16th

IChO

International Chemistry Olympiad

8 theoretical problems
2 practical problems

THE SIXTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
1–10 JULY 1984, FRANKFURT AM MAIN, GERMAN FEDERAL REPUBLIC

THEORETICAL PROBLEMS

PROBLEM 1

A)

The element carbon consists of the stable isotopes ^{12}C (98.90 percent of atoms) and ^{13}C (1.10 percent of atoms). In addition, carbon contains a small fraction of the radioisotope ^{14}C ($t_{1/2}$= 5730 years), which is continuously formed in the atmosphere by cosmic rays as CO_2. ^{14}C mixes with the isotopes ^{12}C and ^{13}C via the natural CO_2 cycle.

The decay rate of ^{14}C is described by (N = number of ^{14}C atoms; t = time; λ = decay constant):

$$\text{decay rate} = -\frac{dN}{dt} = \lambda N \qquad (1)$$

Integration of (1) leads to the well-known rate law (2) for the radioactive decay:

$$N = N_0\, e^{-\lambda t} \qquad (2)$$

N_o = number of ^{14}C atoms at t = 0

1.1 What is the mathematical relationship between the parameters α and $t_{1/2}$ (= half l life)?

1.2 The decay rate of carbon, which is a part of the natural CO_2 cycle, is found to be 13.6 disintegrations per minute and gram of carbon. When a plant (e. g. a tree) dies, it no longer takes part in the CO_2 cycle. As a consequence, the decay rate of carbon decreases.

In 1983, a decay rate of 12.0 disintegrations per minute and gram of carbon was measured for a piece of wood which belongs to a ship of the Vikings. In which year was cut the tree from which this piece of wood originated?

1.3 Assume that the error of the decay rate of 12.0 disintegrations per minute and gram of carbon is 0.2 disintegrations per minute and gram of carbon. What is the corresponding error in the age of the wood in question b)?

1.4 What is the isotope $^{12}C/^{14}C$ ratio of carbon, which takes part in the natural CO_2 cycle (1 year = 365 days)?

B)

The elements strontium and rubidium have the following isotope composition:

Strontium: 0.56 % ^{84}Sr ; 9.86 % ^{86}Sr ; 7.00 % ^{87}Sr ; 82.58 % ^{88}Sr (these isotopes are all stable).

Rubidium: 72.17 % ^{85}Rb (stable) ; 27.83 % ^{87}Rb (radioactive; $t_{1/2} = 4.7 \times 10^{10}$ years).

The radioactive decay of ^{87}Rb leads to ^{87}Sr.

In Greenland one finds a gneiss (= silicate mineral) containing both strontium and rubidium.

1.5 What is the equation rate law describing the formation of ^{87}Sr from ^{87}Rb as a function of time?

1.6 Assume that the isotope ratio $^{87}Sr/^{86}Sr$ (as determined by mass spectrometry) and the isotope ratio $^{87}Rb : ^{86}Sr$ are known for the gneiss. What is the mathematical relationship with which one can calculate the age of the gneiss?

SOLUTION

A)

1.1 The relationship is:

$$\alpha = \frac{\ln 2}{t_{1/2}}$$

1.2

$$t = \frac{t_{1/2}}{\ln 2} \times \ln\left(\frac{N_0}{N}\right) = \frac{5730}{0.6930} \times \ln\left(\frac{13.6}{12.0}\right) = 1035 \text{ years}$$

1.3 For N_o/N = 13.6/12.0 t = 1035 years

For N_o/N = 13.6/12.2 t = 898 years

For N_o/N = 13.6/11.8 t = 1174 years

Thus, the tree was cut 1035 (+ 139/–137) years ago.

