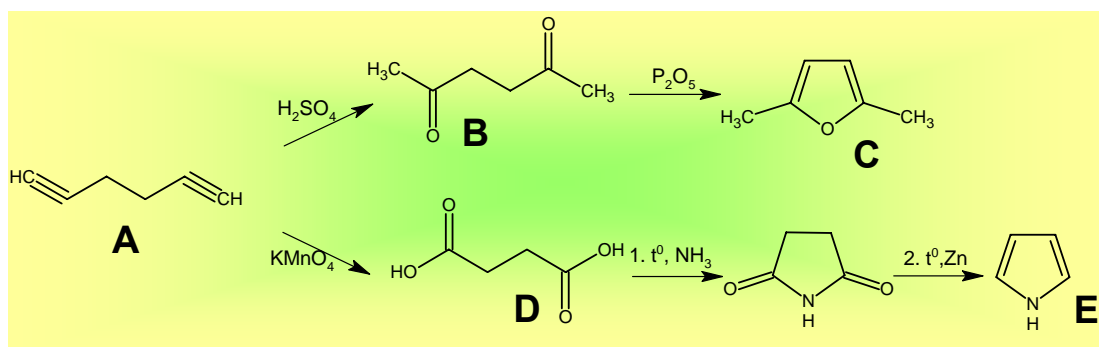


*Devoted to 65th Anniversary of the Victory
of the Soviet Union in the Great Patriotic War*

47th Ukrainian Chemistry Olympiad

Final National Competition

*THEORETICAL EXAM FOR STUDENTS
OF THE 11th FORM*



Ivano-Frankivsk

2010

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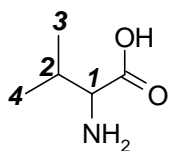
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I round

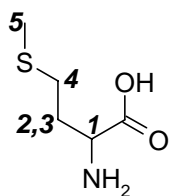
Task 1. Spectra ^1H NMR

^1H NMR spectra of five natural aminoacids are presented below: valine, methionine, isoleucine, lysine, leucine. Find, which spectrum corresponds to each of the aminoacids. Perform as complete assigning as possible and indicate the multiplicity of signals in the spectra. Use the attached form for the answer.

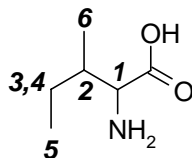
Note: deuterated water was used as a solvent in NMR experiments, and for this reason the spectra do not contain the signals of solvent and the protons, capable to exchange.



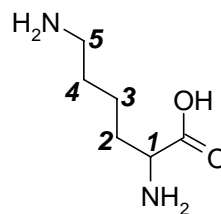
Valine



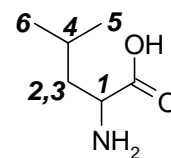
Methionine



Isoleucine

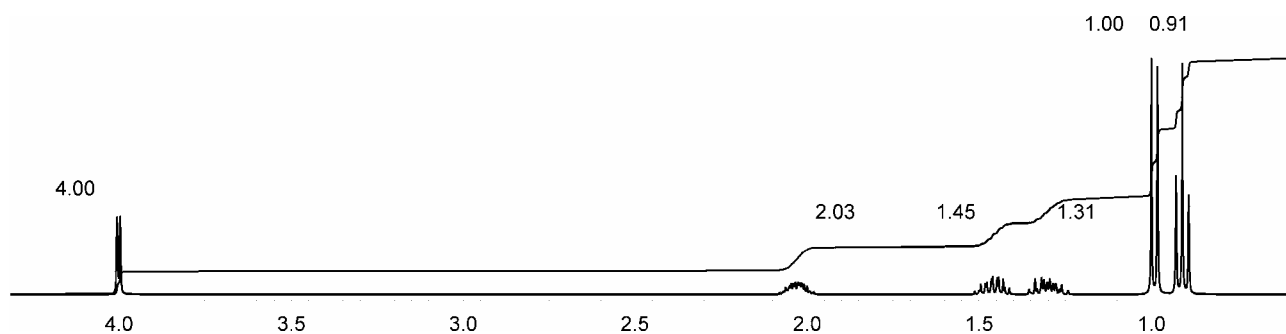


Lysine

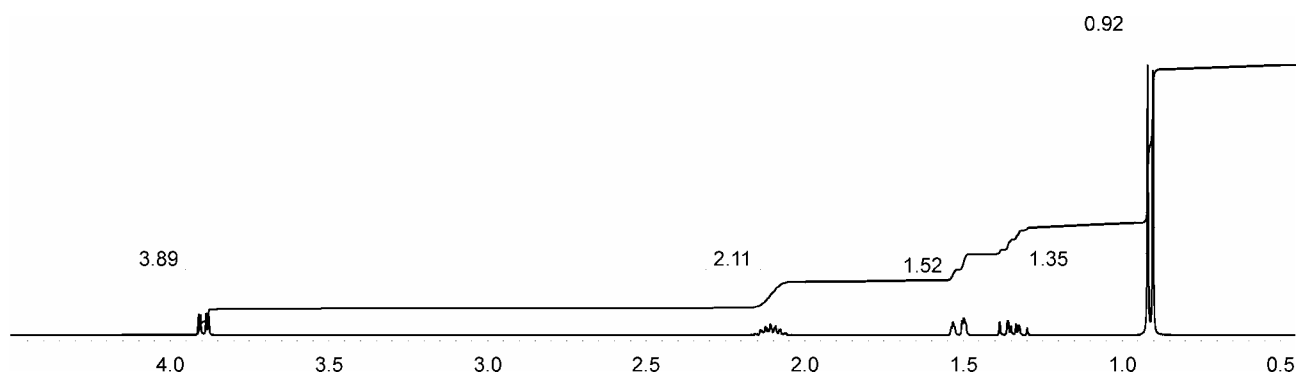


Leucine

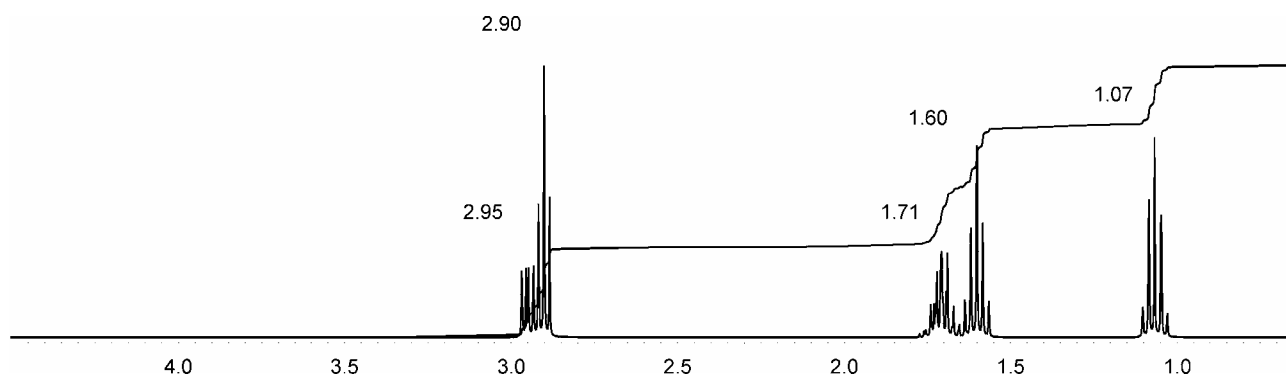
No. 1



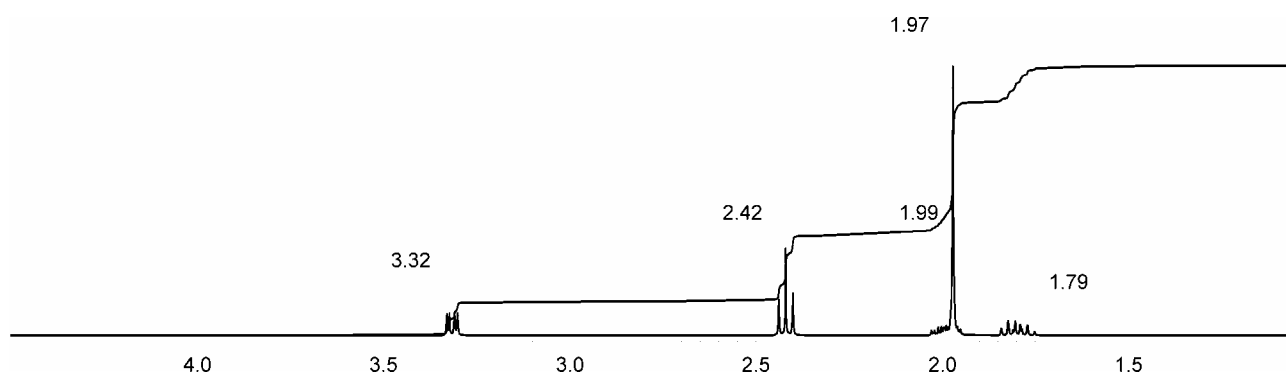
No. 2



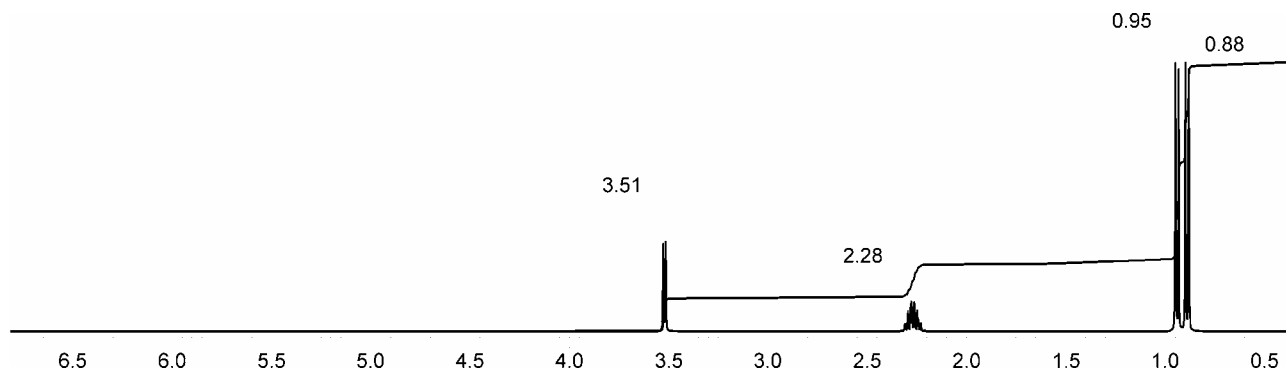
No. 3



No. 4



No. 5

*Form for answers**Spectrum No. 1*

Aminoacid:

Signal	4.00	2.03	1.45	1.31	1.00	0.91
Multiplicity		multiplet				
Number(s) of protons		2				

Spectrum No. 2

Aminoacid:

Signal	3.89	2.11	1.52	1.35	0.92
Multiplicity					
Number(s) of protons					

Spectrum No. 3

Aminoacid:

Signal	2.95	2.90	1.71	1.60	1.07
Multiplicity					
Number(s) of protons					

Spectrum No. 4

Aminoacid:

Signal	3.32	2.42	1.99	1.97	1.79
Multiplicity					
Number(s) of protons					

Spectrum No. 5

Aminoacid:

