

XII BALTIC CHEMISTRY OLYMPIAD

Tartu, April 29 - May 2, 2004

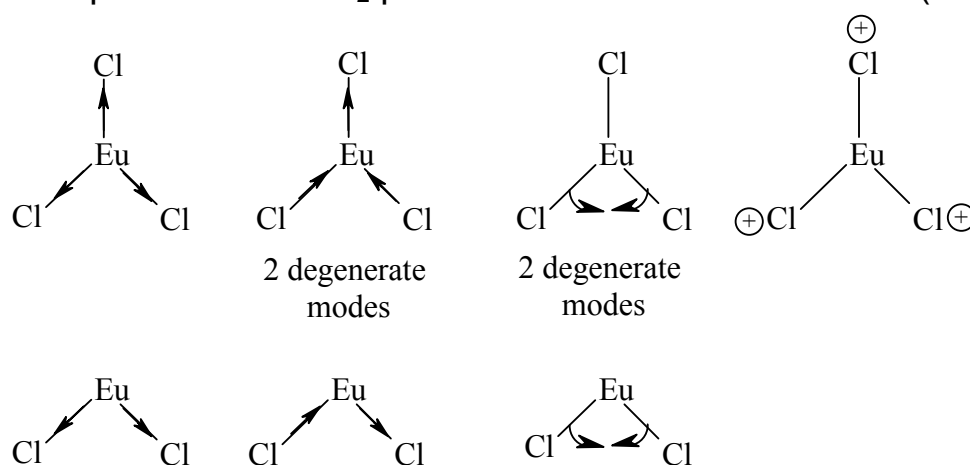
Theoretical problems

SOLUTIONS

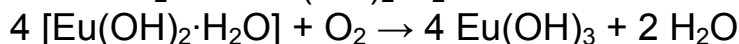
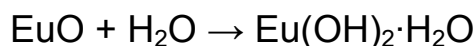
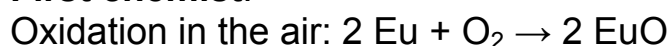
PROBLEM 1

a) Eu ($M = 152 \text{ g}\cdot\text{mol}^{-1}$)

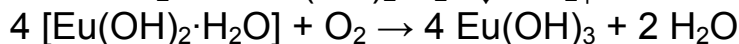
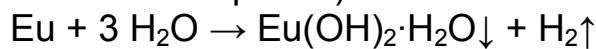
b) The IR spectrum of EuCl_2 proves that the molecule is bent (*not linear*).



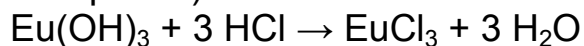
c) **First chemist:**



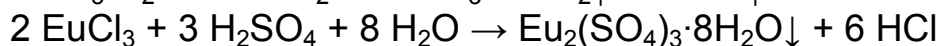
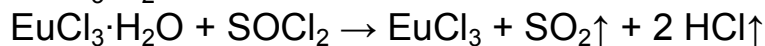
(simplified reaction schemes showing formation of Eu_2O_3 or Eu(OH)_3 are also acceptable)



(a simplified reaction scheme showing formation of Eu(OH)_3 is also acceptable)

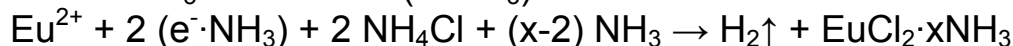


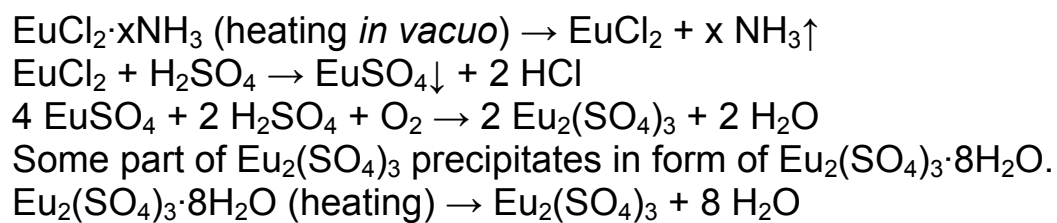
The white crystals obtained by evaporation of the solution are $\text{EuCl}_3 \cdot \text{H}_2\text{O}$.



