

IChO 1973

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Problem 1: Nitration product of a hydroxybenzene and its electroreduction

In nitrating a hydroxy derivative of benzene a compound is formed which contains 49.0 % by mass of oxygen. A charge of 4350 C is required for a total electroreduction of 0.458 g of the compound, efficiency being 80 %.

Problem:

1.1 Determine the stoichiometric as well as structural formulas of the compound if the product of the electrochemical reduction is an aromatic hydroxy amino derivative.

F (Faraday's charge) = $96\,500\text{ C mol}^{-1}$

Official English text of the problem.

Answers

- 1.1** The stoichiometric formula is $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$. The expected nitration product is **2,4,6-trinitrophenol (picric acid)**, Oc1c([N+](=O)[O-])cc([N+](=O)[O-])cc1[N+](=O)[O-]. Its structural formula is $\text{HO}-\text{C}_6\text{H}_2(\text{NO}_2)_3$, with the hydroxyl group at position 1 and nitro groups at positions 2, 4 and 6.

Solution

1.1

Let the nitration product contain h hydroxyl groups and n nitro groups on a benzene ring. It therefore contains six carbon atoms, $6 - n$ hydrogen atoms, n nitrogen atoms and $h + 2n$ oxygen atoms. Using the usual rounded atomic masses, its molar mass is

$$M = [6(12) + (6 - n) + 14n + 16(h + 2n)]\text{g mol}^{-1} = (78 + 16h + 45n)\text{g mol}^{-1}.$$

Reduction of a nitro group to an amino group changes the nitrogen oxidation state from +3 to -3, requiring **six electrons per nitro group**.

Only 80 % of the supplied charge effects the desired reduction:

$$Q_{\text{effective}} = 0.80(4350\text{ C}) = 3480\text{ C}.$$

Thus the amount of electrons used is

$$n(e^-) = \frac{3480 \text{ C}}{96\,500 \text{ C mol}^{-1}} = 0.0360622 \text{ mol}.$$

Each mole of compound requires $6n$ moles of electrons, so

$$\frac{0.458 \text{ g}}{M}(6n) = 0.0360622 \text{ mol},$$

giving

$$\boxed{\frac{M}{n} = 76.20 \text{ g mol}^{-1}}.$$

The oxygen mass fraction supplies a second relation:

$$0.490 = \frac{(16.0 \text{ g mol}^{-1})(h + 2n)}{M}.$$

Consequently,

$$\frac{h}{n} = \frac{0.490(76.2017)}{16.0} - 2 = 0.33368.$$

Combining this result with the molar-mass expression, with masses expressed numerically in g mol^{-1} ,

$$76.2017 = \frac{78}{n} + 16(0.33368) + 45,$$

which yields

$$n \simeq 3.016, \quad h \simeq 1.006.$$

The required integer group counts are therefore

$$\boxed{n = 3, \quad h = 1}.$$

The compound is a trinitrophenol, with molecular—and also empirical—formula

$$\boxed{\text{C}_6\text{H}_3\text{N}_3\text{O}_7}, \quad M = 229 \text{ g mol}^{-1}.$$

The corresponding checks are

$$w_{\text{O}} = \frac{7(16)}{229} \times 100\% = 48.91\%,$$

and

$$Q = \frac{(0.458/229) \text{ mol} \times 18 \times 96\,500 \text{ C mol}^{-1}}{0.80} = 4342.5 \text{ C},$$

both close to the supplied values.

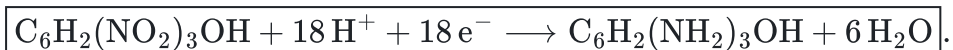
The starting hydroxybenzene is **phenol**, Oc1ccccc1. Its hydroxyl group directs nitration to the two ortho positions and the para position. Introducing three nitro groups therefore gives the expected product **2,4,6-trinitrophenol**, identified above. To draw its structure, place hydroxyl at carbon 1 of a benzene ring, nitro groups at carbons 2, 4 and 6, and hydrogen atoms at carbons 3 and 5.

The balanced nitration equation is



Here the reagent is **nitric acid**, $\text{O}=[\text{N}^+](\text{O}^-)_2$, and the coproduct is **water**, O .