Signal	3.51	2.28	0.95	0.88
Multiplicity				
Number(s) of protons				

Solution**Spectrum No. 1**

Aminoacid: isoleucine

Signal	4.00	2.03	1.45	1.31	1.00	0.91
Multiplicity	d	m	m	m	d	t
Number(s) of protons	1	2	3(4)	4(3)	6	5

Spectrum No. 2

Aminoacid: leucine

Signal	3.89	2.11	1.52	1.35	0.92
Multiplicity	dd	m	m	m	d
Number(s) of protons	1	4	2(3)	3(2)	5,6

Spectrum No. 3

Aminoacid: lysine

Signal	2.95	2.90	1.71	1.60	1.07
Multiplicity	dd	t	m	quint	quint
Number(s) of protons	1	5	2	4	3

Spectrum No. 4

Aminoacid: methionine

Signal	3.32	2.42	1.99	1.97	1.79
Multiplicity	dd	t	m	s	m
Number(s) of protons	1	4	2(3)	5	3(2)

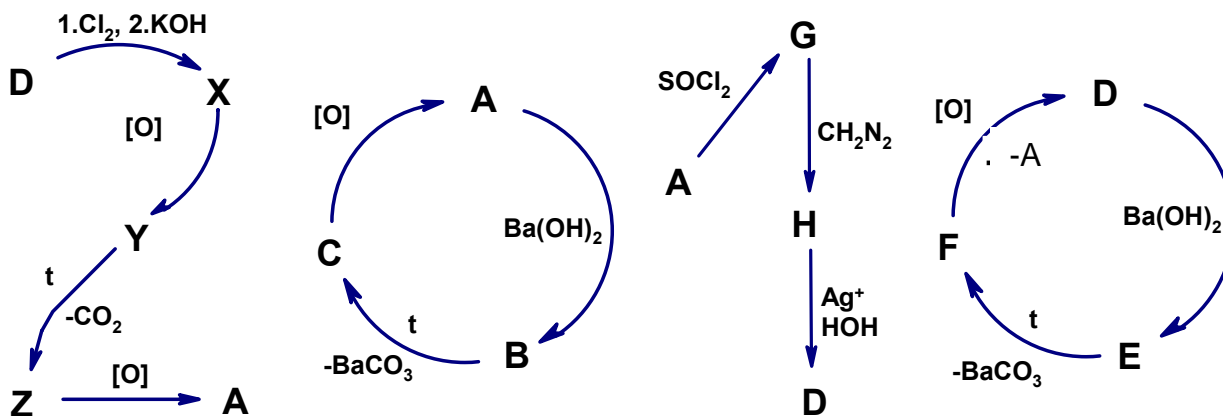
Spectrum No. 5

Aminoacid: valine

Signal	3.51	2.28	0.95	0.88
Multiplicity	d	m	d	d
Number(s) of protons	1	2	3(4)	4(3)

Task 2. Transformation-2010

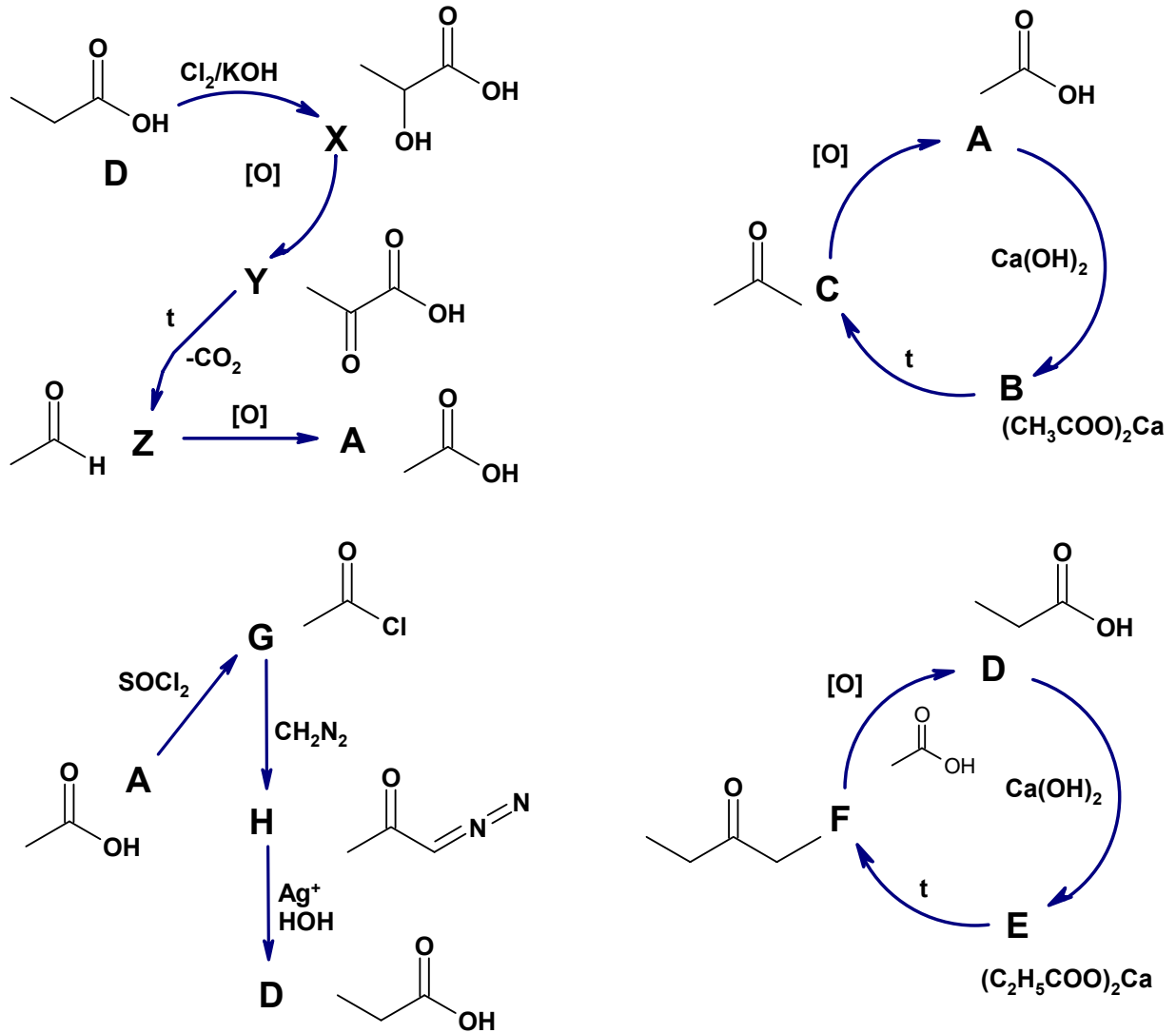
Below find the scheme of transformations of some organic compounds.



1. Find compounds **A-H** and **X, Y, Z**.
2. If the transformations from the first circle of number 2010 are considered, assuming, that all its reactions go on 100%, which portion of compound **A** will remain after five circles of transformations $A \rightarrow B \rightarrow C \rightarrow A$?
3. Write the mechanism of transformation $H \rightarrow D$.
4. From which compound **C** and **F** can be obtained at the same time?
5. Put required oxidizers instead of $[O]$.

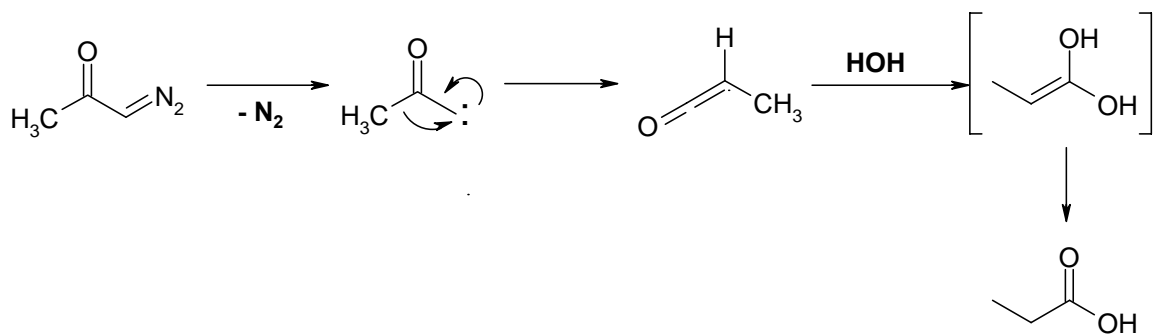
Solution

1. It can be understood from the scheme of transformations, that **A** and **D** are referred to the same class of chemical compounds, have acidic properties (react with hydroxide), and **A** also reacts with $SOCl_2$. It is reasonable to assume that it is carboxylic acid, then **B** is barium salt, which eliminates barium carbonate on heating and is transformed to ketone, and ketone forms this acid again on heating.
2. This fits well for acetone, which at oxidation gives only acetic acid. So:
A – acetic acid, **B** – barium acetate, **C** – acetone. Then **D** is propionic acid, **E** – barium propionate, **F** – diethyl ketone.

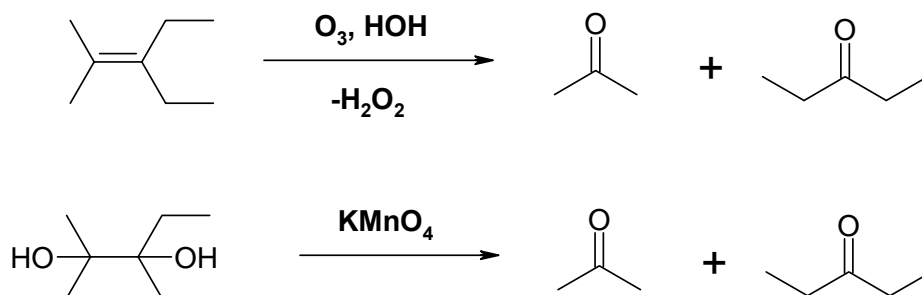


3. Assuming, that all stages go on 100%, in each transformation cycle 1 equivalent of acetic acid is transformed into 0.5 equivalents of acetic acid, so in each cycle the quantity of acid becomes two times lower, so after the fifth cycle only $1/2^5 = 1/32$ portion of **A** remains.

4.



5. C and F can be obtained at the same time by ozonolysis of alkene or diol:

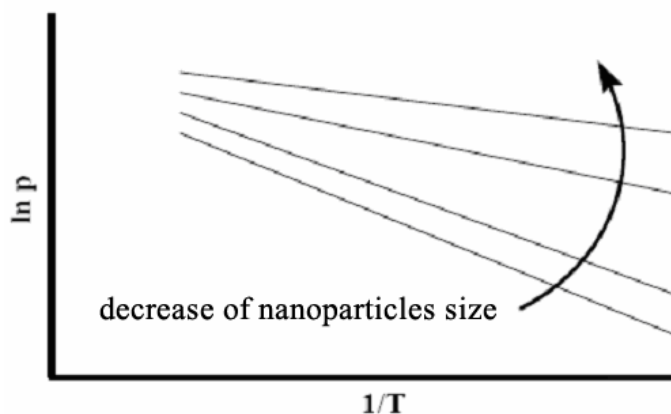


6. For oxidation of ketones into acids such strong oxidizers can be used as nitric acid or acidic solutions of potassium dichromate or permanganate. There is wide choice of mild oxidizers for oxidation of aldehyde into acid, for example, ammonium solution of silver hydroxide. And copper oxide can be used for oxidation of hydroxyacid into ketoacid.