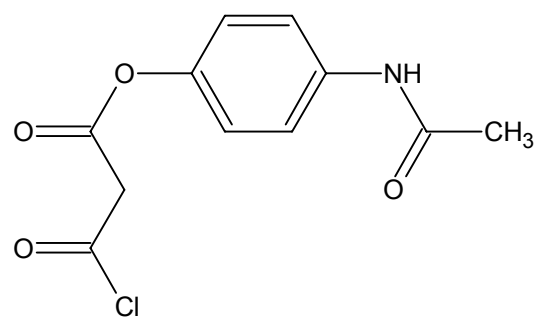
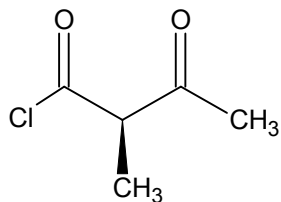
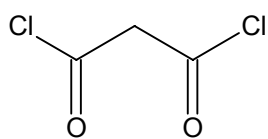
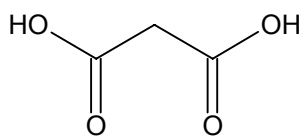
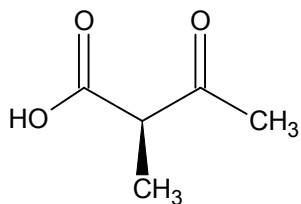
$\text{Eu}_2(\text{SO}_4)_3 \cdot 8 \text{ H}_2\text{O}$ is slightly soluble in water, so precipitation is not complete.

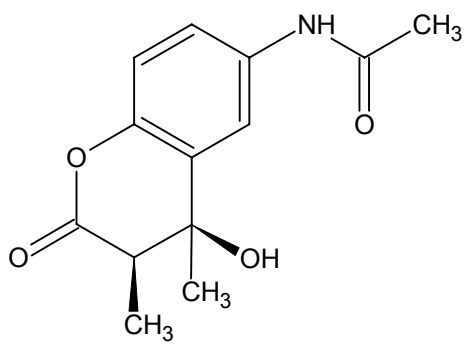
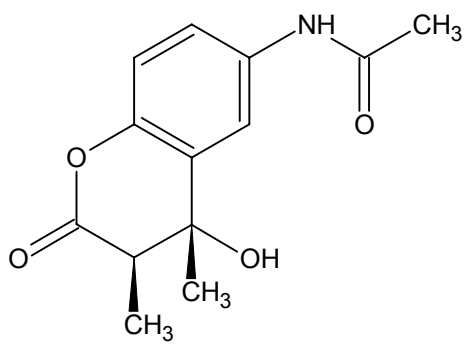
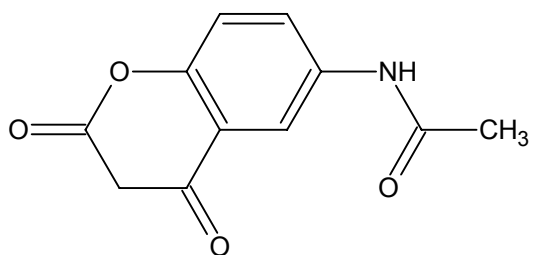
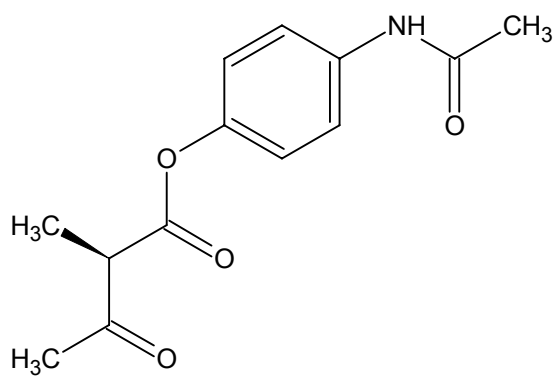
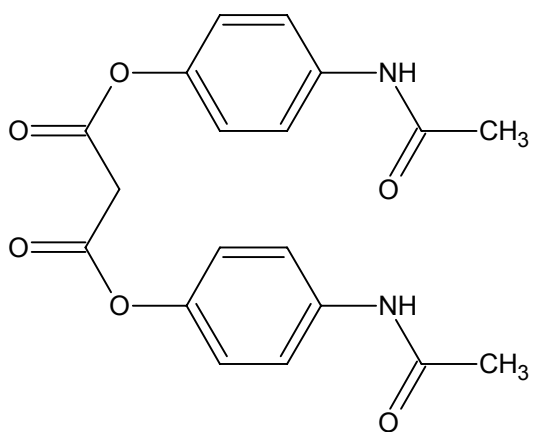
Second chemist:

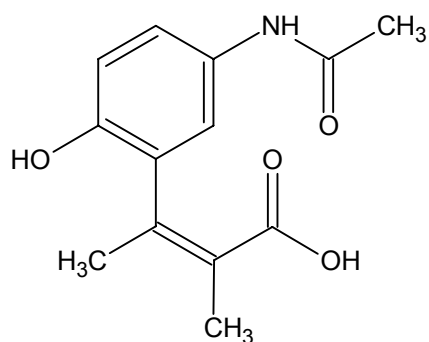
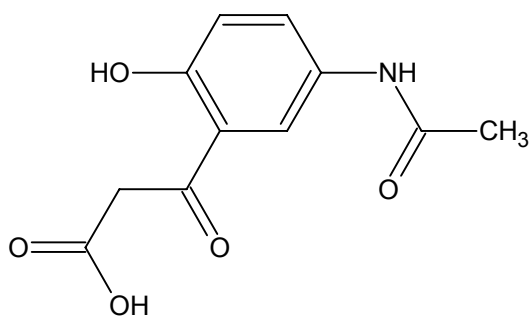




PROBLEM 2





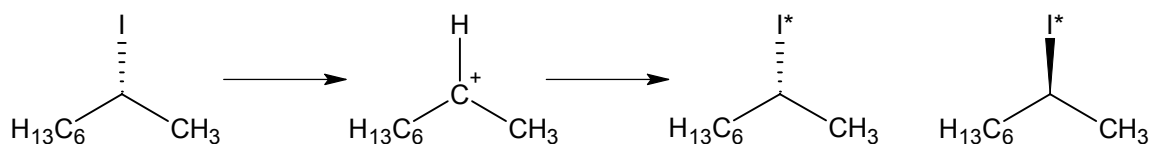


AlCl_3 is a catalyst. It acts as a Lewis acid, stabilizes intermediate carbocatione.

$\text{HF}+\text{SbF}_5$ is a superacid, which also stabilizes intermediate carbocatione.

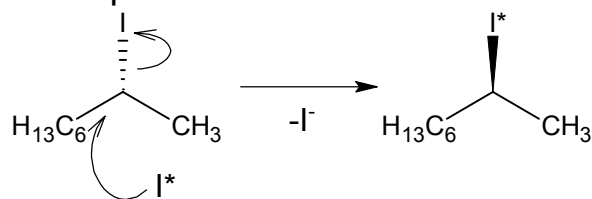
PROBLEM 3

- The fact, that specific rotation changes, does not give ability to discard neither mechanism. When $\text{S}_{\text{N}}1$ mechanism takes place, intermediate planar carbocation is formed and iodide ion can attach from both side with equal possibilities. Therefore during reaction racemization takes place.



When $\text{S}_{\text{N}}2$ mechanism takes place, iodide anion attacks from opposite side to the leaving group (iodine). Formally, radioactive iodine does not differ from “regular” iodine, therefore the product of reaction is (2S)-2-iodooctane – enantiomer of original compound. Therefore racemization

takes place in this case.



- The fact, that racemization is two times faster than replacement with radioactive iodine shows that reaction goes through S_N2 mechanism. When S_N2 mechanism takes place, with a radioactive iodide attack enantiomer of starting compound is forming. Thus, when the half of starting compound will have radioactive iodine, racemization will be full.
- After the reaction will end, specific rotation will be 0.
- The water phase will have inorganic salt NaI (in fact it will be mixture of NaI and NaI^*).
Water should be cold:
 - When reaction mixture is diluted with cold water, temperature is dropped down and therefore reaction practically stops.
 - secondly, alkyl iodides are very reactive compounds and thus with cold water hydrolysis is avoided.
- When reaction is performed in methanol, methanol can be not only solvent, but also nucleophile. During this reaction, 2-methoxyoctane will form, specific rotation of which isn't equal to specific rotation of 2-iodooctane (even may have different sign). As in this case there are two concurrent reactions, specific rotation and radioactivity are not linearly dependent.
- $\kappa = \lambda v(\alpha_0/\alpha)/t$, and $k = k'/[NaI^*]$
 $k' = 5E-5$, and $k = 0,03057$

PROBLEM 4

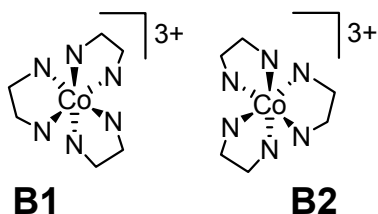
1. Solid **A** elemental analysis yields: C:H:Cl = 1:5:1. 1H NMR data suggest that there is a CH_2 group attached to the electronegative atom X such as Cl, O, N. Assuming only one additional atom X in **A** molecule yields C:H:Cl:X = 1:5:1:14.0/M(X), and assumption that X is nitrogen gives C:H:Cl:N = 1:5:1:1 and finally $C_2H_{10}Cl_2N_2$, which is $NH_2CH_2CH_2NH_2 \cdot 2HCl$, ethylenediamine dihydrochloride (en-2HCl).

C:H:Cl ratio in **B** is 6:26:3. 1H and ^{13}C NMR chemical shifts in **A** and **B** are similar, which suggest that original molecule **A** did not change significantly in

B. If so, nitrogen is also present in **B**, and the number of N atoms is equal to the number of C atoms. This reasonable assumption gives C:H:Cl:N = 6:26:3:6, and the rest of 20.6% can be either Co or O or both. The presence of Na in **B** can be ruled out. One Co atom per **B** molecule yields 16.2%, and the rest 4.4% accounts for one O. Thus the molecular formula for **B** is $C_6H_{26}Cl_3N_6CoO$. Obviously, there are 3 molecules of en present, and compound **B** is Co complex: $[Co(en)_3]Cl_3 \cdot H_2O$.

Let's see what we know about **C**: (a) C:H:Cl = 4:10:1; (b) 2 types of C atoms in molecule; (c) obtained from **B**, thus contains Co.