Complete electroreduction gives **2,4,6-triaminophenol**, Oc1c(N)cc(N)cc1N, with formula $C_6H_9N_3O$. The balanced reduction half-equation is



The hydrogen ions in this acidic-medium half-equation are **protons**, $[H^+]$.

The solution was checked against the official solution.

Problem 2: Combustion of a gaseous hydrocarbon in a closed vessel

A mixture of a gaseous hydrocarbon and oxygen is in a vessel of a volume of 1 dm^3 at a temperature of 406.5 K and a pressure of $101\,325 \text{ Pa}$. There is twice as much oxygen in the mixture as is needed for the reaction with the hydrocarbon. After combustion of the hydrocarbon the pressure in the vessel (at the same temperature) is increased by 5% .

Problem:

2.1 What hydrocarbon was in the mixture when the mass of water formed by the combustion was 0.162 g .

Official English text of the problem.

Answers

- 2.1** The molecular formula is C_3H_6 . The hydrocarbon can be **propene** C=CC or **cyclopropane** C1CC1; the given data cannot distinguish these two isomers.

Solution

2.1

Let the hydrocarbon be C_xH_y , with a moles initially present. Its complete combustion consumes oxygen $O=O$ and produces carbon dioxide $O=C=O$ and water O :



At 406.5 K and the stated pressures, the water formed remains gaseous. Treating the gases as ideal, pressure is proportional to total gas amount at fixed temperature and volume.

The initial total amount is

$$n_i = \frac{pV}{RT} = \frac{(101325 \text{ Pa})(1.00 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1})(406.5 \text{ K})} \approx 3.00 \times 10^{-2} \text{ mol}.$$

The amount of water formed is

$$n_{\text{water}} = \frac{0.162 \text{ g}}{18.0 \text{ g mol}^{-1}} = 9.00 \times 10^{-3} \text{ mol} = \frac{ay}{2}.$$

Because the initial oxygen amount is twice the amount required for combustion,

$$n_{\text{oxygen},i} = 2a \left(x + \frac{y}{4} \right).$$

Thus,

$$n_i = a + 2a \left(x + \frac{y}{4} \right) = a \left(1 + 2x + \frac{y}{2} \right).$$

After combustion, half the initial oxygen remains. Adding this excess oxygen to the carbon dioxide and water gives

$$n_f = ax + \frac{ay}{2} + a \left(x + \frac{y}{4} \right) = a \left(2x + \frac{3y}{4} \right).$$

Consequently,

$$n_f - n_i = a \left(\frac{y}{4} - 1 \right) = \frac{n_{\text{water}}}{2} - a.$$

The pressure increase of 5% gives

$$n_f - n_i = 0.05n_i \approx 1.50 \times 10^{-3} \text{ mol.}$$

Therefore, the initial hydrocarbon amount was

$$a = \frac{9.00 \times 10^{-3}}{2} - 1.50 \times 10^{-3} = 3.00 \times 10^{-3} \text{ mol.}$$

The hydrogen subscript follows from the water yield:

$$y = \frac{2n_{\text{water}}}{a} = \frac{2(9.00 \times 10^{-3})}{3.00 \times 10^{-3}} = 6.$$

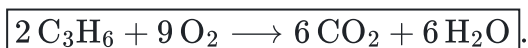
Using the initial total amount,

$$1 + 2x + \frac{y}{2} = \frac{n_i}{a} \approx 10,$$

so

$$1 + 2x + 3 = 10 \implies x = 3.$$

Hence the molecular formula is C_3H_6 , and its balanced combustion equation is



As a check, per mole of hydrocarbon the initial mixture contains $1 + 9 = 10$ moles of gas. After combustion it contains $3 + 3 + 4.5 = 10.5$ moles, giving exactly the stated 5% pressure increase.

Both propene $\text{C}=\text{CC}$ and cyclopropane C1CC1 have this formula and satisfy the conditions.

The solution was checked against the official solution.

Problem 3: Ionisation of acetic and hypochlorous acids in a mixture

Equal volumes (10 cm^3) of 0.01-molar solutions of CH_3COOH and HClO were mixed and then diluted to a total volume of 100 cm^3 . Ionisation constant of CH_3COOH is equal to 1.8×10^{-5} and that for HClO is 3.7×10^{-8} .