Task 3. Hydride

Hydrogen is considered as promising fuel. One of the lacks of such fuel is the problem of its storage and transportation. The most simple solution is to use reversible process of some metal hydride formation for this purpose.

For the reaction $\text{Me}(\text{solid}) + \text{H}_2(\text{g}) = \text{MeH}_2(\text{solid})$ it can be obtained from Van't Hoff equation, that $\ln p_{\text{H}_2} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$. It is problematic to find metal, which has solid stable hydride that decomposes, for example, at 200 °C, but the situation can be improved with the help of nanotechnology. The figure shows schematic dependency of $\ln p_{\text{H}_2}$ on $\frac{1}{T}$ for four samples with different nanoparticles size.



For reference: entropy change ΔS in the process of isothermal compression of ideal gas from the volume $V_{starting}$ to V_{final} is calculated as $\Delta S = R \ln \frac{V_{final}}{V_{starting}}$.

1. Discuss the advantages and lacks of hydrogen as fuel.
2. Write the expression for equilibrium constant of mentioned reaction and obtain the equation for p_{H_2} , shown in the task, explain the meaning of abbreviations.
3. Estimate the value of enthalpy for mentioned reaction, at which the hydride decomposes (hydrogen pressure over it will be equal to atmospheric) at 200 °C. Assume that entropy of this reaction is entirely determined by hydrogen's compression to the volume of metal hydride (take its density to be equal to 1.45 g/cm³, as for MgH₂). Is this value fall into technologically acceptable range of "hydrogen bonding energy" 10–60 kJ/mol?
4. What is the view of the member appearing in the right part of the equation, provided in the task, corrected for nanoparticles chemistry description? Explain the answer and write this equation.
5. What, in your opinion, is chemical nature of this member? Explain the answer.
6. Which other scientific achievements of Van't Hoff can you remind?

Solution

1. Hydrogen is ecologically pure, non-poisonous fuel, which in the case of available energy can be obtained from the compound, which is very widespread on the Earth – water. Its main important lacks are the following: volatility, due to which hydrogen can form explosive gas (explosive mixture with air or oxygen) in wide concentration range, low boiling point (20 K), low density of liquid hydrogen and its fluidity. Complex problems of hydrogen storage and transporting are only technological. At high temperatures (working temperatures for internal combustion engine) the solubility of hydrogen in metals may become a problem. It is also worth to remember that greenhouse effect is caused, among other reasons, by water vapor.

2. Equilibrium constant $K = \frac{1}{p_{\text{H}_2}}$. After its combining with integral form of

Van't Hoff's equation $\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$, we get the formula from the task. In

it ΔH and ΔS – are enthalpy and entropy of reaction of hydride formation, R is universal gas constant, T is thermodynamic temperature.

3. Calculate the entropy of hydrogen compression at 200°C. For 1 mole of gas

starting volume is $22.4 \cdot \frac{473}{273} = 38.8$ (l), and final volume is $1.45 \cdot 26 = 37.7$

(cm³ or ml). So, $\frac{V_{\text{final}}}{V_{\text{starting}}} = \frac{37.7}{38.8 \cdot 1000} = 9.72 \cdot 10^{-4}$ and $\Delta S = 8.314 \cdot \ln(9.72 \cdot 10^{-4}) = -57.7$

(J/K·mol). At atmospheric pressure $p_{\text{H}_2} = 1$ atm we get $\frac{\Delta H}{RT} - \frac{\Delta S}{R} = 0$ and

$\Delta H = T\Delta S$, from which $\Delta H = -27.3$ kJ/mol, which falls into technologically-acceptable range.

4. Linear dependency $\ln p_{\text{H}_2} - \frac{1}{T}$ is not broken, that is why the member may

contain only temperature related members like a and/or $\frac{a}{T}$. In the first case the

lines should be parallel, in the second they should go through the same point on vertical axis. As it can be seen from the graph, the second case is real one.

Since ΔH and tilting angle are negative, and particle size reduction r leads to decrease of line's tilt angle, the member should be positive and grow with

decrease of r . (By the way, physical arguments allow to specify: it also should be proportional to total area of nanoparticles' surface, which, in turn, is

proportional to $\frac{V_M}{r}$, where V_M is molar volume of solid, as well as surface

tension coefficient, or, more exactly, its change in the reaction). So, the following form of corrected equation may be determined from the graph:

$$\ln p_{\text{H}_2} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} + \frac{a}{r^n T}, \text{ where } a > 0, n > 0.$$

5. In fact, this member corrects for process enthalpy. This takes place due to additional energy of surface tension, which grows with decrease of the nanoparticle's size.
6. Isotonic Van't Hoff's coefficient in the formulas for colligative properties of the solutions (osmotic pressure, cryoscopy, etc.). The first Noble's Prize in chemistry in 1901. Stereochemistry: the principles of chirality, as well as achievements in physical chemistry (kinetics, equilibrium, diluted solutions).

Task 4. Metal for Ford

"If there was no metal X, there would be no my car"

Henry Ford



Once after racing in England in 1905 Henry Ford, future "motor king", was looking on crashed French car. He was interested in the rests of engine, which was made from rather firm, viscous and light material. In Ford's laboratory it was found soon, that this material was steel with some additive of metal X. After additional studied Henry Ford put this new steel into production, which allowed him to make his cars more light, increase their firmness and improve the productivity, which allowed to attract many consumers.

The chemistry of compounds of metal **X** is very interesting. Electrolysis of the solution of 1.092 g of oxide of this metal **A** in hydrochloric acid produces green gas on anode, and the same quantity of violet chloride **B**, which is chloride of metal **X**, with mass 1.890 g forms on cathode. Reduction of compound **B** with magnesium in the atmosphere of carbon monoxide (under 200 atm pressure) leads to yellow complex compound **C** (weight portion of magnesium is 5.195%, does not contain chlorine) with mass 2.772 g. At treatment of compound **C** by the solution of

hydrochloric acid, hydrogen and green compound **D** are formed (2.628 g). Its heating in inert atmosphere gives metal **X**. At low temperatures compound **D** dimerizes.

1. Find metal **X**, write the equations of reactions, which go at its interaction with the mixture of HNO₃ and HF. Why does not this reaction go at the presence of only HNO₃?
2. Determine compounds **A-D**.
3. Write the reactions of mentioned transformations.
4. Write structural formula of complex **C**.
5. Write reactions of interaction of liquid **D**: a) with hydrogen; b) with oxygen.
6. How **X** is obtained from oxide **A** in the industry?
7. Explain the reason of dimerization of **D**.

Solution

1-3. There are sufficient data about electrolysis of the solution of oxide **A** to determine unknown metal. Yellowish-green gas is chlorine. Since the quantity of chlorine is the same as of chloride **B**, it can be concluded that oxidation state of metal in chloride is lower on 2 than in oxide:



$$\text{Molar mass of oxide } M(\text{A}) = 2x + 16 \cdot n,$$

$$\text{molar mass of chloride } M(\text{B}) = x + 35,5 \cdot (n-2), \text{ where } x \text{ is atomic mass of metal,}$$

$$\frac{1,092}{1,89} = \frac{2x + 16n}{2(x + 35,5(n-2))} \Rightarrow x = 29,63n - 97,16$$

n	x, g/mol	Me
4	21.3	
5	51.0	V
6	80.6	
7	108	Ag ???
8	140	

So, **A** – V₂O₅, **B** – VCl₃.

Determined mass fraction of V in complex **C**, taking into account that all vanadium from chloride transformed to **C**:

$$w(\text{V}) = \frac{m(\text{V})}{m(\text{C})} \cdot 100\% = \frac{m(\text{B}) \cdot \frac{M(\text{V})}{M(\text{VCl}_3)}}{m(\text{C})} \cdot 100\% = \frac{1,89 \cdot \frac{51}{157,5}}{2,772} \cdot 100\% = 22,078\%$$

Since the complex does not contain chlorine, its ligands are CO. Determined to composition of complex **C**:

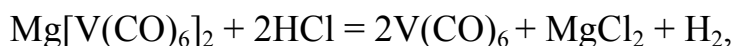
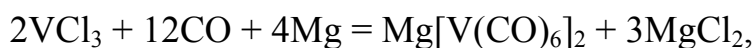
$$n(\text{Mg}) : n(\text{V}) : n(\text{CO}) = \frac{5,195}{24} : \frac{22,078}{51} : \frac{72,727}{28} = 0,216 : 0,432 : 2,597 = 1 : 2 : 12$$

So, **C** is Mg[V(CO)₆]₂. In this complex vanadium has oxidation state –1.

The quantity of compound **C** $n(\text{C}) = \frac{2,772}{462} = 0,006$ mol. Mass of compound **D** is

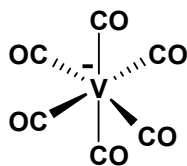
lower than mass of compound **C** on the mass of magnesium, which was in **C**. So, from 1 mole of Mg[V(CO)₆]₂ 1 mole of „V₂(CO)₁₂” forms, or 2 moles of V(CO)₆. Thus, **D** is V(CO)₆.

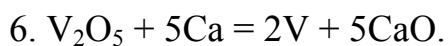
Equations of reactions:



The surface of vanadium is covered by dense passivating film, and due to this vanadium is stable in aggressive media. The role of HF is to dissolve this film.

4.





7. In $V(CO)_6$ vanadium contains 17 electrons, formation of 18-electron shell occurs at dimerization.

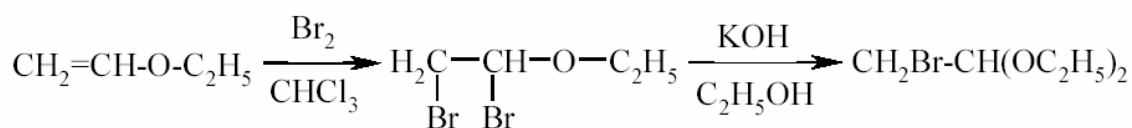
Task 5. Chain

Compound **A** is obtained from vinyl ethyl ether in two stages: first it is treated by bromine without heating, and then – by alcohol solution of potassium hydroxide. At the presence of sulfuric acid **A** vigorously reacts with methylphenyl ether without heating. The product of reaction **B** at heating with alcohol solution of alkaline forms compound **C**, and at heating in the solvent with high boiling point under reflux, for example, in pentanol-1, it forms compound **D**. In the latter case water is formed as by-product, and vapor temperature falls down due to formation of triple azeotrope. At its reaction with hydrogen bromide only one product can form. The solubility and other physical properties of **C** and **D** are significantly different, but their mass-spectra contain the ions of the same mass. Only one compound can form at its interaction with hydrogen bromide. The solubility and other physical properties of **C** and **D** are significantly different, but their mass-spectra contain molecular ions of the same mass. Only one product can form at its interaction with hydrogen bromide. The solubility and other physical properties of **C** and **D** are significantly different, but their mass-spectra contain molecular ions of the same mass.