1.4

$$N = \frac{13.6 \times t_{1/2}}{\ln 2} = 5.91 \times 10^{10} \text{ atoms } ^{14}\text{C /g carbon}$$

$$1 \text{ g} \approx 0.989 \text{ g } ^{12}\text{C}; \quad 0.989 \text{ g } ^{12}\text{C} \approx (0.989/12) \times 6.023 \times 10^{23} \text{ atoms } ^{12}\text{C}$$

$$^{12}\text{C} / ^{14}\text{C} = \frac{0.989 \times 6.023 \times 10^{23}}{12 \times 5.91 \times 10^{10}} = 8.40 \times 10^{11} : 1$$

B)

1.5 Equation (2) describes the decay of the ^{87}Rb:

$^{87}\text{Rb} = ^{87}\text{Rb}_o \,.\, \exp(-\lambda t)$

The symbol ^{87}Rb stands for the number of atoms of this nuclide.

Consequently, one obtains for the formation of ^{87}Sr from ^{87}Rb:

$^{87}\text{Sr} = ^{87}\text{Rb}_o - ^{87}\text{Rb} = ^{87}\text{Rb} \,.\, \exp(\lambda t) - ^{87}\text{Rb}$ (a)

1.6 The formation of the radiogenic ^{87}Sr follows equation (a).

One has to take into account that at time t = 0, when the mineral was formed, there was some non-radiogenic strontium in it already:

$^{87}\text{Sr} = (^{87}\text{Sr})_o + ^{87}\text{Rb} \,.\, [\exp(\lambda t) - 1]$

The isotope ratio $(^{87}\text{Sr}/ ^{86}\text{Sr})_o$ follows from the isotope composition of strontium. The time t in this equation corresponds to the age of the gneiss.

PROBLEM 2

Ludwig Mond discovered before the turn of this century that finely divided nickel reacts with carbon monoxide forming tetracarbonylnickel, $Ni(CO)_4$, a colourless, very volatile liquid. The composition of $Ni(CO)_4$ provides an example of the noble gas rule ("EAN rule").

Problems:

2.1 Use the eighteen-electron rule (noble gas rule) to predict the formula of the binary carbonyls of Fe(0) and Cr(0).

2.2 What composition would the eighteen-electron rule predict for the most simple binary chromium(0)-nitrosyl compound?

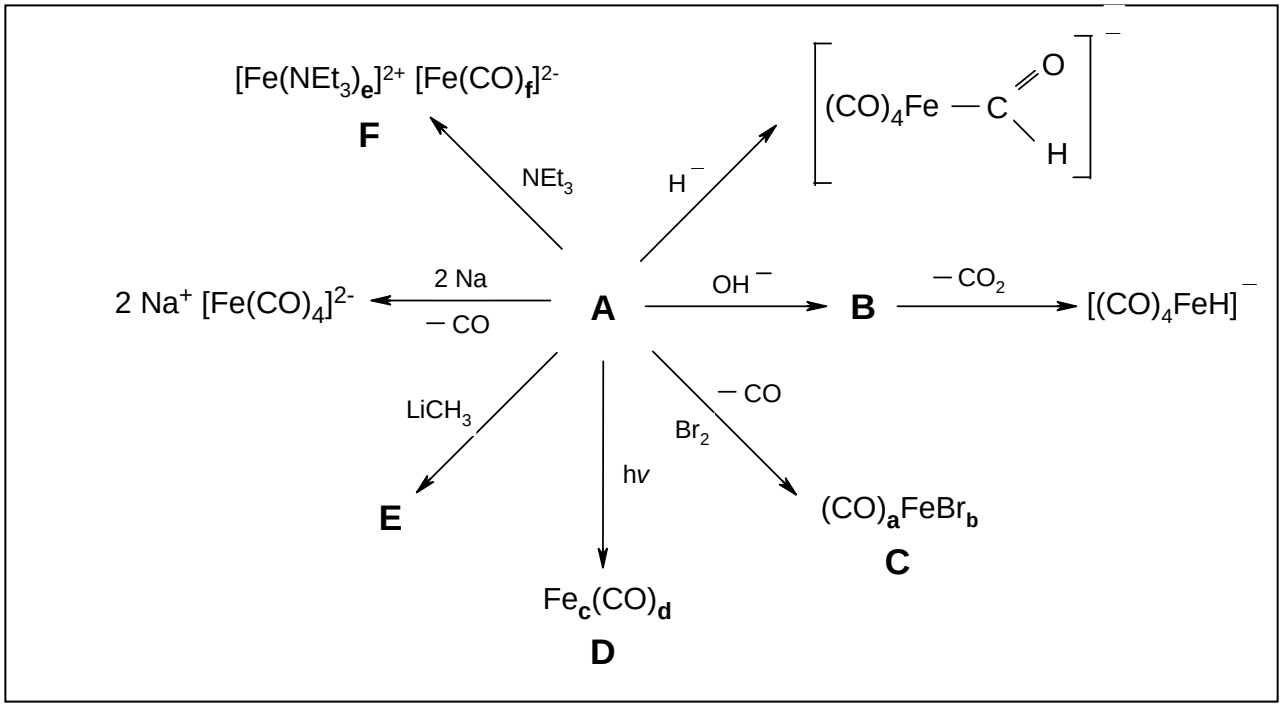
2.3 Explain why Mn(0) and Co(0) do not form so-called mononuclear carbonyl complexes of the type $M(CO)_x$ (M = metal), but rather compounds with metal-metal bonding.