Problems:

Calculate:

3.1 degree of ionisation for each of the acids in the solution,

3.2 degree of ionisation of HClO if the diluted solution would not contain CH_3COOH ,

3.3 pH value for the solution containing at the same time CH_3COOH and HClO .

Official English text of the problem.

Answers

- **3.1** In the mixture:
 - Acetic acid, $\text{CC}(=\text{O})\text{O}$: $\alpha = 0.125$, or 12.5%.
 - Hypochlorous acid, OCl : $\alpha = 2.94 \times 10^{-4}$, or 0.0294%.
- **3.2** Hypochlorous acid alone: $\alpha = 6.06 \times 10^{-3}$, or 0.606%.
- **3.3** The mixture has $\text{pH} = 3.90$.

Solution

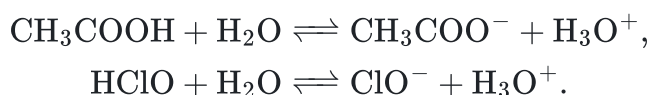
We use concentrations in place of activities and neglect water's self-ionisation. Besides the two acids named above, the species involved are water, O ; hydronium ion, $[\text{OH}_3^+]$; acetate ion, $\text{CC}(=\text{O})[\text{O}^-]$; and hypochlorite ion, $[\text{O}^-]\text{Cl}$.

3.1 Degree of ionisation of each acid in the mixture

Dilution gives the same analytical concentration for each acid:

$$C = (0.01 \text{ mol dm}^{-3}) \frac{10 \text{ cm}^3}{100 \text{ cm}^3} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}.$$

The ionisation equilibria are



Both equilibria share the same hydronium-ion concentration,

$$h = [\text{H}_3\text{O}^+].$$

Let α_1 and α_2 be the degrees of ionisation of acetic acid and hypochlorous acid, respectively. Their equilibrium concentrations are

$$\begin{aligned} &= C\alpha_1, & [\text{CH}_3\text{COOH}] &= C(1 - \alpha_1), \\ [\text{ClO}^-] &= C\alpha_2, & [\text{HClO}] &= C(1 - \alpha_2).\end{aligned}$$

Consequently,

$$K_1 = \frac{h\alpha_1}{1 - \alpha_1}, \quad K_2 = \frac{h\alpha_2}{1 - \alpha_2},$$

so that

$$\alpha_1 = \frac{K_1}{h + K_1}, \quad \alpha_2 = \frac{K_2}{h + K_2}.$$

Here and below, concentrations entering the equilibrium expressions are expressed in mol dm^{-3} .

Electrical neutrality requires

$$h = [\text{CH}_3\text{COO}^-] + [\text{ClO}^-] = C(\alpha_1 + \alpha_2).$$

Thus h satisfies

$$h = C \left(\frac{K_1}{h + K_1} + \frac{K_2}{h + K_2} \right).$$

Substituting $C = 1.0 \times 10^{-3}$, $K_1 = 1.8 \times 10^{-5}$, and $K_2 = 3.7 \times 10^{-8}$, the positive solution is

$$h = 1.25623 \times 10^{-4} \text{ mol dm}^{-3}.$$

Therefore,

$$\alpha_1 = \frac{1.8 \times 10^{-5}}{1.25623 \times 10^{-4} + 1.8 \times 10^{-5}} = 0.125328 \approx \boxed{12.5\%},$$

$$\alpha_2 = \frac{3.7 \times 10^{-8}}{1.25623 \times 10^{-4} + 3.7 \times 10^{-8}} = 2.94446 \times 10^{-4} \approx \boxed{0.0294\%}.$$

Acetic acid is sufficiently ionised that retaining its depletion, through the factor $1 - \alpha_1$, improves the calculation appreciably.