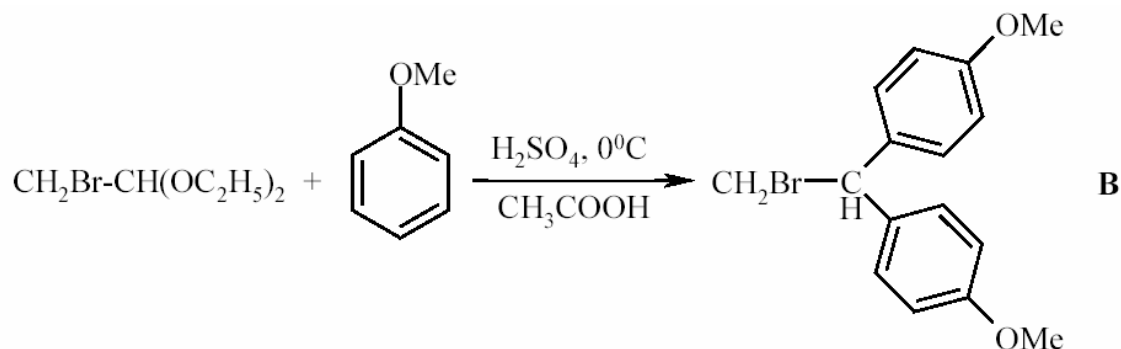
1. Determine the structure of compounds **A** – **D**. Write equations of reactions.

Solution

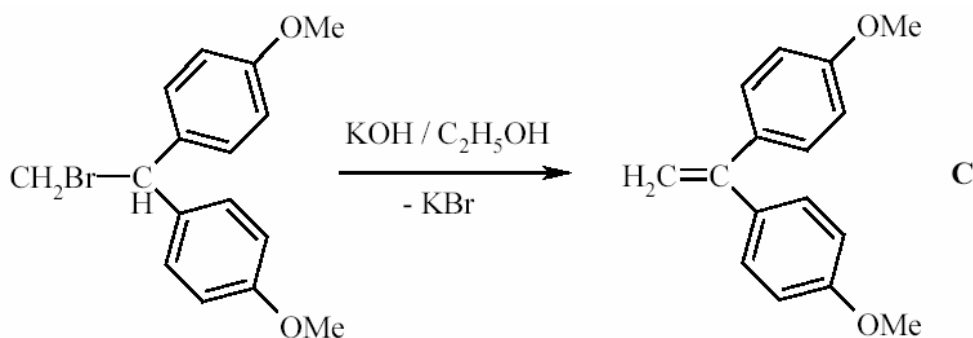
Compound **A** is diethylacetal of bromobenzaldehyde. The scheme of its preparation:



At the presence of sulfuric acid it can react with phenyl ethers, participating in electrophilic substitution reaction:

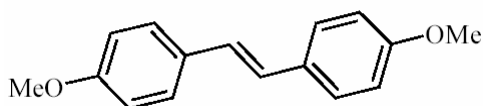


Obtained 1,1-disubstituted-2-bromoethane at interaction with alcohol solution of alkaline undergoes normal dehydrobromination, forming 1,1-di(*p*-anisyl)ethylene:



Hydrogen bromide elimination also occurs at reflux of B in pentanol. It immediately reacts with alcohol, forming corresponding bromoalkane and water, which results in formation of triple azeotrope pentanol-bromopentane-water. Since molar masses of C and D are the same, but their properties are different, C and D are isomers.

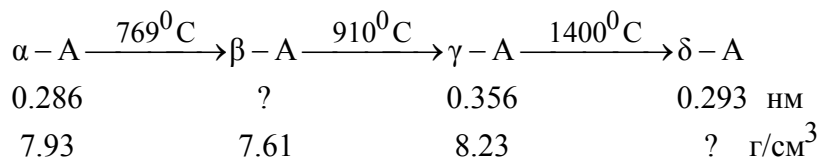
D is trans-isomer of 1,2-di(*p*-anisyl)ethylene (dimethoxystylbene):



The examples of reaction of stylobenes synthesis:

Task 6. Modifications of metal

Metal **A** forms several modifications. Transition between them may be shown in the form of the scheme below, where unit cell parameters and densities are indicated:



At heating of **A** in the flow of gas **B** at 150°C and 15 atm yellow volatile liquid **C** forms. **C** is not soluble in water and decomposes at 300°C. Chemical properties of **C** can be illustrated by the following reactions:



1. Determine metal **A** and unknown compounds, marked as "?", if α , β , δ are modifications with body-centered cubic cell (one atom in the center of cube and eight - in the corners). Which cell does γ -modification possess?
2. Find all compounds, if it is known that **E** and **D** are salts, and molecule **B**, in a contrast to isoelectronic molecule **G**₂, has dipole moment $\mu = 0.04 \cdot 10^{-29} \text{ C} \cdot \text{m}$ ($q_e = 1.602 \cdot 10^{-19} \text{ C}$).
3. Describe the structure of molecule **B** by the method of molecular orbits and determine the charges on atoms, if the distance between nuclei is 1.128 Å.
4. What is the structure of the molecule **C** (indicate hybridization and oxidation states of all atoms, electronic configuration and the quantity of unpaired electrons of central atom, geometric shape of the molecule)? What is dipole moment of molecule **C**?

Solution

The mass of unit cell for body-centered cubic cell is $2m_A^0$, cell volume is a^3 ,

$$\text{from this } 2m_A^0 = \rho \cdot a^3, \quad M_A = \frac{N_a \cdot \rho \cdot a^3}{2} = \frac{6.02 \cdot 10^{23} \cdot 7.93 \cdot (0.286 \cdot 10^{-7})^3}{2} = 55.8 \text{ (g/mol)},$$

which corresponds to Fe.

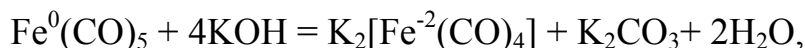
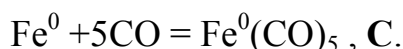
$$a_{\beta-A} = \sqrt[3]{\frac{2M_{\text{Fe}}}{N_{\text{a}} \cdot \rho}} = \sqrt[3]{\frac{2 \cdot 55.8}{6.02 \cdot 10^{23} \cdot 7.61}} = 0.290 \text{ nm},$$

$$\rho_{\delta-A} = \frac{2M_{\text{Fe}}}{N_{\text{a}} \cdot a^3} = \frac{2 \cdot 55.8}{6.02 \cdot 10^{23} \cdot (0.293 \cdot 10^{-7})^3} = 7.37 \text{ g/cm}^3.$$

$$n = \frac{N_{\text{a}} \cdot \rho \cdot a^3}{M_{\text{A}}} = \frac{6.02 \cdot 10^{23} \cdot 8.23 \cdot (0.356 \cdot 10^{-7})^3}{55.8} = 4,$$

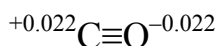
which corresponds to face-centered cubic cell (one atom in the centers of each side of cube and eight - in its corners).

It is easy to understand that **B** is CO, and **G**₂ is N₂.



Electronic structure of CO molecule: $\sigma_{\text{O}}^2 \sigma_{\text{S}}^2 \pi_{\text{X,Y}}^4 \sigma_{\text{C}}^2$ (one σ - and two π -bonds,

two non-bonding orbitals). Charges on atoms $\frac{0.04 \cdot 10^{-29}}{1.128 \cdot 10^{-10} \cdot 1.602 \cdot 10^{-19}} = 0.022$,



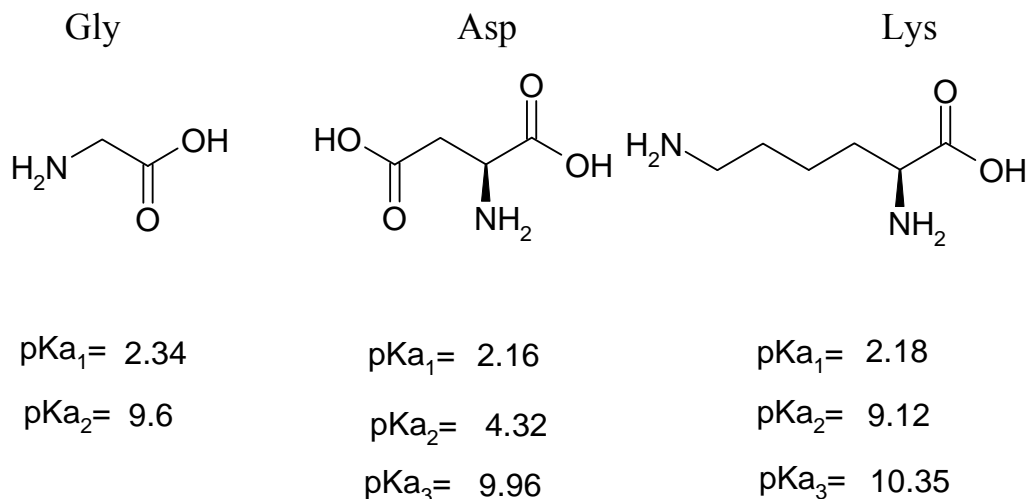
$\text{Fe}^0(\text{C}^{+2} \equiv \text{O}^{-2})_5$, dsp^3 -hybridization of Fe atom, sp -hybridization for C and O, trigonal bipyramide. $\text{Fe}^0 - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^0 4p^0$, no unpaired electrons, dipole moment $\mu=0$.

Task 7. Aminoacids

Aminoacids (AA) are components of proteins, which play critical role for construction of living organisms. Determination of the sequence of aminoacids in natural proteins requires such methods of aminoacids separation, which provide for suitable and efficient way for AA isolation in pure state. Electrophoresis has been one of the most suitable methods, despite of it was the first one. This method is based on the fact that total charge of AA molecule, mobility of AA molecules in respect to stationery electrodes depend on pH of the medium.

One of the basic characteristics of AA molecule in this method is so-called isoelectric point (IP), that is the value of pH, at which AA molecule has zero overall charge.

The representatives of the most wide-spread aminoacids, which can be found in proteins, are glycine (Gly), aspartic acid (Asp), lysine (Lys):

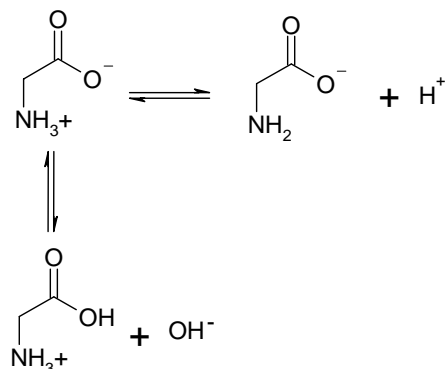


In solutions AA exist predominantly as zwitterions (bipolar compounds).

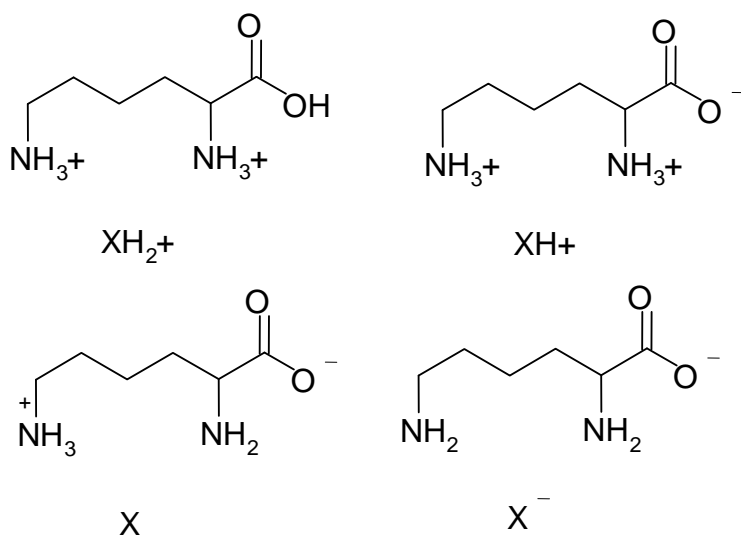
1. Draw the scheme of equilibria, which exist in glycine solution.
2. Draw the structures of lysine forms, which exist in solutions, and write the equations for corresponding equilibrium constants.
3. What is pH of 0.01M solution of aspartic acid?
4. Estimate IP values for each of AA. Make respective conclusions and propose the method for separation of these AA by electrophoresis.
5. How many possible tripeptides can be obtained from these three AAs?
6. Heating of glycine leads to its polycondensation. Average molar mass of obtained polymer on the data of analysis is about 2000 g/mol. Calculate the quantity of glycine molecules, required for obtaining of 1 molecule of this polymer.

Solution

1. There is equilibrium between three forms of glycine in the solution. The content of each form varies according to the change of pH of the medium. Neutral molecule of AA predominantly exists in the solution as zwitter-ion.



2. Equilibrium between four forms is set in lysine solution:

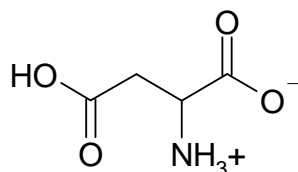


It is worth to draw attention to distribution of charges on aminogroups of Lys depending on protonation level. Zwitter-ion, in which ϵ -aminogroup has positive charge, will be dominating from in the solution ("Protonation steps for Lys at the ϵ - and α -amino groups are not completely separated. ...Lys with the deprotonated α -amino and protonated ϵ -amino groups predominates over Lys with the protonated α -amino and deprotonated ϵ -amino groups", O. Yamauchi and A. Odani, Pure & Appl. Chem., V. 68, No. 2, pp. 469-496, 1996).

The expression for equilibrium constants:

$$K_1 = [\text{XH}^+] [\text{H}^+] / [\text{XH}_2^+], K_2 = [\text{X}] [\text{H}^+] / [\text{XH}^+], K_3 = [\text{X}^-] [\text{H}^+] / [\text{X}].$$

3. The following zwitter-ion will be dominating form in the solution of aspartic acid:



Acidity of the solution is caused by dissociation of γ -carboxygroup (α -aminogroup and carboxygroup, connected with it, are deactivated because of formation of stable zwitter-ionic system due to ion-ion interaction and formation of H-bonds system). Thus, $[H^+] \approx (K_2 \cdot c)^{0.5}$, $pH = -\lg[H^+] = 3.16$.

4. For bifunctional aminoacids, such as glycine, $IP = (pK_1 + pK_2)/2 = 5.97$. Obtaining of this formula is based in the equity of concentrations of protonated and deprotonated forms of Gly.

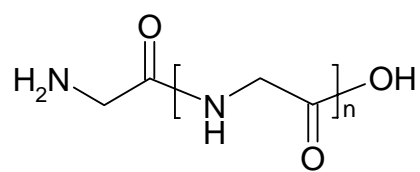
IP for trifunctional aminoacids is almost equal to the expression, similar to the one for Gly, however it should be mentioned that IP for Asp is in acidic medium, which is explained by zwitter-ion content increase at H^+ ions concentration growth, and for Asp $IP \approx (pK_1 + pK_2)/2 = 3.24$.

IP for lysine is in alkaline solution. The existence of terminal aminogroup causes protonation of Lys molecule, which provides some total positive charge to the molecule. Positive charge should be deactivated in order to get electro-neutral molecule. This takes place in the media with high pH, for $IP \approx (pK_2 + pK_3)/2 = 9.74$.

So, for separation of the mixture of these aminoacids, certain pH should be created (optimal value is 5.97), and put two electrodes in the solution. At this pH value Asp molecules will predominantly move to positively charges electrode, and Lys molecules will move to another electrode. Gly molecules will not move to any of the electrodes. This is the basis of one of AA separation methods. Relative speeds of AA molecules movement will also be different.

5. $27 = 3^3$

6. The molecule which formed has the structure



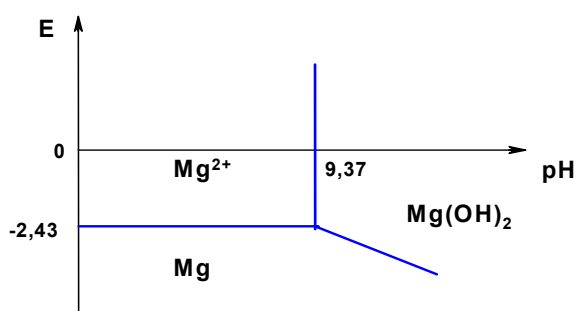
It is easy to show that $n = 33$. Approximately 34 Gly molecules are required for obtaining of 1 molecule of this polymer.

II round

Task 1. Pourbaix diagram

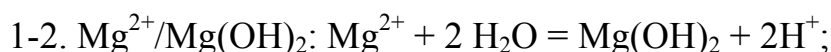
Pourbaix diagram shows the dependency of redox-potential (E) on pH of the solution. Pourbaix diagrams are very convenient for demonstration of thermodynamically stable forms of ions or molecules at certain pH and E at certain temperature.

Below you can find Pourbaix diagram for magnesium (T = 298K), concentration of Mg^{2+} ions is 0.02 mol/l.



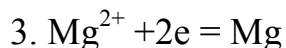
1. Write equations of processes, which take place on three borders.
2. Why the potential of Mg^{2+}/Mg pair does not depend on pH, while the potential of $\text{Mg}(\text{OH})_2/\text{Mg}$ depends?
3. Find standard potential of Mg^{2+}/Mg pair (T = 298K).
4. Calculate Solubility Product for $\text{Mg}(\text{OH})_2$ (T=298K).
5. Find the potential of $\text{Mg}(\text{OH})_2/\text{Mg}$ border at pH=12.
6. Will Mg be subjected to corrosion at potential E = 0 and pH = 13?

Solution



Mg^{2+}/Mg : $\text{Mg}^{2+} + 2e = \text{Mg}$ (H^+ ions do not participate in the process, that is why E does not depend on pH).

$\text{Mg}(\text{OH})_2/\text{Mg}$: $\text{Mg}(\text{OH})_2 + 2\text{H}^+ + 2e = \text{Mg} + 2 \text{H}_2\text{O}$ (H^+ participate in the process, E depends on pH).



Write Nernst equation:

$$E_{\text{Mg}^{2+}/\text{Mg}} = E^0_{\text{Mg}^{2+}/\text{Mg}} + \frac{0.059}{2} \lg C_{\text{Mg}^{2+}} \Rightarrow E^0_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}} - \frac{0.059}{2} \lg C_{\text{Mg}^{2+}}$$

$$E^0_{\text{Mg}^{2+}/\text{Mg}} = -2.43 - \frac{0.059}{2} \lg 0.02 = -2.38 \text{ (V)}.$$

4. $\text{Mg}(\text{OH})_2 / \text{Mg}^{2+}$ exists at $\text{pH}=9.37$. Dissolving of hydroxide occurs below this value.

$$\text{SP}(\text{Mg}(\text{OH})_2) = [\text{Mg}^{2+}] \cdot [\text{OH}^-]^2 = [\text{Mg}^{2+}] \cdot \left(\frac{K_w}{[\text{H}^+]} \right)^2 = 2 \cdot 10^{-2} \cdot \left(\frac{10^{-14}}{10^{-9.37}} \right)^2 = 1.1 \cdot 10^{-11}$$

5. $\text{Mg}(\text{OH})_2 + 2\text{H}^+ + 2\text{e} = \text{Mg} + 2\text{H}_2\text{O}$.

According to Nernst equation,

$$\begin{aligned} E &= E^0_{\text{Mg}(\text{OH})_2/\text{Mg}} + \frac{0.059}{2} \cdot \lg [\text{H}^+]^2 = E^0_{\text{Mg}(\text{OH})_2/\text{Mg}} + 0.059 \cdot \lg [\text{H}^+] = \\ &= E^0_{\text{Mg}(\text{OH})_2/\text{Mg}} - 0.059 \cdot \text{pH} \end{aligned}$$

At pH increase on 1, potential decreases on 0.059 V, then, comparing with the value of potential at $\text{pH}=9.37$, for $\text{pH} = 12$ we get:

$$E = -2.43 - 0.059 \cdot (12 - 9.37) = -2.59 \text{ (V)}.$$

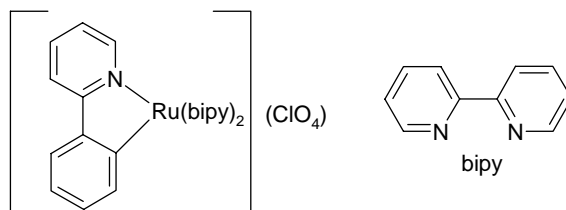
6. At $E=0$, $\text{pH}=13$ metal is covered by hydroxide and is passivated. Corrosion does not take place.

Task 2. Catalysis

Reaction of compound **A**, which contains Ru(II), with hydrogen peroxide occurs at the presence of catalyst **K** and results in formation of compound **B**, which contains Ru(III). The following dependency of concentration of **A** on time was found in one of the experiments:

t, s	10	30	60	120
[A], M	0.170	0.124	0.077	0.029

- Determine reaction order on **A**. Calculate rate constant and concentration of **A** at $t = 0$.
- Compound **A** has the formula, shown below:



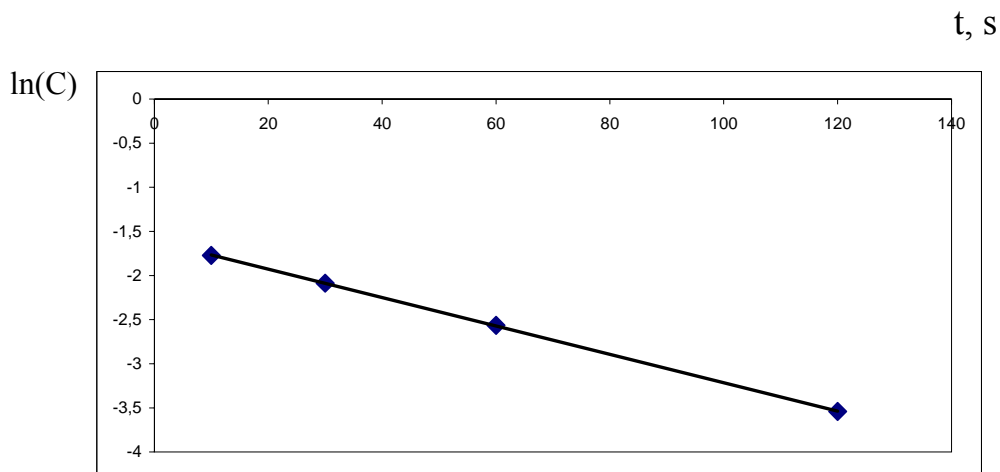
To which class of chemical compounds can **A** be referred? Write equations of reaction, mentioned in the task, and propose formula of **B**.

- Compound **A** can exist in the form of two isomers and in the solution can slowly isomerize into compound **A'**. Equilibrium mixture contains **A** and **A'** in 1:1 ratio. Explain the difference between **A** and **A'**.
- If the solution of **A**, which was stored during several months, is used for reaction with H₂O₂, reaction rate (at the presence of catalyst **K**) decreases in 1.7 times compared to fresh solution (other conditions are the same). Determine rate constant for reaction of **A'** with H₂O₂ (k').
- Propose the most probable reason for the difference between k and k', if catalyst **K** is natural enzyme - horse radish peroxidase.

Solution

1. Check, how kinetic equations for the reactions of different orders fit experimental data. For the first order: $c = c_0 e^{-kt}$; $\ln c = \ln c_0 - kt$.

t, s	10	30	60	120
ln[A]	-1.772	-2.087	-2.564	-3.540



Linear dependency of $\ln[A]$ on t was obtained, so reaction has the first order. Check shows that the equations for other orders do not fit experimental data.

The constant is equal to tangent of slope angle of obtained line:

$$k = \operatorname{tg}\alpha = (3.540 - 1.772)/(120 - 10) = 0.016 \text{ s}^{-1}.$$

It is not necessary to build graph for solution of this task, it is sufficient to calculate constant for different pairs of experimental points and to be sure that obtained values are the same.

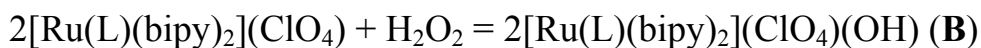
Calculate initial concentration.

$\ln c_0 = \ln c + kt$, for example, calculation using the first point gives:

$$\ln c_0 = -1.772 + 0.016 \cdot 10 = -1.612; c_0 = 0.2 \text{ M}.$$

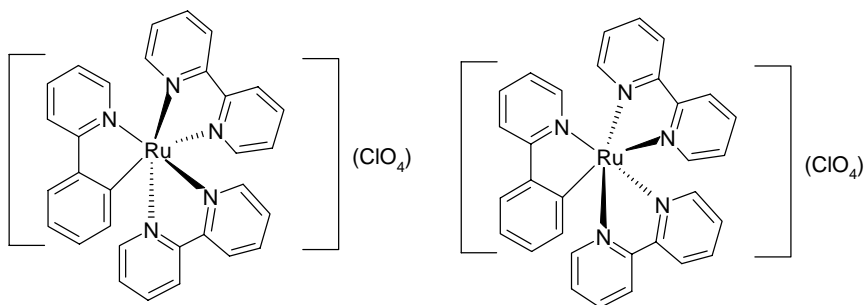
2. **A** contains Ru–C bond and is referred to metalloorganic compounds.

Equations of reactions:



where LH is 2-phenylpyridine

3. **A** and **A'** are optical isomers:



The bond marked as \longleftarrow is directed to the reader, and the bond \longleftarrow is directed from the reader. It is clear that it is impossible to make conclusion which isomer is **A** and which is **A'** from the text of the task.

$$4. v_{\text{initial}} = k[A]_{\text{initial}},$$

$$v_{\text{mixture}} = k[A]_{\text{equilibrium}} + k'[A']_{\text{equilibrium}} = [A]_{\text{equilibrium}}(k + k') = 0.5[A]_{\text{initial}}(k + k'),$$

$$v_{\text{initial}} / v_{\text{mixture}} = (k[A]_{\text{initial}}) / (0.5[A]_{\text{initial}}(k + k')) = 2k / (k + k') = 1.7,$$

$$2k = 1.7k + 1.7k',$$

$$2k - 1.7k = 1.7k',$$

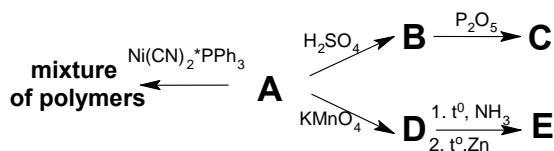
$$k' = 0.176k,$$

$$k' = 0.0028 \text{ s}^{-1}.$$

5. Catalytic center is probably asymmetric (chiral) and reacts with different optical isomers of **A** in different ways.

Task 3. Polymerization

Hydrocarbon **A** (C_6H_6) is easily transformed into aromatic compounds **C** ($\text{C}_6\text{H}_8\text{O}$) and **E** ($\text{C}_4\text{H}_5\text{N}$) according to the following scheme. At the presence of the complex of nickel(II) cyanide with triphenylphosphine hydrocarbon **A** forms the mixture of polymers, consisting of elementary units of two types. It is interesting that the polymer, obtained from the homologue of compound **A**, which contains 8 carbon atoms, is built from three types of elementary units, and in this case trimer is also formed along with it.



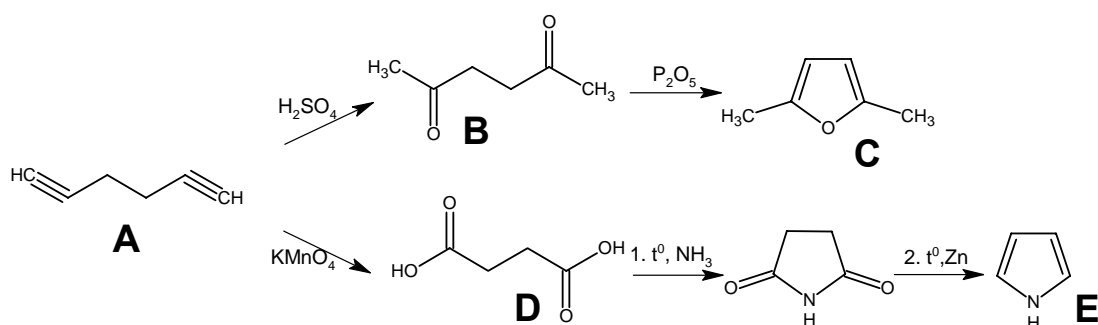
(H_2SO_4 – water solution, KMnO_4 – acidified water solution at heating)

1. Determine compounds **A** - **E**.
2. Draw the mechanism of polymer formation. Will polymerization occur at addition of ammoniac to reaction mixture? Provide some grounds for the answer.

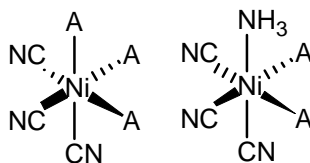
3. Show the structures of elementary units, which are in the polymers, obtained from hydrocarbon **A**.
4. Explain the differences in the structure of polymer, obtained from the homologue, containing 8 carbon atoms, as well as trimer formation.

Solution

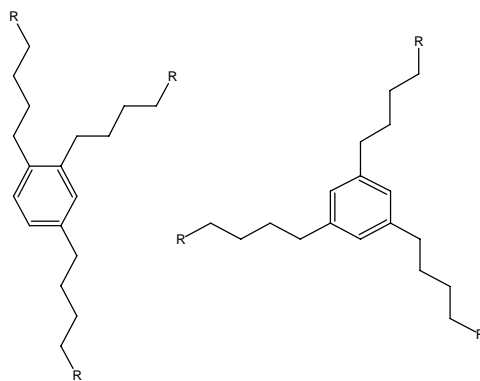
1.



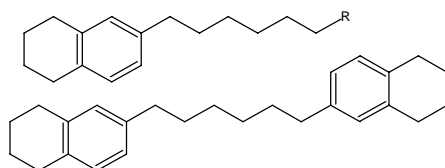
2. At polymerization at the presence of $\text{Ni}(\text{CN})_2 \cdot \text{PPh}_3$ transition complex forms, in which Ni has octahedral structure; CN^- and PPh_3 , as well as the molecules of **A**, coordinated to Ni due to π -bonds, are located in the vertices of the polyhedron. Lability of the complex favors to formation of the fragment of polymers, containing benzene ring, from the fragments, containing triple bonds. At addition of ammoniac one of the places in coordination sphere is taken by NH_3 , that is why benzene ring does not form.



3. Polymers, obtained from hydrocarbon **A** contain 1,3,5- and 1,3,4-substituted benzene rings, in this case each molecule of **A** takes part in formation of two benzene rings, so each ring forms from three molecules of **A**.

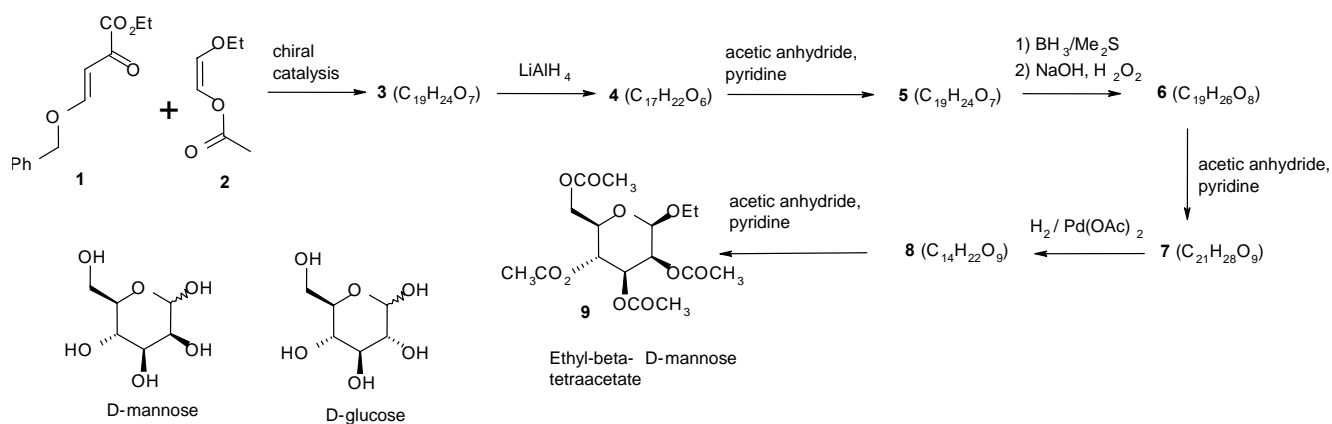


4. At polymer formation from corresponding homologue, except the units, containing 1,3,5-substituted and 1,3,4-substituted benzene rings, the units containing tetrahydronaphtalene system also form. Such system formed at reaction of not three, but two molecules of homologue. Formation of trimer is also explained by the same reaction. In the case of **A** this pathway does not take place because of formation of strongly strained cyclobutane ring.



Task 4. Dutch mannose

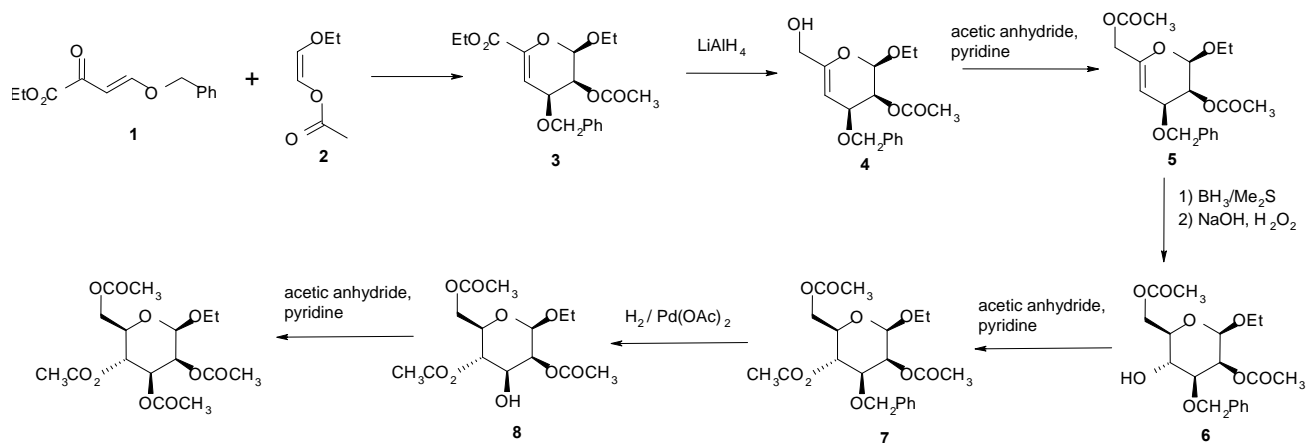
A group of scientists under the supervision of Karl Anker Jorgensen from Denmark proposed efficient method for the synthesis of hydrocarbon derivatives. Key stage, which forms carbon core of saccharide, is so called Diels-Alder heteroreaction between compounds **1** and **2** with the use of chiral metal-complex catalysts, providing formation of only one enantiomer **3**. The use of this method for the synthesis of derivative of D-mannose **9** is presented below.



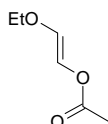
1. Draw (with stereo-chemical details) space structure of compounds **3-8**.
2. Which starting compound should be taken instead of compound **2** in order to obtain (according to presented scheme) tetraacetate of ethyl-beta-D-glucose?
3. Propose the method for preparation of mannose from compound **9**.
4. Draw (with stereo-chemical details) space structure of the products of reaction of D-mannose with a) NaBH₄; b) HNO₃; c) EtSH, H⁺; d) NH₂OH; e) acetone, H⁺; f) benzaldehyde, H⁺.
5. In the case of the latter two reactions explain, why five-membered cyclic ketal is selectively formed with acetone, while six-membered cyclic acetal is selectively formed with benzaldehyde.

Solution

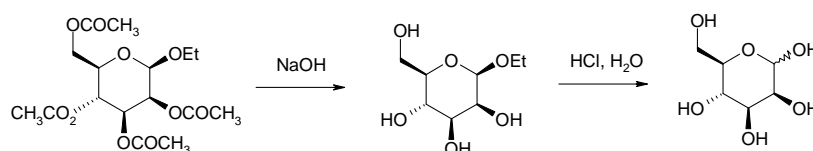
1.



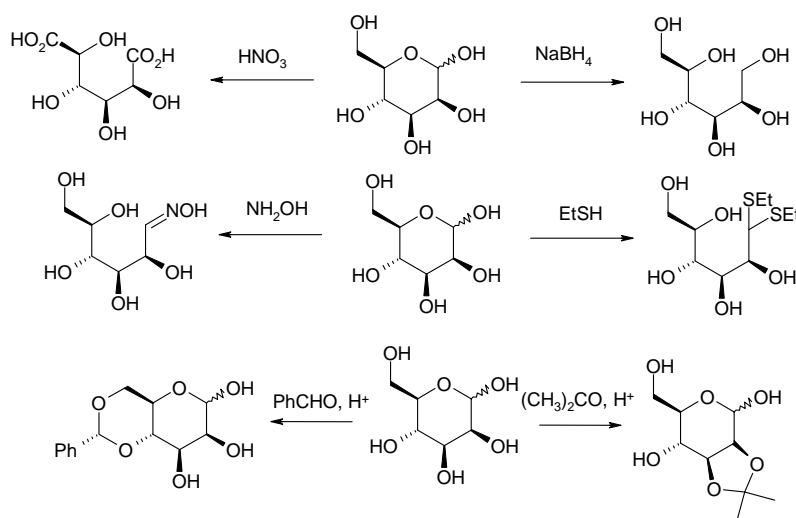
2. *Cis*-orientation of 2-ethoxy- and 3-acetoxy substituents in the product **3** is caused by *cis*-configuration of alkene **2**. In order to obtain tetraacetate of ethyl-beta-D-glucose in corresponding product of Diels-Alder hetero-reaction, there should be *trans*-orientation of 2-ethoxy and 3-acetoxy substituents. So, *trans*-2-ethoxyvinylacetate should be used.



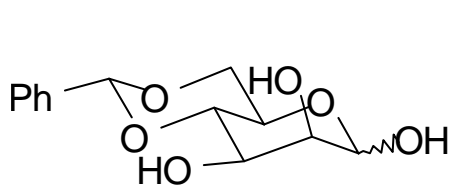
3. Mannose may be obtained in two stages: 1) alkaline hydrolysis of acetoxy-groups; 2) acidic hydrolysis of acetal group:



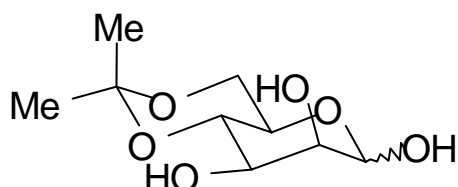
4.



5. Formation of six-membered acetal cycle is favored in the case of benzaldehyde (phenyl substituent takes equatorial position), but is not favorable in the case of acetone (in these conditions one of methyl groups takes axial position). So in the case of acetone formation of five-membered ketal cycle occurs. In turn, formation of such ketal cycle is possible only in the case of *cis*-orientation of OH-groups in 1,2-diol fragment, that is why reaction goes on hydroxy-groups at C-2 and C-3.



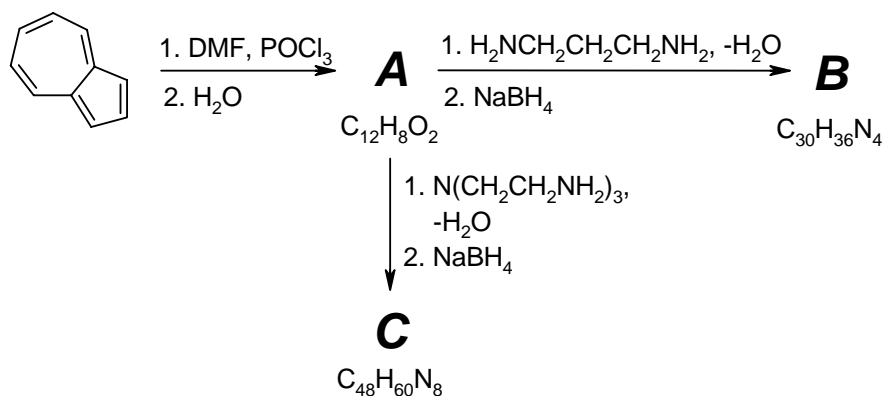
favorable



not favorable

Task 5. Etude in blue colors

Coronand **B**, based on azulene core, was obtained for the first time in 2001 with 50% yield. The same authors with 12% yield obtained cryptand **C**. The scheme of compounds **B** and **C** obtaining starting from azulene is presented below (DMF is N,N-dimethylformamide; NaBH₄ is sodium borohydride, reducer).

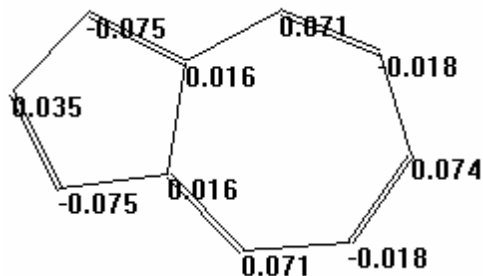


Brief description of PMR spectrum of compound **B** has the following form:

1.74 (4H, multiplet), 2.18 (4H, wide singlet), 2.74 (8H, triplet), 4.17 (8H, singlet), 7.01 (4H, triplet), 7.45 (2H, triplet), 7.67 (2H, singlet), 8.26 (4H, doublet), where the figures mean chemical shift of signals, and their integral intensity and multiplicity is presented in brackets.

1. Calculation of azulene molecule were performed using molecular orbits method in

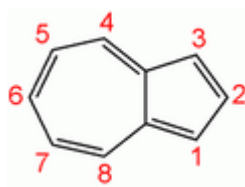
Hueckel approximation and charges on carbon atoms were determined. Using these data predict, in which positions will azulene be attacked by electrophilic and nucleophilic reagents.



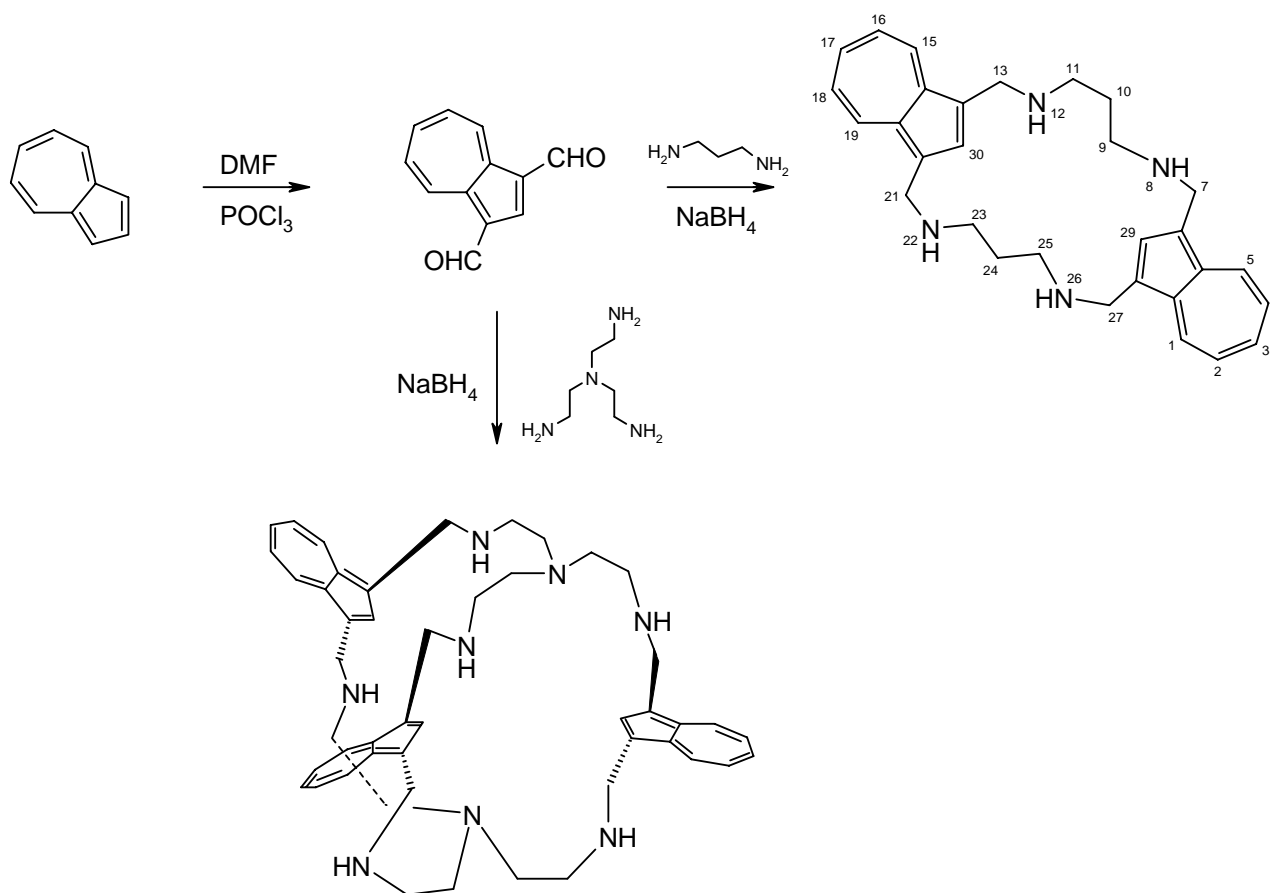
2. Write the scheme and draw the structures of compounds **A** – **C**. Explain the difference in the yields of reactions of **B** and **C** formation.
3. Which particle attacks azulene molecule in the reaction of obtaining of compound **A**? What is the role of this particle in the reaction (electrophyl or nucleophyl)?
4. Refer the signals in PMR spectrum of compound **B** as completely as possible. Show that these spectral data confirm the results of quantum-chemical calculations.
5. What are cryptands and coronands? For what are they used?