2.4 Suggest structures of $Ni(CO)_4$, $Mn_2(CO)_{10}$ and $Co_2(CO)_8$.

2.5 State whether $V(CO)_6$ and the compounds mentioned in a) and d) are diamagnetic or paramagnetic.

2.6 Why are the carbon monoxide ligands bound to metals much more strongly than to boron in borane adducts (e.g. R_3B-CO; R = alkyl)?

2.7 Determine the composition of the compounds labeled **A** - **F** in the following reaction scheme:



Hints:

a) **C** has the following analysis: C, 14.75 % ; Br, 48.90 % .

b) **D** contains 30.70 % Fe; the molecular mass is 363.8 a.m.u.

c) Excess triethylamine is used for the synthesis of **F**. **F** contains 5.782 % C and 10.11 % N.

2.8 Why is the compound **F** formed in the disproportional reaction (given in g)), and not the compositional isomer $[Fe(CO)_f]^{2+}[Fe(NEt_3)_e]^{2-}$?

2.9 The eighteen-electron rule is also satisfied by a compound prepared from elementary chromium and benzene.

i) Draw the formula of this complex.

ii) Which complex with the analogous structure is prepared by the reaction of iron powder with cyclopentadiene? Write the chemical equation for its formation.

SOLUTION

2.1 $Fe(CO)_5$, $Cr(CO)_6$

2.2 $Cr(NO)_4$

2.3 Explanation: the odd number of electrons in the $Mn(CO)_5$ and $Co(CO)_4$ fragments.

2.4 $Ni(CO)_4$: tetrahedral geometry

$Mn_2(CO)_{10}$: - octahedral $Mn(CO)_5$-structure having a Mn-Mn bond,

- relative orientation (conformation) of the carbonyl groups.

$Co_2(CO)_{10}$: CO-bridges and Co-Co bond

2.5 $Fe(CO)_5$, $Cr(CO)_6$, $Ni(CO)_4$, $Mn_2(CO)_{10}$, $Co_2(CO)_{10}$ are diamagnetic,

$V(CO)_6$ is paramagnetic.

2.6 Explanation using the so-called "back-bonding concept"

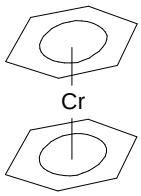
2.7 **A** = $[Fe(CO)_5]$ **B** = $[HOCOFe(CO)_4]$ **C** = $[FeBr_2(CO)_4]$

D = $[Fe_2(CO)_9]$ **E** = $[(CO)_4Fe{=}C(OLi)CH_3]$ **F** = $[Fe(NEt_3)_6]$ $[Fe(CO)_4]$

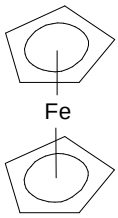
2.8 This observation is due to differing back bonding capability of NEt_3 and CO.

2.9

i) Structural formula of dibenzenechromium



ii) Structural formula of ferrocene.



PROBLEM 3

A weak acid of total concentration 2×10^{-2} M is dissolved in a buffer of pH = 8.8. The anion A^- of this acid is coloured and has a molar decadic absorption coefficient ε of 2.1×10^4 cm^2 mol^{-1}. A layer *I* of the solution with 1.0 cm thickness absorbs 60 percent of the incident luminous intensity I_o.