3.2 Degree of ionisation of hypochlorous acid alone

Its analytical concentration remains

$$C = 1.0 \times 10^{-3} \text{ mol dm}^{-3}.$$

With no acetic acid present, let

$$x = [\text{H}_3\text{O}^+] = [\text{ClO}^-].$$

Then $[\text{HClO}] = C - x$, giving

$$K_2 = \frac{x^2}{C - x}.$$

Rearranging and taking the positive root,

$$\begin{aligned} x^2 + K_2x - K_2C &= 0, \\ x &= \frac{\sqrt{K_2^2 + 4K_2C} - K_2}{2} = 6.06429 \times 10^{-6} \text{ mol dm}^{-3}. \end{aligned}$$

Hence

$$\alpha = \frac{x}{C} = 6.06429 \times 10^{-3} \approx \boxed{0.606\%}.$$

The greater ionisation in this case illustrates the common-ion effect: hydronium ions supplied by acetic acid suppress the ionisation of hypochlorous acid in the mixture.

3.3 pH of the mixture

Using the hydronium-ion concentration obtained in part 3.1,

$$\text{pH} = -\log_{10} \left(\frac{[\text{H}_3\text{O}^+]}{1 \text{ mol dm}^{-3}} \right) = -\log_{10}(1.25623 \times 10^{-4}) = 3.90093.$$

Thus,

$$\text{pH} = 3.90$$

The solution was checked against the official solution.

Problem 4: Precipitate and dry residue from two unknown solutions

When solutions of two unknown substances are mixed together in stoichiometric ratio, 1.25 g of a precipitate are formed which contain a salt of a bivalent metal M. The precipitate when heated to 1100 °C is decomposed to 0.70 g of a solid metal oxide MO and another gaseous oxide. After evaporation of the filtrate, a dry residue with a mass of 2.0 g remains which yields two products by thermal decomposition at 215 °C: a gaseous oxide and 0.90 g of water vapour. The total volume of the gaseous mixture is 1.68 dm³ (at STP).

Problem:

4.1 Determine the unknown compounds and write chemical equations for the above mentioned reactions.

Official English text of the problem.

Answers

- 4.1** The original solutes are **calcium nitrate** and **ammonium carbonate**. The metal is **calcium**, the precipitate is **calcium carbonate**, and the dry residue is **ammonium nitrate**.

Role	Compound	Formula	SMILES
Original solute	Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	<chem>[Ca+2].[O-][N+](=O)[O-].[O-][N+](=O)[O-]</chem>
Original solute	Ammonium carbonate	$(\text{NH}_4)_2\text{CO}_3$	<chem>[NH4+].[NH4+].[O-]C(=O)[O-]</chem>
Precipitate	Calcium carbonate	CaCO_3	<chem>[Ca+2].[O-]C(=O)[O-]</chem>
Solid decomposition product	Calcium oxide	CaO	<chem>[Ca+2].[O-2]</chem>
Gas from the precipitate	Carbon dioxide	CO_2	<chem>O=C=O</chem>
Dry filtrate residue	Ammonium nitrate	NH_4NO_3	<chem>[NH4+].[O-][N+](=O)[O-]</chem>
Oxide from the dry residue	Nitrous oxide	N_2O	<chem>N#[N+][O-]</chem>
Other decomposition product	Water	H_2O	<chem>O</chem>

The disconnected SMILES specify the constituent ions of the salts; they do not encode their crystal lattices.

Solution

4.1

Use the conventional STP molar volume $22.4 \text{ dm}^3 \text{ mol}^{-1}$ and rounded atomic molar masses. Guard digits are retained in intermediate calculations.

Identification of the dry residue

Interpreting the stated volume as the equivalent STP volume of both products from the dry residue,

$$n_{\text{total}} = \frac{1.68 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.0750 \text{ mol}.$$

The amount of water formed is

$$n(\text{H}_2\text{O}) = \frac{0.90 \text{ g}}{18.0 \text{ g mol}^{-1}} = 0.0500 \text{ mol}.$$

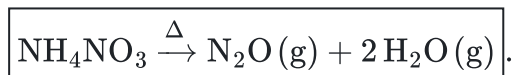
Therefore, the gaseous oxide has

$$\begin{aligned} n_{\text{oxide}} &= 0.0750 - 0.0500 = 0.0250 \text{ mol}, \\ m_{\text{oxide}} &= 2.0 - 0.90 = 1.1 \text{ g}, \end{aligned}$$

and hence molar mass

$$M_{\text{oxide}} = \frac{1.1 \text{ g}}{0.0250 \text{ mol}} = 44 \text{ g mol}^{-1}.$$

The oxide-to-water mole ratio is 1 : 2. Decomposition at 215°C into an oxide of molar mass 44 g mol^{-1} and water in this ratio identifies **ammonium nitrate**, yielding **nitrous oxide**:



Its molar mass is 80.0 g mol^{-1} , so the residue contains

$$n(\text{NH}_4\text{NO}_3) = \frac{2.0 \text{ g}}{80.0 \text{ g mol}^{-1}} = 0.0250 \text{ mol}.$$

This gives 0.0500 mol , or 0.90 g , of water and a total equivalent gas volume of

$$(0.0250 + 0.0500) \times 22.4 = 1.68 \text{ dm}^3,$$

as required.

Identification of the metal and precipitate

The soluble product is ammonium nitrate. Since nitrates and ammonium salts are soluble, the original solutes are a nitrate of the bivalent metal and an ammonium salt of the precipitating anion.

Each mole of metal nitrate supplies two nitrate groups and therefore produces two moles of ammonium nitrate. Thus,

$$n(\text{MO}) = \frac{n(\text{NH}_4\text{NO}_3)}{2} = 0.0125 \text{ mol}.$$

The molar mass of the metal oxide is

$$M(\text{MO}) = \frac{0.70 \text{ g}}{0.0125 \text{ mol}} = 56 \text{ g mol}^{-1}.$$

Subtracting oxygen's contribution gives

$$M(M) = 56 - 16 = 40 \text{ g mol}^{-1},$$

identifying the metal as **calcium**.

The precipitate's mass per mole of calcium is

$$\frac{1.25 \text{ g}}{0.0125 \text{ mol}} = 100 \text{ g mol}^{-1}.$$

This matches calcium carbonate:

$$M(\text{CaCO}_3) = 40 + 12 + 3(16) = 100 \text{ g mol}^{-1}.$$

At 1100 °C, it decomposes according to



The predicted masses are

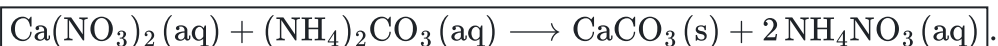
$$m(\text{CaO}) = 0.0125 \times 56 = 0.70 \text{ g},$$

$$m(\text{CO}_2) = 0.0125 \times 44 = 0.55 \text{ g}.$$

Their sum is 1.25 g, confirming the precipitate identification.

Original reaction

The two unknown compounds are consequently calcium nitrate and ammonium carbonate:



Evaporating the filtrate removes the solvent and leaves solid ammonium nitrate. The predicted residue mass is

$$2(0.0125 \text{ mol})(80.0 \text{ g mol}^{-1}) = 2.0 \text{ g},$$

in agreement with the problem.

The solution was checked against the official solution.

Problem 5: Shortest syntheses of ethyl benzoate and aminobenzoic acids

Using your knowledge about the properties of benzene and its derivatives, write chemical equations for reactions by which ethyl ester of benzoic acid as well as o-, m-, and p-amino benzoic acids are prepared in the shortest way.

Official English text of the problem.

Answers

Taking **benzene as the common starting material**, the conventional short routes are:

- **Ethyl benzoate**, CCOC(=O)c1ccccc1: benzene → toluene → benzoic acid → ethyl benzoate. **Three reactions.**

- **o-Aminobenzoic acid (2-aminobenzoic acid, anthranilic acid)**, Nc1ccccc1C(=O)O: benzene → toluene → 2-nitrotoluene → 2-nitrobenzoic acid → 2-aminobenzoic acid. **Four reactions.**
- **m-Aminobenzoic acid (3-aminobenzoic acid)**, Nc1cccc(C(=O)O)c1: benzene → toluene → benzoic acid → 3-nitrobenzoic acid → 3-aminobenzoic acid. **Four reactions.**
- **p-Aminobenzoic acid (4-aminobenzoic acid)**, Nc1ccc(C(=O)O)cc1: benzene → toluene → 4-nitrotoluene → 4-nitrobenzoic acid → 4-aminobenzoic acid. **Four reactions.**

Physical separation of isomers is not counted as a chemical reaction.