Solution

1. It is clear that attack by electrophylic reagents will take place at the atoms with the lowest charge, and by nucleophylic - at the atoms with the highest charges, that is electrophyls react with atoms 1 and 3, and nucleophyls – with 4, 6 and 8.



2.



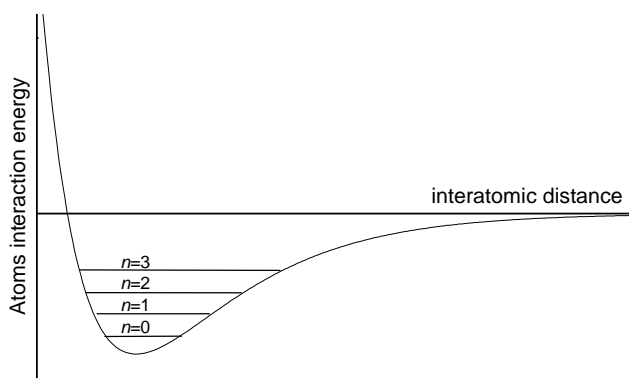
Low yield in the reaction of **C** formation (compared to **B**) is caused by noticeably lower ΔS_{act} at formation of bicyclic structure compared to monocyclic structure. In another words, pre-organizing of reagents, required for obtaining of macrocyclic structure **C**, is more complicated.

3. $\text{HC}(\text{Cl})=\text{N}(\text{CH}_3)_2^+$ is so-called Wilsmeier complex (cation). It has the role of electrophyl.

4. 1.74 (10- and 24-CH₂), 2.18 (8-, 12-, 22- and 26-NH), 2.74 (9-, 11-, 23- and 25-CH₂), 4.17 (7-, 13-, 21- and 27-CH₂), 7.01 (2-, 4-, 16- and 18-CH), 7.45 (3- and 17-CH), 7.67 (29- and 30-CH), 8.26 (1-, 5-, 15- and 19-CH). Analysis of signals of aromatic protons indicates that exactly 1,3-disubstituted azulene formed: first, there is rather high symmetry of the molecule, second, only in the case when both substituents are in five-membered ring, there is only one singlet in the part of the spectrum above 7 ppm.

5. Coronands and crypands are macrocyclic polydentate compounds, able to form stable complexes with metal cations. In a contrast to coronands, containing one macrocycle, macrocyclic systems of cryptands is bi- or polycyclic. They are used as interphase transfer catalysts, selective reagents for metals extraction etc.

Task 6. Diatomic molecules



The figure schematically presents potential curve for diatomic molecule. Atoms, as quantum objects, according to Heisenberg uncertainty principle, are in continuous movement. This movement in diatomic molecule may be compared to oscillations of spring

pendulum with characteristic frequency $\omega = \sqrt{\frac{k}{\mu}}$ (here k is force constant of the

molecule, μ is reduced mass, related to masses m_1, m_2 of atoms: $\mu = \frac{m_1 m_2}{m_1 + m_2}$). The

energy of such oscillations is determined by formula $E = \frac{h}{2\pi} \omega \left(n + \frac{1}{2} \right)$, where h is Plank constant, n is integer number, which takes the values 0, 1, 2...; these levels, plotted from the lowest point of the graph, are schematically shown on the figure by horizontal lines.

The frequencies of molecule's vibrations were determined from IR-spectra (1 Hz = 1 s⁻¹):

Molecule	H ₂	HD	D ₂	H ³⁵ Cl	D ³⁵ Cl
ω , THz	829.4	720.1	588.1	563.8	404.5

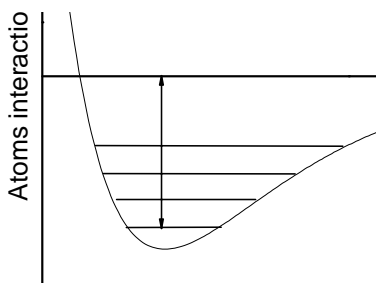
1. Give determinations of kinetic and potential components of the energies of atoms in diatomic molecule. At which ratio between them dissociation of molecule occurs?

2. Indicate the energy of dissociation of vibrationally non excited molecule on the graph.
3. Calculate force constants of the molecules, presented in the table (consider that relative atomic mass is the same as nuclonic number). Explain the result.
4. Taking into account that dissociation energy for H₂ is 432 kJ/mol, calculate the dissociation energies for D₂ and HD molecules.
5. Calculate energy change in the reaction: HCl + D₂ = DCl + HD. Classify this reaction as exo- or endothermal.
6. In your opinion, why does the temperature make influence of heat effect of reaction?

Solution

1. Kinetic energy is mainly the energy of movement (intra-molecular, that is vibrations) of atoms' nuclei, formula for its calculation is provided in the text of the task. Potential energy is the energy of interaction of atoms; even approximate formula for its calculation is quite complicated, that is why its dependency on interatomic distance is presented in graphical form in the task. At the moment of dissociation kinetic energy should be not less than potential (in absolute value).

2. This is the distance from zero vibration level to "zero energy level", which corresponds to non-interacting atoms.



3. $\mu[\text{kg}] = \mu[\text{a.m.u.}] / 1000 N_A$. It can be seen from calculated values of force constants, that force constants do not depend on atomic masses (the discrepancy is within the error), but depend only on electronic shell of the molecule, i.e. on nuclei charges and the quantity of electrons.

Molecule	H ₂	HD	D ₂	H ³⁵ Cl	D ³⁵ Cl
μ, a.m.u.	0.5	0.66667	1.0	0.97222	1.89189
k, kg·s ²	571.3	574.3	574.5	513.3	514.2

4. Dissociation energies of the molecules H₂, D₂ and DH will differ only due to the energies of zero ($n = 0$) vibrations, whereas potential curve for these molecules is the same. So (see scheme in the answer to question 2), the energy of zero vibrations ($E_0[\text{J/mol}] = \frac{h\bar{\omega}}{4\pi} \cdot N_A$) of this molecule should be added to dissociation energy of H₂, and the energy of zero vibrations of the molecule of D₂ or HD should be subtracted.

Molecule	H ₂	HD	D ₂	H ³⁵ Cl	D ³⁵ Cl
E_0 , kJ/mol	26.3	22.9	18.7	17.9	12.8
E_{dis} , kJ/mol	432	435.4	439.6		

5. Calculate the change in reaction energy as the difference between dissociation energies of its participants:

$$17.9 + 18.7 - 12.8 - 22.9 = 0.9 \text{ (kJ/mol), exothermic reaction.}$$

6. Higher vibrational levels of the molecules become to be populated at the temperature above absolute zero (vibrations with $n = 1, 2, \dots$ are excited). Since these levels are not the same for the reagents and the products, they will be populated in different way. This fact in our scheme leads to the change of energy characteristics of chemical reaction.

Task 7. Important element

Calcination of compound **A** with the weight equal to 2.00 g leads to formation of simple compound with the weight equal to 0.25 g, formed by the element **X**, and binary compound **A**₁, in which weight fraction of element **X** $w(\text{X}) = 42.86\%$. Hydrolysis of **A**₁ gives the mixture of gases **B**₁ and **B**₂.

At interaction of **B**₁ with ammonia solution of copper (I) oxide yellowish-brown precipitate **C** forms. Gas **B**₁ can participate in Kucherov reaction, producing ketone **D**. At addition of concentrated sulfuric acid to **D** aromatic hydrocarbon **D**₁

forms (weight fraction $w(\mathbf{X}) = 90\%$). Gas \mathbf{B}_2 reacts with water in acidic medium, forming compound \mathbf{E} , which is not stable and rearranges to \mathbf{D} .

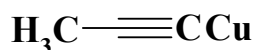
It is also known that only \mathbf{B}_1 forms at heating of \mathbf{B}_2 with metallic sodium in $(\text{C}_2\text{H}_5)_2\text{O}$.

1. Determine all compounds and chemical element \mathbf{X} .
2. Write equation of hydrolysis of \mathbf{A}_1 .
3. Write structural formula of the anion, which is a component of compound \mathbf{A}_1 .
4. Which allotropic modifications of element \mathbf{X} do you know? Write not less than five answers.

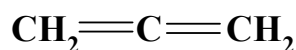
Solution

1. Element \mathbf{X} is carbon, \mathbf{B}_1 is acetylenic hydrocarbon. Aromatic hydrocarbons are formed in acidic medium from methylketones. So, \mathbf{D}_1 is C_xH_y , $w(\text{C}) = 12x/(12x+y) = 0.9$, from this $x=1.33y$, \mathbf{D}_1 is $(\text{C}_3\text{H}_4)_n$. At $n = 3$ \mathbf{D}_1 is 1,3,5-trimethylbenzene. \mathbf{D} is acetone; \mathbf{B}_1 is methylacetylene.

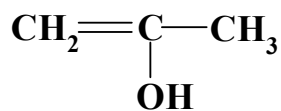
Compound \mathbf{B} :



Compound \mathbf{B}_2 is allene:



Compound \mathbf{E} :



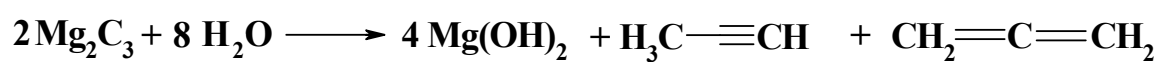
Compound \mathbf{A}_1 is carbide E_xC_y .

$$w(\text{E}) = x \cdot M(\text{E}) / (x \cdot M(\text{E}) + 12y) = 1 - 0.4286 = 0.5714;$$

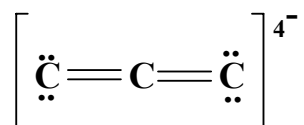
$$0.5714 \cdot x \cdot M(\text{E}) + 6.8568y = x \cdot M(\text{E}); \quad M(\text{E}) = 16y/x.$$

The conditions of the task can be satisfied at $y=3$; $x=2$. So, compound \mathbf{A}_1 is Mg_2C_3 . By the way of not difficult calculations we can obtain that compound \mathbf{A} is MgC_2 .

2.



3.



4. Diamond, graphite, carbene, fullerene, carbon nanotubes.