate constant is determined (denoted as k_1 and k_2).

Then, the experiment with the more concentrated hydrogen peroxide solution is repeated in an ice bath (the temperature has to be measured). The rate constant is determined (denoted as k_3) and the activation energy is calculated by Arrhenius equation $k = A \cdot e^{-\frac{E_a}{R \cdot T}}$.

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Part 1 – **Determination of the percentage of hydrogen peroxide solution**

Complete and balance the following reaction equation:

__ $KMnO_4$ + __ H_2O_2 + __ H_2SO_4 → ____

For the analysis transfer 10 mL of the hydrogen peroxide solution into the 100 mL volumetric flask, dilute to the mark and mix thoroughly. For each titration take 10 mL of the diluted solution, add ~10 mL of 1 M sulfuric acid that contains a small quantity (~0.3%) of manganese(II) sulfate and titrate with 0.02 M $KMnO_4$, until the solution attains a faint pink color that persists for ~1 minute. Summarize titration results in Table 1.

Why no indicator is used in this titration?

What is the role of Mn^{2+} ions in the reaction? Why only ~0.5 mL of potassium permanganate solution is used if no Mn^{2+} ions are added?

Table 1

Results of titration of the hydrogen peroxide solution with potassium permanganate

No.	Burette readings ($KMnO_4$)		
	V_{start}, mL	V_{end}, mL	V, mL
1.			
2.			
3.			
..			
..			

The volume of potassium permanganate solution used in calculations V = _________ mL

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Calculation of the molar concentration of the hydrogen peroxide solution:

Part 2 – **Kinetics of hydrogen peroxide decomposition**

Catalytic decomposition of hydrogen peroxide can be studied by measuring the volume of liberated oxygen and calculating the amount of decomposed hydrogen peroxide from the reaction equation. The quantity of oxygen is calculated by the ideal gas law (R = 8.314 J / (mol · K)).

Write reaction equation for the decomposition of hydrogen peroxide!

Draw Lewis structure of hydrogen peroxide, determine oxidation numbers of the elements and hybridization of oxygen, and estimate bond angles!

Student's name, surname: [ ] Country: [ ]

Procedure:

1. Open the stopcock of the separating funnel and fill the funnel with water whose temperature is equal to room temperature (it is not necessary to use distilled water).
2. Fill the crystallizing dish on the magnetic stirrer with the same water to half-height. Measure water temperature in the crystallizing dish.
3. With volumetric pipettes transfer into the 50 mL conical flask:

   10 mL of 0.25 M potassium iodide solution

   15 mL of distilled water

   Place the flask into the water bath. Set a uniform stirring speed and do not change it through the entire experiment.
4. Record the burette reading (it is sufficient to take readings with one decimal place).
5. With a 5 mL pipette transfer 5 mL of the titrated hydrogen peroxide solution into the conical flask and immediately place in the neck of the flask the rubber stopper with a gas outlet tube for transferring the liberated oxygen into the burette. Start the stop-watch.
6. To keep the pressure in the burette equal to the atmospheric pressure (record the barometer reading), slowly move down the separating funnel, so that the water level in the burette and in the separating funnel remains at the same height. It is suggested that you hold the separating funnel in your left hand, while recording the time with your right hand. If you are a lefthander, change the experiment set-up correspondingly.
7. When the first 5 mL of gas have been collected, start recording the time necessary for the evolution of each milliliter of oxygen. First, record the time on your draft paper, then, record it in Table 2. Go on, until 30 mL of oxygen have been collected.
8. Remove the stopper from the neck of the conical flask, stop stirring, wash the conical flask and repeat the experiment with another quantity of hydrogen peroxide.
9. With volumetric pipettes transfer into the 50 mL conical flask:

   10 mL of 0.25 M potassium iodide solution

   10 mL of distilled water

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Table 2

Time necessary for the evolution of the indicated volume of oxygen

Experiment 1			Experiment 2			Experiment 3		
t, ^{o}C			t, ^{o}C			t, ^{o}C		
p, kPa			p, kPa			p, kPa		
$V(O_2)$, mL	Time		$V(O_2)$, mL	Time		$V(O_2)$, mL	Time	
	min.	s		min.	s		min.	s

10. With the 10 mL pipette transfer into the conical flask 10 mL of the same hydrogen peroxide solution and proceed as described previously. Finish the experiment, when 30 mL of oxygen have been collected.

11. Put into the crystallizing dish several ice-cubes and place into it the 50 mL conical flask, containing a magnetic stirring bar and the following solutions:

    10 mL of 0.25 M potassium iodide solution

    10 mL of distilled water

    Let the temperature become steady for 5 minutes, stop stirring and measure the temperature in the conical flask.

12. With the 10 mL pipette transfer into the conical flask 10 mL of the same hydrogen peroxide solution and proceed as described previously. Measure the temperature in the conical flask after the end of the experiment.

13. Record the atmospheric pressure. Summarize all experimental results in Table 2. Determine the reaction order.

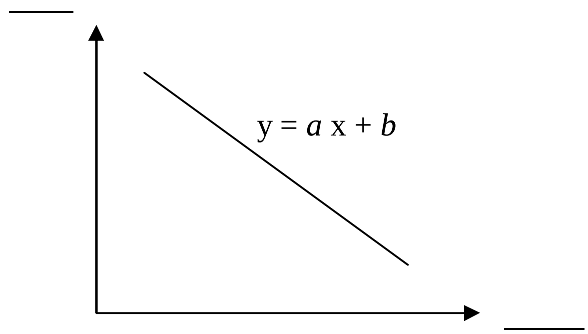
14. Hand in to the observer Table 2, the coordinates to be used for the graph, and the calculation formula. The observer will record the time you hand in the data. In approximately one hour you will receive three graphs in the indicated coordinates, containing a straight line and the corresponding equation in the form $y = a x + b$.

15. From the received graphs determine the rate constants (k_1, k_2, and k_3; measurements made during the evolution of the first 5 mL of oxygen are not used in the calculations, but they have to be included in Table 2) and calculate the activation energy.

Determination of the reaction order:

Student’s name, surname: [ ] Country: [ ]

Coordinates to be used for drawing graphs for the determination of the rate constants and explanation of how the rate constant k_i can be elucidated from the coefficients a and b:



Formulas for the calculation of quantities displayed in the graph (explain precisely the designations and your reasoning for obtaining the formulas):

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Calculation example (put your data into the obtained formulas and indicate the units):

The determined reaction rate constants:

k_1 = ______

k_2 = ______

k_3 = ______

Calculation of the activation energy: