

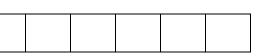
# Uniting Elements, Strengthening Bonds, Shaping Tomorrow!



30<sup>th</sup> Baltic Chemistry Olympiad Tartu, Estonia, May 4<sup>th</sup>-6<sup>th</sup>, 2024

# Theoretical exam solutions

Student's code:



Problem	1	2	3	4	5	6
Points						

May 5<sup>th</sup>, 2024 Tartu, Estonia

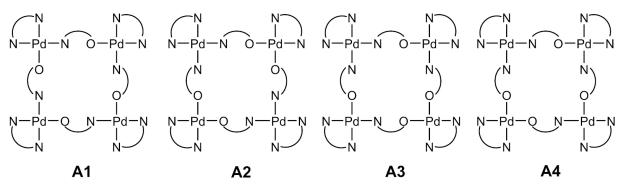
## Problem 1. Polygonal chemistry. Author: Siim Kaukver

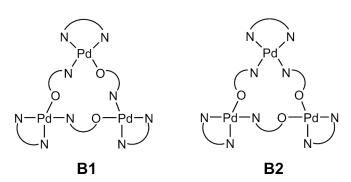
**a)** Dinitro(*N*,*N*,*N*',*N*'-tetramethylethylenediamine)palladium(II)

(2 pts)

(18 pts)

b) Structures of A1–A4 and B1–B2: Each correct structure gives 3 points.





c) a = 3, b = 4

**d)** First,  $\Delta H$  has to be found using the Van't Hoff equation:

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Substituting  $T_1 = 313$  K,  $T_2 = 333$  K,  $K_1 = 21.5$  and  $K_2 = 32.1$  and calculating, we get  $\Delta H = 17.38 \text{ kJ} \cdot \text{mol}^{-1}$ .

A new equation can now be written to calculate  $K_3$ . It can be assumed  $\Delta H$  is constant in the given temperature range. Whether  $K_3$  is found via  $K_1$  or  $K_2$  makes no difference – both approaches are equally valid.

$$\ln\left(\frac{K_3}{K_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_3} - \frac{1}{T_1}\right)$$

By substituting known parameters and calculating, we get  $K_3 = 26.4$ . (3 pts)

- e) Equilibrium constant *K* for the reaction  $3\mathbf{A} \rightleftharpoons 4\mathbf{B}$  can be written as  $K = \frac{[\mathbf{B}]^4}{[\mathbf{A}]^3}$ . (1 *pt*)
  - Let the ratio  $\frac{[\mathbf{B}]}{[\mathbf{A}]}$  be equal to *x*. Hence,  $K = [\mathbf{B}] \cdot x^3$ . (2 pts)

Mass balance for Pd: 
$$c_0 = 4 \cdot [\mathbf{A}] + 3 \cdot [\mathbf{B}].$$
 (2 pts)

By dividing the mass balance equation by [**B**], the following equation is obtained:

$$\frac{c_0}{|\mathbf{B}|} = \frac{4}{x} + 3$$
, from which  $[\mathbf{B}] = \frac{c_0 x}{3x + 4}$ . (2 pts)

Now, *K* can be expressed as:  $K = [\mathbf{B}] \cdot x^3 = \frac{c_0 x^4}{3x+4}$ . (1 *pt*)

(2 pts)

Finding the exact solution is impossible under exam conditions, but a simplification can be made.

As 3x >> 4, it can be assumed that  $3x + 4 \approx 3x$ . Therefore,  $K = \frac{c_0 x^4}{3x + 4} \approx \frac{c_0 x^3}{3}$ . (3 *pts*)

Finally, 
$$x = \sqrt[3]{\frac{3K}{c_0}} = \sqrt[3]{\frac{3 \cdot 26.4}{1.154 \cdot 10^{-3}}} \approx 41.$$
 (1 pt)

Note: the exact solution is x = 41.38, hence the simplification is justified.

## Problem 2. Unknown amino acid. Author: Andreas Päkk

- a)  $n(N) = n(NH_3) = n(HCl) n(NaOH)$  (1 pt)  $n(N) = 0.1350 \text{ mol} \cdot dm^{-3} \cdot 0.04000 \text{ dm}^3 - 0.1500 \text{ mol} \cdot dm^{-3} \cdot 0.01683 \text{ dm}^3 = 0.002875 \text{ mol}$  $w(N) = \frac{0.002875 \text{ mol} \cdot 14.01 \text{ g} \cdot \text{mol}^{-1}}{0.3425 \text{ g}} \cdot 100\% \approx 11.76\%$  (1 pt)
- **b)** Ammonium ions, which remain in the titrated solution, act as a weak acid:  $NH_4^+ \rightleftharpoons NH_3 + H^+$

As the equilibrium is considerably shifted to the left,  $[H^+]_{eq} = [NH_3]_{eq}$ , therefore:

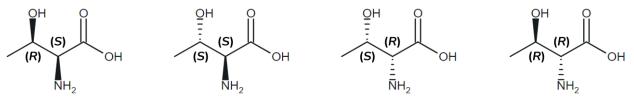
$$K_{a} = \frac{[\mathrm{NH}_{3}][\mathrm{H}^{+}]}{[\mathrm{NH}_{4}^{+}]} = \frac{[\mathrm{H}^{+}]^{2}}{[\mathrm{NH}_{4}^{+}]} \implies [\mathrm{H}^{+}] = \sqrt{K_{a} \cdot c(\mathrm{NH}_{4}^{+})} = \sqrt{K_{a} \cdot \frac{n(\mathrm{HCl}) - n(\mathrm{NaOH})}{V(\mathrm{HCl}) + V(\mathrm{NaOH})}}$$
(2 pts)

$$pH = -\log[H^+] = -\log\left(\sqrt{5.6 \cdot 10^{-10} \cdot \frac{0.002875 \text{ mol}}{0.05683 \text{ dm}^3}}\right) \approx 5.27$$
(1 pt)

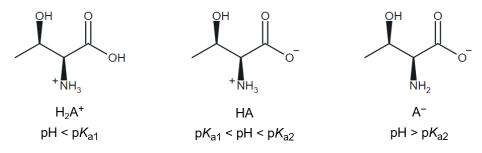
c) Since **X** has two given dissociation constants, it can be assumed that there is only one ionizable amino group in its structure. The general formula of amino acids is R-CH(NH<sub>2</sub>)COOH or R-CH(NH<sub>3</sub><sup>+</sup>)COO<sup>-</sup> (zwitterionic form), where the R group represents a specific side chain.  $M(R) = \frac{1 \cdot 14.01 \text{ g} \cdot \text{mol}^{-1} \cdot 100\%}{11.76\%} - M(C_2H_4NO_2) = 45.07 \text{ g} \cdot \text{mol}^{-1}$ (1 pt)

R corresponds to the hydroxylated carbon chain  $CH_3CH(OH)$ –, thus the condensed structural formula of **X** is  $CH_3CH(OH)CH(NH_2)COOH$  or  $CH_3CH(OH)CH(NH_3^+)COO^-$  (Thr). (1 pt)

**d)** Each correctly drawn stereochemical structure gives 1 point – in total 4 points. **Each pair** of correct configuration indications (S/R) gives 0,5 points – in total 2 points.



e) Each correctly drawn stereochemical ionic form gives 1 point – in total 3 points.



**f)** Two-step dissociation of **X**:

1. 
$$H_2A^+ \rightleftharpoons H^+ + HA$$
  $K_{a1} = \frac{[H^+][HA]}{[H_2A^+]} \Rightarrow [H_2A^+] = \frac{[H^+][HA]}{K_{a1}}$   
2.  $HA \rightleftharpoons H^+ + A^ K_{a2} = \frac{[H^+][A^-]}{[HA]} \Rightarrow [A^-] = \frac{K_{a2}[HA]}{[H^+]}$ 

At the isoelectric point  $[H_2A^+] = [A^-]$ , therefore:

$$\frac{[\mathrm{H}^+][\mathrm{HA}]}{K_{a1}} = \frac{K_{a2}[\mathrm{HA}]}{[\mathrm{H}^+]} \implies \frac{[\mathrm{H}^+]}{K_{a1}} = \frac{K_{a2}}{[\mathrm{H}^+]} \implies [\mathrm{H}^+] = \sqrt{K_{a1}K_{a2}} = \frac{K_{a1}K_{a2}}{2}$$
$$\mathrm{pH} = -\mathrm{log}[\mathrm{H}^+] = \frac{-\mathrm{log}K_{a1} - \mathrm{log}K_{a2}}{2} = \frac{\mathrm{pK}_{a1} + \mathrm{pK}_{a2}}{2} = \frac{2.09 + 9.10}{2} \approx \mathbf{5.60}$$

## Problem 3. Reverse engineering. Author: Ritums Cepītis

- a)  $\ln[A] = \ln[A]t kt$ , where  $k = \frac{\ln(0.05) \ln(1)}{30 \text{ s}} = 0.1 \text{ s}^{-1}$  (2 pts) b)  $k_{300} = 0.1 \text{ s}^{-1}$ ;  $k_{2024} = 1.0 \text{ s}^{-1}$
- $\ln\left(\frac{k_{300}}{k_{2024}}\right) = \frac{E_a}{8.314} \left(\frac{1}{2024} \frac{1}{300}\right), \text{ where } E_a = 6.7 \text{ kJ} \cdot \text{mol}^{-1}$ (3 pts)
- **c)**  $T_1$  and  $t_2$ .

(2 pts)

(4 pts)

- **d)** If  $T_1$  is chosen, the answer is  $T_1 = 1230$  K. (2 pts)
  - If  $t_2$  is chosen, the answer is  $t_2 = 3.79 \cdot 10^{-8}$  s. (2 pts)
- e) The equations for the missing elementary steps:

$$A \rightarrow A' + B \qquad k_1$$
  

$$A' + B \rightarrow A \qquad k_{-1}$$
  

$$A' + B \rightarrow B' + B + C \qquad k_2$$
  

$$A' + B' \rightarrow 2B \qquad k_3$$

Mechanism correspondance to the given reaction law:

$$\begin{aligned} \frac{d(B')}{dt} &= 0 = k_2[A'][B] - k_3[A'][B'] \implies [B'] = \frac{k_2[A'][B]}{k_3[A']} = \frac{k_2[B]}{k_3} \\ \frac{d(A')}{dt} &= 0 = k_1[A] - k_{-1}[A'][B] - k_2[A'][B] - k_3[A'][B'] = \\ &= k_1[A] - k_{-1}[A'][B] - k_2[A'][B] - k_2[A'][B'] = \\ &= k_1[A] - [A'](k_{-1}[B] + 2 \cdot k_2[B]) \\ &\Rightarrow [A'] = k_1[A] \\ - \frac{d(A)}{dt} &= k_1[A] - k_{-1}[A'][B] = k_1[A] - \frac{k_{-1}k_1[A]}{(k_{-1} + 2 \cdot k_2)} = \left(\frac{2 \cdot k_{-1}k_1}{k_{-1} + 2 \cdot k_2}\right)[A] \end{aligned}$$

(2 pts)

(4 pts)

# Problem 4. Have you heard about cerium? Author: Deimantas Šmigelskas

#### Part I. Minerals

- a) There are 4 tetrahedral PO<sub>4<sup>3-</sup></sub> ions and 4 Ce atoms in a unit cell which consists of 24 atoms in total.
   (1 pt)
- **b) Th** isotopes are radioactive while La and Nd have stable isotopes. (1 *pt*)
- **c)**  $\Delta m = n(U) \cdot M(U) n(Ce) \cdot M(Ce) = 4.53 \text{ g}$

$$97.91n = 4.53 \Rightarrow n = 0.0463$$
 (1 pt)

$$\frac{n}{n_0} = \frac{0.0463}{\frac{m(\text{CePO}_4)}{M(\text{CePO}_4)}} = 0.71$$
(1 pt)

**d)**  $N_n(^{238}_{92}\text{U}) = N_0 e^{-\lambda_U t}$ 

Since there was no pre-existing lead in the mineral:  $N_0 = N_n \begin{pmatrix} 238\\92 \end{pmatrix} + N_n \begin{pmatrix} 206\\82 \end{pmatrix}$  (1 *pt*)

$$\frac{N_{n}\binom{238}{92}U}{N_{n}\binom{238}{92}U + N_{n}\binom{206}{82}Pb} = e^{-\lambda_{U}t} \implies \ln\left(\frac{N_{n}\binom{238}{92}U}{N_{n}\binom{238}{92}U + N_{n}\binom{206}{82}Pb}\right) = -\lambda_{U}t \implies t = \frac{\ln\left(\frac{N_{n}\binom{238}{92}U}{N_{n}\binom{238}{92}U + N_{n}\binom{206}{82}Pb}\right)}{-\lambda_{U}} = \frac{\ln\left(\frac{N_{n}\binom{238}{92}U + N_{n}\binom{206}{82}Pb}{N_{n}\binom{238}{92}U}\right)}{\lambda_{U}} = \frac{\ln\left(1 + \frac{N_{n}\binom{206}{82}Pb}{N_{n}\binom{238}{292}U}\right)}{\lambda_{U}} \qquad (2 \ pts)$$

$$\lambda = \frac{\ln(2)}{t_{0.5}}$$

Moles of atoms can be used instead of the number of atoms and Pb mass is 206 because of  $^{238}U \rightarrow ^{206}Pb$  decay.

$$t = \frac{\ln\left(1 + \frac{n_n\binom{206}{82}\text{Pb}}{n_n\binom{238}{92}\text{U}}\right)}{\frac{\ln(2)}{t_{0.5}}} = \frac{\ln\left(1 + \frac{\frac{6.05 \text{ g} \cdot 0.0001}{222 \text{ g} \cdot \text{mol}^{-1}}\right)}{\frac{6.05 \text{ g} \cdot 0.0001}{524 \text{ g} \cdot \text{mol}^{-1}}\right)}{\ln(2)} \cdot t_{0.5} = 0.0453 \cdot t_{0.5} = 0.202 \text{ billion}$$
(1 pt)

e) 1 mol of  $CO_3^{2-}$  produces 1 mol of  $CO_2$ , which gives:

$$n(\text{CO}_3^{2-}) = \frac{m(\text{CO}_2)}{M(\text{CO}_2)} = 0.014224 \text{ mol}$$
 (0.5 pts)

$$M(\text{Ce}_{0.48}\text{La}_{0.37}\text{Nd}_{0.1}\text{Pr}_{0.04}\text{Sm}_{0.01}\text{CO}_3\text{F}) = \frac{m}{n(\text{CO}_3^{2-})} = 219.235 \text{ g}\cdot\text{mol}^{-1}$$
(0.5 pts)

Mass balance:

$$x \cdot M(\text{La}) + y \cdot M(\text{Nd}) = 219.235 - n(\text{Ce}) \cdot M(\text{Ce}) - n(\text{Pr}) \cdot M(\text{Pr}) - n(\text{Sm}) \cdot M(\text{Sm}) - n(\text{C})$$

(1.5 pts)

(0.5 pts)

$$M(C) - n(0) \cdot M(0) - n(F) \cdot M(F)$$
 (0.5 pts)

$$x \cdot M(\text{La}) + y \cdot M(\text{Nd}) = 65.827 \tag{1 pt}$$

Charge balance:

$$3 \cdot [n(Ce^{3+}) + n(La^{3+}) + n(Nd^{3+}) + n(Pr^{3+}) + n(Sm^{3+})] = 2 \cdot n(CO_3^{2-}) + n(F^{-})$$
  
(La<sup>3+</sup>) + n(Nd<sup>3+</sup>) = 0.47 (1 pt)

The system of equations yields:

$$\begin{cases} x \cdot M(\text{La}) + y \cdot M(\text{Nd}) = 65.827\\ x + y = 0.47 \end{cases} \Rightarrow (x; y) = (0.37; 0.1)$$

#### $Ce_{0.48}La_{0.37}Nd_{0.1}Pr_{0.04}Sm_{0.01}CO_{3}F$

- f) There are 6 atoms closely located to cerium in the same plane plus 3 above and 3 below the plane – in total 12 atoms, which means the coordination number of Ce is 12. (1 pt)
- g)  $2\text{CeO}_2 + 8\text{HCl} \rightarrow 2\text{CeCl}_3 + 4\text{H}_2\text{O} + \text{Cl}_2$

$$n(\text{HCl}) = 4 \cdot n(\text{CeO}_2) = 4 \cdot \frac{5.0 \cdot 10^3 \text{ kg} \cdot w(\text{Ce})}{M(\text{Ce}) \cdot 100\%} = 45675.14 \text{ mol}$$

$$V(\text{HCl}) = \frac{n}{2} = 91350.27 \text{ dm}^3 \approx 93 \text{ m}^3 \qquad (1 \text{ pt})$$

**h**)  $\beta$ -cerium (*a* = 0.3681 nm, *c* = 1.1857 nm). DHCP structure can be subdivided into 6 rhombic prism unit cells each of which has 2 atoms inside it: (2.5 pts)

$$\rho = \frac{m(\text{atoms})}{V(\text{unit cell})} = \frac{2 \cdot \frac{M(\text{Ce})}{N_A}}{\frac{\sqrt{3}}{2} a^2 \frac{c}{2}} = 6.69 \text{ g} \cdot \text{cm}^{-3}$$

 $\gamma$ -cerium (*a* = 0.5161 nm). FCC unit cell contains 4 atoms of Ce: (2 pts)

$$\rho = \frac{m(\text{atoms})}{V(\text{unit cell})} = \frac{4 \cdot \frac{M(\text{Ce})}{N_A}}{a^3} = 6.77 \text{ g} \cdot \text{cm}^{-3}$$

Thus,  $\gamma$ -cerium is more dense than  $\beta$ -cerium.

#### Part II. Cerium loves redox

i)  $H^+ + [Ce(NO_3)_6]^{2-} + Fe(OH)_2 + Cu_2O \rightarrow Ce^{3+} + Fe^{3+} + Cu^{2+} + H_2O + NO_3^{-}$ 

Oxidation half-equations:

 $2H^+ + Fe(OH)_2 \rightarrow Fe^{3+} + 2H_2O + e^-$ (0.5 pts)

 $2H^+ + Cu_2O \rightarrow 2Cu^{2+} + + 2e^-$ (0.5 pts)

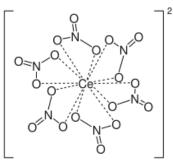
**Reduction half-equation:** 

 $[Ce(NO_3)_6]^{2-} + e^- \rightarrow Ce^{3+} + 6NO_3^ |\cdot 6$ (0.5 pts)

The sum of oxidation and reduction half-equations:

 $10H^{+} + 6[Ce(NO_3)_6]^{2-} + 4Fe(OH)_2 + Cu_2O \rightarrow 6Ce^{3+} + 4Fe^{3+} + 2Cu^{2+} + 9H_2O + 36NO_3^{-}$  (0.5 pts)

**j)** The structrure of the anion of CAN:



**k)** Each identified compound **A**–**C** gives 1 point. (3 pts)A must contain Ce and O. Hydrogen in water is a weak oxidizing agent, so Ce will be in +3 form, and out of Ce<sub>2</sub>O<sub>3</sub>, CeO(OH), Ce(OH)<sub>3</sub>, or other non-polymeric formulas, Ce(OH)<sub>3</sub> gives the right answer. In the second reaction peroxide ion is consumed and water is produced, meaning that

(1 pt)

(1 pt)

(1 pt)

(0.5 pts)

the HO<sub>2</sub><sup>-</sup> ion has lost its hydrogen and replaced two OH<sup>-</sup> ions in hydroxide resulting in **B** 

Ce(O<sub>2</sub>)OH (Ce cannot be +4 here because no oxidation occurrs for cerium). However, anhydride Ce<sub>2</sub>(O<sub>2</sub>)<sub>2</sub>O formed after dimerization of Ce(O<sub>2</sub>)OH followed by H<sub>2</sub>O abstraction is also a possible choice. Ce must be +4 in **C** due to oxidation and since all oxygens have the same oxidation number CeO<sub>2</sub> or Ce(OH)<sub>4</sub> are possible. The absence of stronger base to deprotonate OH<sup>-</sup> leaves us with the choice of Ce(OH)<sub>4</sub>.

Balanced reaction equations:

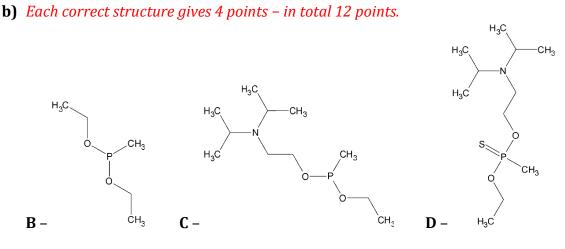
a)  $A - [PCl_3CH_3]^+ [AlCl_3I]^-$ 

- i)  $2Ce + 6H_2O \rightarrow 2Ce(OH)_3 + 3H_2$
- ii)  $Ce(OH)_3 + HO_2^- \rightarrow Ce(O_2)OH + H_2O + OH^$ or  $2Ce(OH)_3 + 2HO_2^- \rightarrow Ce_2(O_2)_2O + 3H_2O + 2OH^-$
- iii)  $2Ce(O_2)OH + 3H_2O + OH^- \rightarrow 2Ce(OH)_4 + HO_2^$ or  $Ce_2(O_2)_2O + 4H_2O + OH^- \rightarrow 2Ce(OH)_4 + HO_2^-$
- I) Ceria (CeO<sub>2</sub>) plays a special role in heterogeneous catalysis. In the ideal cell of CeO<sub>2</sub>, the structure consists of a **face-centered** cubic unit cell of cations with anions occupying the **tetrahedral** holes. In the structure, each cerium cation is coordinated by **8** nearest-neighbor oxygen anions, while each oxygen anion is coordinated by **4** nearest-neighbor cerium cations. Ceria can also be doped with other metal cations to alter electric conductivity. When cerium cations are replaced with lower oxidation state elements (M<sup>2+</sup>/M<sup>3+</sup>), the lattice oxygen atoms in CeO<sub>2</sub> are **removed**. The ceria crystal usually exhibits a few defects due to the co-existence of Ce<sup>4+</sup> and **Ce<sup>3+</sup>** ions. /.../ Because the metal surfaces are essentially saturated in CO when excess CO is present, the rate-limiting step for the reaction is **2**. /.../ (3 pts)

<b>m)</b> I – NO <sub>x</sub> (NO, NO <sub>2</sub> ); J – O <sub>2</sub> ; K – O; I – Ce <sub>2</sub> O <sub>3</sub> ; M – H <sub>2</sub> .	(3 pts)
<b>n) 5.</b> $2CeO_2 \rightarrow O_{ad} + Ce_2O_3$	(1 pt)
<b>6.</b> $Ce_2O_3 + 0.5O_2 \rightarrow 2CeO_2$	(1 pt)

- 7.  $Ce_2O_3 + H_2O \rightarrow 2CeO_2 + H_2$  (1 pt)
- o) Ce(5,5'-(Cl)<sub>2</sub>-salen)<sub>2</sub> is a stronger oxidizing agent, because methoxy-substituted aromatic rings are more electron-rich, therefore, stabilizing central Ce(IV).
   (1 pt)

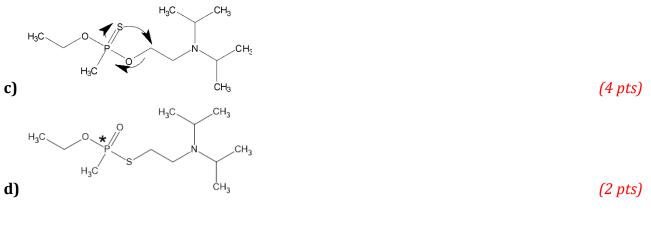
## Problem 5. Poisonous chemicals. Author: Denis Sokol

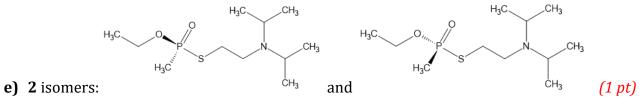


(3 pts)

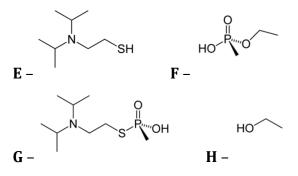
(4 pts)

(12 pts)

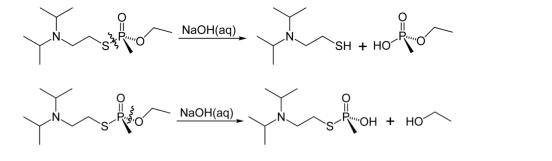




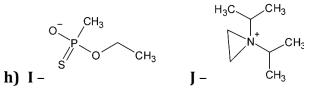
f) Each correct structure gives 2 points – in total 8 points.



Hydrolysis reactions with aqueous sodium hydroxide:



g) G



 $\begin{array}{c}
1 \\
CH_3 \\
1 \\
H_3C \\
H_3C \\
H_3C \\
H_3C \\
CH_31 \\
H_3C \\
CH_31 \\
H_3C \\
CH_32 \\
CH_32$ 

(8 pts)

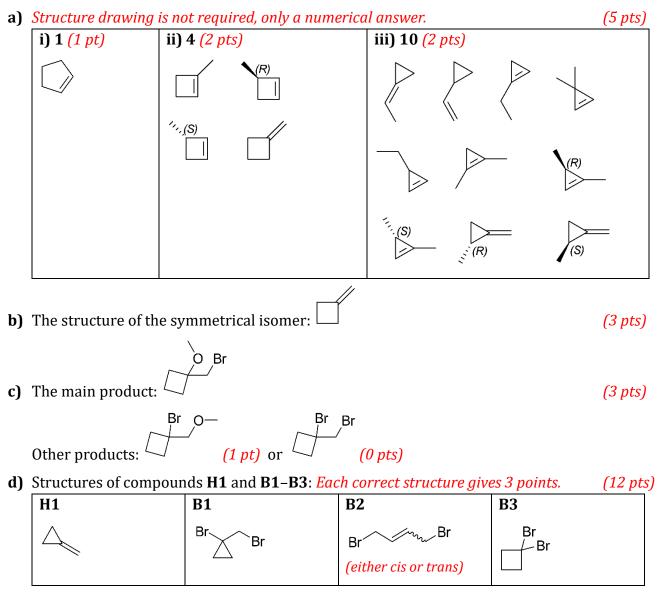
(2 pts)

(8 pts)

(4 pts)

j) Phosphorus	(4 pts)
<b>k) qd</b> , <b>sept</b> , <b>s</b> (should be multiplate in a real spectrum), <b>d</b> , <b>t</b> , <b>d</b> .	(2 pts)
<b>l)</b> LD = $\frac{7 \text{ mg} \cdot 30 \text{ dm}^3}{1000 \text{ dm}^3} = 0.21 \text{ mg} = 0.00021 \text{ g}$	(1 pt)
<b>m)</b> LD = $\frac{0.00021 \text{ g}}{80 \text{ kg}}$ = 2.62 · 10 <sup>-6</sup> g·kg <sup>-1</sup>	(1 pt)
n) 3816 lethal doses.	(1 pt)

# Problem 6. Simple organic chemistry. Author: Nauris Narvaišs

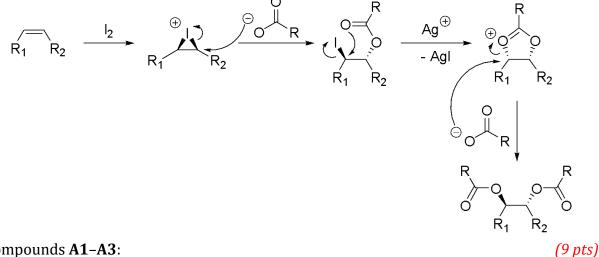


e) Number of possible stereoisomers and products: *1 point for each correct answer.* (4 pts)

	<b>i)</b> (R1 = R2) ≠ H	<b>ii)</b> (R1 ≠ R2) ≠ H
Stereoisomers formed	2	2
Exist in total for product	3	4

f) 1 pt for formation of iodonium, 1 pt for attack on iodonium, 1 pt for cyclization, 1 pt for attack of second carboxylate. If mechanism is just 2  $S_N2$  reactions, then 2 pts total. If relative stereochemistry is incorrect or missing, then 1 pt deduction.

Simplified mechanism:



g) Compounds A1-A3:

A1	A2	A3
HN <sup>CN</sup> Br	HN OEt	
<i>If stereochemistry is incorrect or not specified 2 pts in total.</i>	3 pts	<i>If stereochemistry is incorrect or not specified 2 pts in total.</i>

**h)** 1 pt for bromonium formation, 2 pts for rearrangement, 1 point for elimination. 0.5 pts for  $E_2$ instead of E<sub>1</sub>CB.