3.1 What is the equation relating the extinction to the thickness of the absorbing layer?

3.2 How large is the concentration of the acid anion in the buffer solution?

3.3 How large is the pK_a of the acid?

SOLUTION

3.1 The Lambert-Beer law e.g.:

$\log (I_o/I) = A = \varepsilon \,.\, c \,.\, l$

3.2 $\log [(100-60)/100] = - 2.1 \times 10^4 \times [A^-] \times 1$

$[A^-] = 1.895 \times 10^{-5}$ mol cm^{-3} $= 1.895 \times 10^{-2}$ mol dm^{-3}

3.3 According to the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log \frac{[A^-]_{eq}}{[HA]_{eq}}$$

and with the total concentration

$[HA]_{tot} = [HA]_{eq} + [A^-]_{eq} = 2 \times 10^{-2}$ mol dm^{-3}

$$8.8 = pK_a + \log \frac{1.895 \times 10^{-2}}{2 \times 10^{-2} - 1.895 \times 10^{-2}}$$

$pK_a = 7.5$

PROBLEM 4

15 cm^3 of a gaseous hydrocarbon C_xH_y are mixed with 120 cm^3 oxygen and ignited. After the reaction the burned gases are shaken with concentrated aqueous KOH solution. A part of the gases is completely absorbed while 67.5 cm^3 gases remain. It has the same temperature and pressure as the original unburned mixture.

4.1 What is the composition of the remaining gas? Explain.

4.2 How large is the change in the amount of substance per mole of a hydrocarbon C_xH_y when this is burned completely?

4.3 What is the chemical formula of the hydrocarbon used for the experiment? Give the steps of the calculation.

SOLUTION

4.1 The remaining gas is oxygen since the burning products CO_2 and H_2O are completely absorbed in concentrated KOH solution.

4.2 The general stoichiometric equation for complete combustion of a hydrocarbon C_xH_y is as follows:

$C_xH_y + (x + y/4)\ O_2 \rightarrow x\ CO_2 + (y/2)\ H_2O$

The change in amount of substance per mole of hydrocarbon is

$[x + (y/2) – (1 + x + y/4)]$ mol = $[(y/4) – 1]$ mol

4.3 The equation of chemical conversion at the experimental condition is as follows:

$15\ C_xH_y + 120\ O_2 \rightarrow 15x\ CO_2 + (15/2)y\ H_2O + [(120 – 15x – (15/4)y]\ O_2$

For the residual oxygen:

(1) $120 /b – 15x – (15/4)y = 67.5$

and for the total balance of amount of substance:

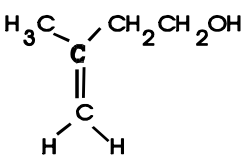
(2) $15x + (15/2)y + 67.5 = 15 + 120 + 15[(y/4) – 1]$

From equation (1) and (2) follows: $x = 2$ and $y = 6$.

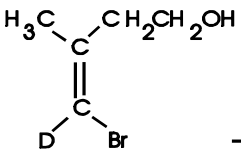
The hydrocarbon in question is ethane.

PROBLEM 5

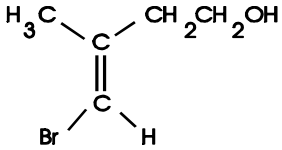
One of the diastereotopic methylene protons at the double bond of **A** was selectively substituted by deuterium. Bromination and subsequent dehydrobromation yields the