2. Optical isomers of $(\pm)[Co(en)_3]Cl_3 \cdot H_2O$ can be resolved into two enantiomers **B1** and **B2**.



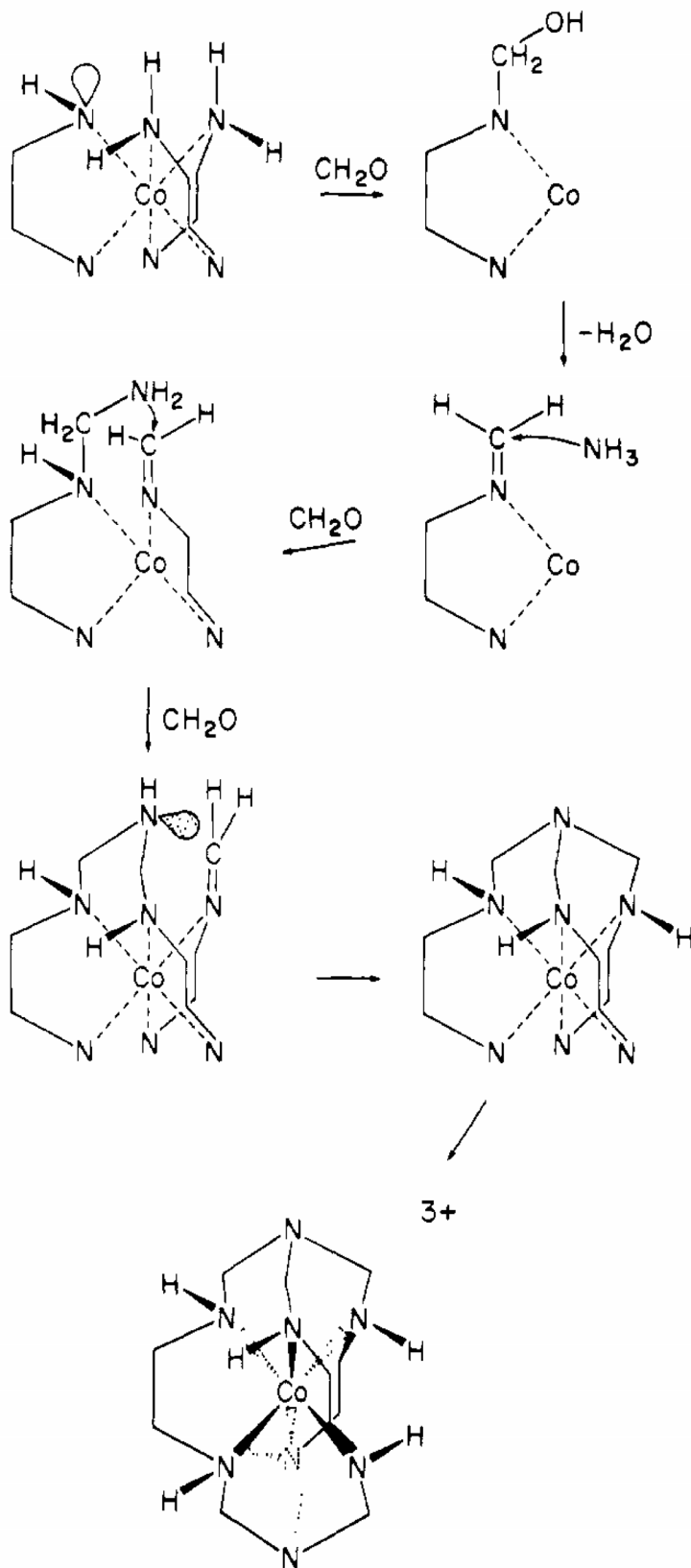
The most common resolution method is converting two enantiomers into two diastereomers. Diastereomers can be separated because they have different physical properties. In this case optically active anion of (2R,3R)-(+)-tartaric acid can be used. $[(+)[Co(en)_3][(+)[tart]Cl]$ is less soluble than $[(-)[Co(en)_3][(+)[tart]Cl]$ and can be precipitated out from solution.

Other resolution methods: (a) "by hand", or Pasteur method is applicable in very few cases; (b) chromatography on a chiral column; (c) chiral catalysis.

3. Upon reduction with Zn amalgam $[Co(en)_3]^{3+}$ is converted to $[Co(en)_3]^{2+}$ (**D**). It cannot be resolved into two enantiomers, since Co^{2+} complex is very labile. The en molecule comes on Co center and off it very fast.

4. The reaction between $[Co(en)_3]^{3+}$, CH_2O and NH_3 leads to macrobicyclic complex in which the ligand completely encapsulates the cobalt ion. See Scheme for details.

The condensation of CH_2O with a bound deprotonated amine to give the coordinated carbinolamine is followed by elimination of H_2O . The resulted imine is then attacked by NH_3 to yield the *gem*-diamine. Addition of another formaldehyde molecule and imine formation allows intramolecular condensation of the *gem*-diamine with imine, and the first six-membered ring system is formed. Formation of another imine followed by intramolecular condensation of the secondary amine leads to the completed cap, and the process is repeated on the opposite octahedral face to give the completely encapsulated metal ion.



PROBLEM 5



2. The amount of reactant moles is n^0 , in equilibrium state n

$$n_{\text{NO}}^0 = n_{\text{NO}} + n_{\text{NOBr}}$$

$$n_{\text{Br}_2}^0 = n_{\text{Br}_2} + 0,5n_{\text{NOBr}}$$

The overall pressure is equal to the sum of partial pressures, hence

$$p_{\text{NO}} + p_{\text{Br}_2} + p_{\text{NOBr}} = 230,0 \text{ mm Hg}$$

If the reaction is not occurred, then the partial pressures at 335 K were, accordingly

$$p_{\text{NO}} = 180 \cdot 335 / 297 = 203,0 \text{ mm Hg and}$$

$$p_{\text{Br}_2} = 0,72 \cdot 62400 \cdot 335 / (1200 \cdot 2 \cdot 80) = 78,4 \text{ mm Hg}$$

Because the partial pressures of gases are proportional to the number of moles, then

$$p_{\text{NO}} + p_{\text{NOBr}} = 203,0 \text{ mm Hg and } p_{\text{Br}_2} + p_{\text{NOBr}} = 78,4 \text{ mm Hg.}$$

We get the following equations:

$$p_{\text{NO}} + p_{\text{Br}_2} + p_{\text{NOBr}} = 230,0 \quad (1)$$

$$p_{\text{NO}} + p_{\text{NOBr}} = 203,0 \quad (2)$$

$$p_{\text{Br}_2} + 0,5p_{\text{NOBr}} = 78,4 \quad (3), \text{ from which}$$

$$p_{\text{Br}_2} = (1) - (2) = 230,0 - 203,0 = 27,0 \text{ mm Hg}$$

$$p_{\text{NOBr}} = (78,4 - 27,0) \cdot 2 = 102,8 \text{ mm Hg}$$

$$p_{\text{NO}} = 230,0 - 27,0 - 102,8 = 100,2 \text{ mm Hg}$$

The equilibrium constant is:

$$K_p = p_{\text{NO}}^2 \cdot p_{\text{Br}_2} / p_{\text{NOBr}}^2 = 100,2^2 \cdot 27,0 / 102,8^2 = 25,7 \text{ mm Hg} = 0,0338 \text{ atm}$$

3. If the pressure is increased, then the equilibrium shifts to the formation of NOBr (smaller number of moles).

4. The partial pressure of NO in equilibrium state is 100,2 mm Hg. Using equation

$pV = nRT$ we find the number of moles:

$$100,2 \cdot 1200 = n \cdot 62400 \cdot 335;$$

$$n = 100,2 \cdot 1200 / (62400 \cdot 335) = 5,75 \cdot 10^{-3} \text{ moles.}$$

PROBLEM 6

1. Cathode: $2\text{H}_3\text{O}^+ (\text{s}) + 2\text{e} = \text{H}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{s})$
Anode: Kolbe reaction: $2\text{CH}_3\text{COO}^- (\text{s}) - 2\text{e} = \text{C}_2\text{H}_6 (\text{g}) + 2\text{CO}_2 (\text{g})$
2. $n(\text{CO}_2) = 5,213/44,01 = 0,1185 \text{ mol}$
 $V(\text{CO}_2) = nRT/p = 0,1185 \cdot 0,0831 \cdot 298,15/1,0 = 2,935 \text{ dm}^3$
 $M(\text{C}_2\text{H}_6) = 2 \cdot 15 = 30 \text{ g/mol}$, $n(\text{C}_2\text{H}_6) = 0,0593 \text{ mol}$; $V(\text{C}_2\text{H}_6) = 1,468 \text{ dm}^3$
3. $Q = 0,1185 \cdot 96485 = 11433 \text{ C (As)}$; $Q = 11433/3600 = 3,176 \text{ Ah}$
4. $T = Q/I = 3,176/0,706 = 4,50 \text{ h}$
 $M = 11433 \cdot 63,55/(2 \cdot 96485) = 3,765 \text{ g}$
5. $[\text{H}_3\text{O}^+] = 1,85 \cdot 10^{-5}/3 = 6 \cdot 10^{-6}$;
 $E(\text{H}^+/\text{H}_2) = 0,059 \cdot \log[\text{H}_3\text{O}^+]$;
 $E(\text{H}^+/\text{H}_2) = 0,059 \cdot (-5,22) = -0,308 \text{ V}$