A



B



C

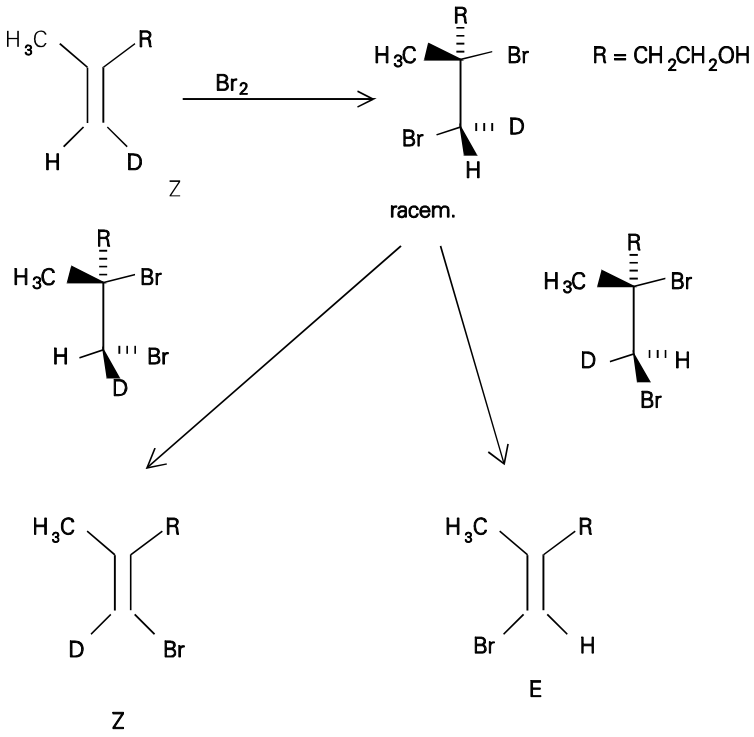
deuteriated product **B** and the non-deuteriated product **C**.

5.1 Which configuration follows for the monodeuteriated **A** from the given reaction products?

5.2 The solution of this question requires the formulation of the reaction and a short argumentation why only **B** and **C** are formed.

SOLUTION

5.1



5.2 The addition of bromine occurs trans (antarafacial). The elimination of HBr via an E2 mechanism also requires an anti-periplanar (= trans) arrangement of H and Br. The products given in this problem are only formed from a Z-configurated adduct.

The bromination of **A** and subsequent dehydrobromination yield both E,Z isomeric bromoolefins that have to be separated. Substitution of the bromine by deuterium in the Z-isomer proceeds by treatment with a metal (best: Na/t-BuOD) under retention to **A**.

PROBLEM 6

A technical interesting C_5 hydrocarbon **A** is separated via dimerization from the for-runnings of the benzene-pyrolysis fraction. This is achieved either by heating to 140 – 150 ^oC under pressure or by heating over several hours at 100^o C. Then it is distilled out at 200 ^oC. Treatment of **A** with peroxyacetic acid under neutral conditions (sodium acetate and sodium carbonate) in dichloromethane at 20^o C yields a product **B**. **B** yields two isomeric products **C** and **D** (summary formula $C_5H_8O_2$) by the reaction with aqueous sodium carbonate solution. The main product **C** contains three different bound carbon atoms whereas in the minor product **D** five different carbon atoms are present. **C** is chiral.

6.1 Write the formulas of **A**, **B**, **C**, and **D** considering the stereochemical representation.

6.2 What is the name of the chemical reaction which is used for the above mentioned separation procedure?

6.3 Which stereochemical rules hold for the dimerization reaction?

6.4 Give the structure of the dimerization product.

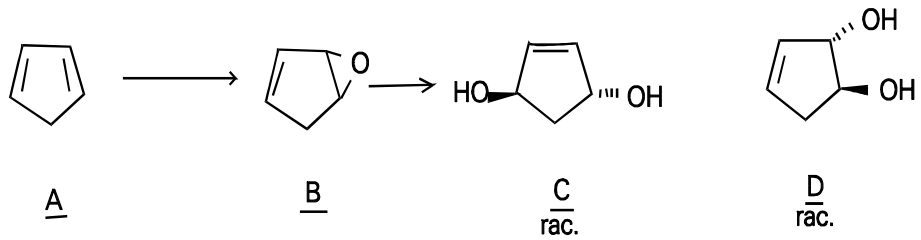
6.5 Give the mechanism of the formation of **C** and **D** from **B**.

6.6 Which kind of isomers are **C** and **D** ?

6.7 How many stereoisomers of **C** and **D** are principally (regardless of their synthetic availability) possible? Give their mutual stereochemical relations. Write their structural formulas.

SOLUTION

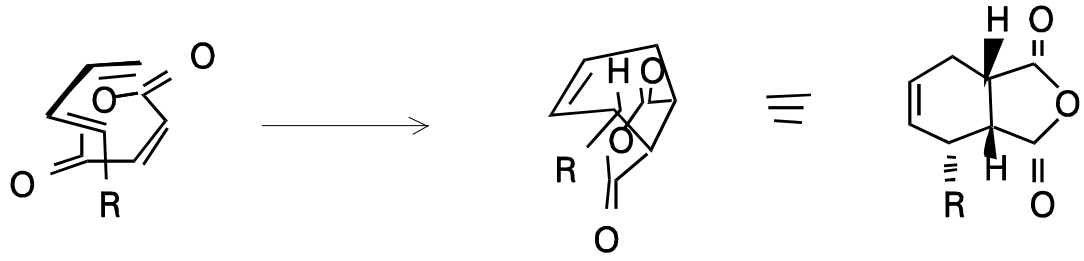
6.1



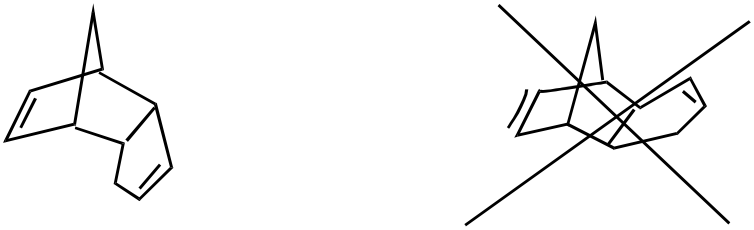
A B C rac. D rac.

6.2 Diels-Alder-reaction, 4+2-cycloaddition

6.3 cis-addition = suprafacial addition with respect to diene and dienophile endo-rule: a substituent at the dienophile is oriented primarilly toward the diene . E.g.



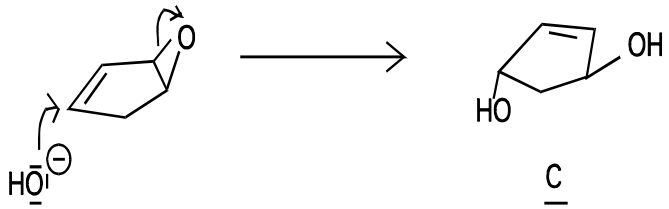
d)



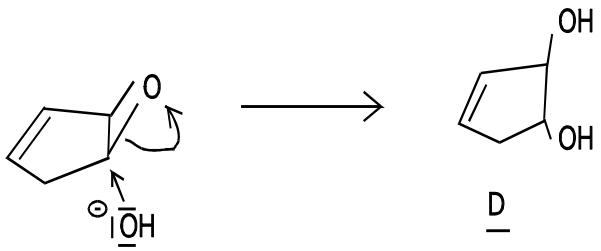
endo exo

6.4

6.5 **C** is formed via a S_N2 reaction. This reaction can lead to a cis or a trans product. Because **C** is chiral, the trans product is formed. **D** is formed via S_N2 reaction.

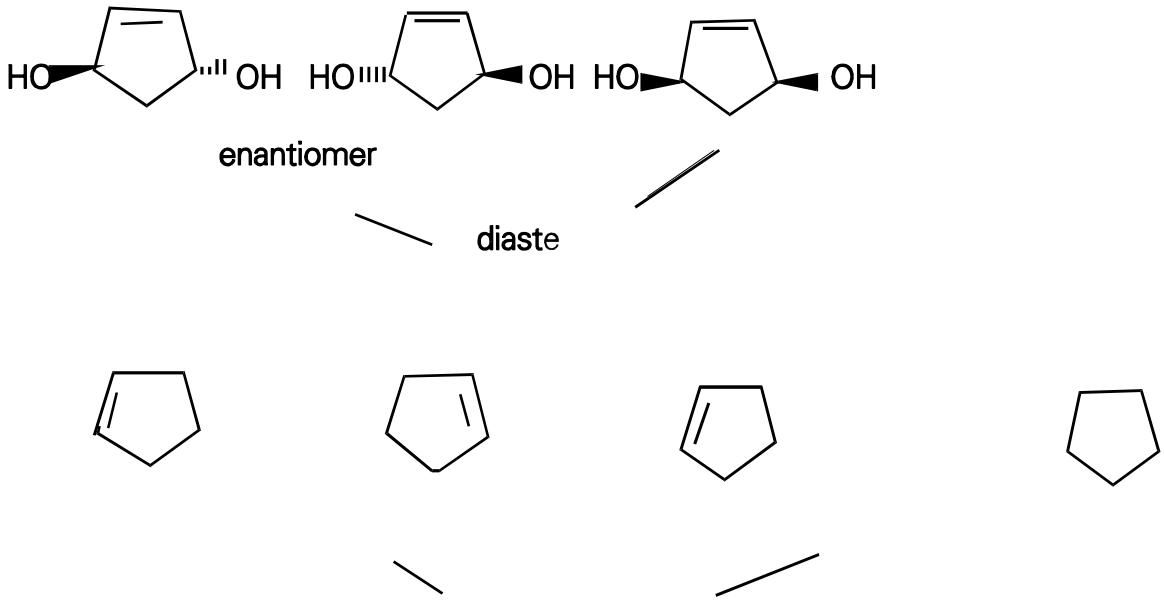


C



D

6.6 **C** and **D** are constitutional isomers.


HO
OH
HO
OH
HO
OH
enantiomer
diaste

NO_2^+ ions. As a result, the equilibrium reactions

$$HONO_2 + HONO_2 \rightleftharpoons H_2O^+\text{-}NO_2 + {}^-O\text{-}NO_2$$

and

$$H_2O^+\text{-}NO_2 \rightleftharpoons {}^+NO_2 + H_2O$$

are shifted far to the left. This effect is counterbalanced by the high reactivity (+M-effect) of phenacetine.

1.3 Phenacetine is oxidized by iron(III) ions and a molecule of p-quinone type and iron(II) ions are formed. The iron(II) ions react immediately with the hexacyanoferrate(III) ions to give Turnbull's Blue.

1.4 Neutralization with sodium or potassium hydroxide solution, use of calcium hydroxide solution and argumentation:

NO_3^--ions, CH_3COO^- ions and 4-ethoxy-2-nitroacetanilide are removed by biological metabolism.

PROBLEM 2 (practical)

Determination of the content of phosphoric acid in a cola drink

Apparatus:

500 ml round-bottom flask with stirrer, reflux condenser, heating mantle, magnetic stirrer, water bath.

Preparation of the sample:

The content of a cola drink bottle is stirred for two or three minutes in a round-bottom flask. Afterwards, 6.0 g powdered active charcoal are added. The entire suspension is carefully heated to reflux and is maintained there for ten minutes. The glass joint of the reflux condenser must not be greased!

The heating mantle is then exchanged with an ice water bath. After the sample has been cooled to 20 ^{o}C, it is filtered through a double fluted filter paper. The initial filtrate should be recycled several times.

Adjustment of the pH-meter:

The pH-meter is adjusted to the working electrode by using two buffer solutions.

Titration:

150 ml of the unknown solution are titrated using pH indication with a standardized sodium hydroxide solution (c(NaOH) = 0.0500 mol dm^{-3}).

The first equivalence point of the phosphoric acid is reached after about 6 ml of the NaOH solution have been consumed. The titration is to be continued until more than about 12 ml of sodium hydroxide solution have been added.

Results of the experiment:

a) Draw the titration curve and determine the first equivalence point.
b) Determine the pH value of the heated cola drink and the pH value at the first equivalence point.
c) Calculate the concentration of phosphoric acid in the cola drink. Write the calculation and the result in your report.

Interpretation of the experiment:

1. Describe and explain your observations during the titration.
2. Is it possible that the active charcoal could have influenced your titration result? Give reasons for your presumption.

Chemicals:

Powdered active charcoal

Sodium hydroxide solution; c(NaOH) = 0.0500 mol dm^{-3}

Buffer solutions