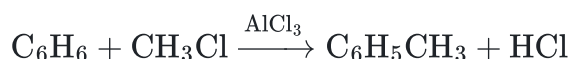
Solution

The essential choice is **when to nitrate**. A methyl group directs electrophilic substitution mainly to the **ortho and para** positions, whereas a carboxyl group directs it mainly to the **meta** position. In each aminobenzoic-acid synthesis, reduce the nitro group after oxidizing the methyl group, so that the amino group is not exposed to the strong oxidant.

The oxidation equations below are balanced **net ionic equations** for hot, acidified dichromate.

Ethyl ester of benzoic acid

First prepare toluene, Cc1ccccc1, by Friedel–Crafts methylation of benzene, c1ccccc1, with chloromethane, CCl, using anhydrous aluminium chloride:

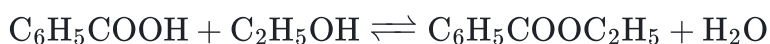


Use excess benzene to limit further methylation.

Oxidize the methyl side chain to obtain benzoic acid, O=C(O)c1ccccc1:



Finally, esterify with ethanol, CCO, by heating with catalytic sulfuric acid:

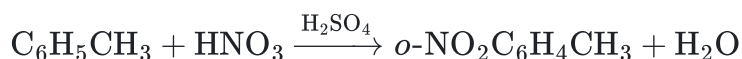


Excess ethanol or removal of water shifts the equilibrium toward ethyl benzoate.

o-Aminobenzoic acid

Prepare toluene by the methylation above, then nitrate it with concentrated nitric acid and sulfuric acid. Nitration gives mainly the ortho and para isomers, together with a small amount of the meta isomer. Separate the required ortho isomer, **2-nitrotoluene**, Cc1ccccc1[N+](=O)[O-].

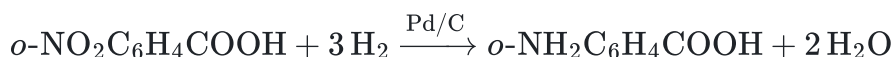
The equation for formation of the ortho product is:



Oxidize its methyl group to give **2-nitrobenzoic acid**, O=C(O)c1ccccc1[N+](=O)[O-]:



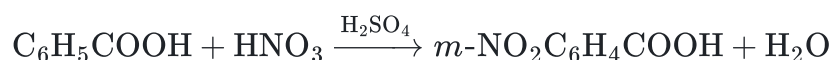
Then selectively hydrogenate the nitro group, for example using hydrogen over palladium on carbon:



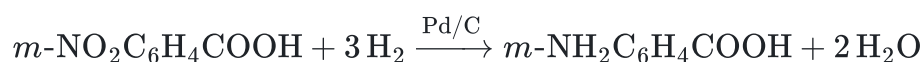
The substituents retain their positions throughout oxidation and reduction, giving 2-aminobenzoic acid.

m-Aminobenzoic acid

Prepare benzoic acid by the first two reactions of the ethyl-benzoate route. Nitrate it with concentrated nitric acid and sulfuric acid, using heat because the carboxyl group deactivates the ring:



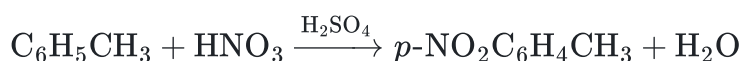
The carboxyl group is meta-directing, so the principal product is **3-nitrobenzoic acid**, O=C(O)c1cccc([N+](=O)[O-])c1. Isolate this product and reduce its nitro group:



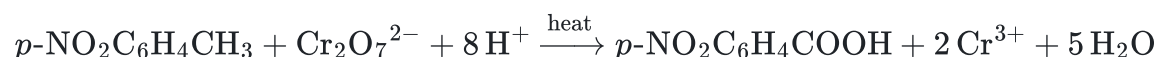
This gives 3-aminobenzoic acid.

p-Aminobenzoic acid

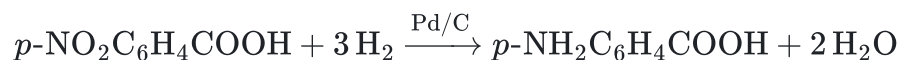
Prepare toluene and nitrate it as above, isolating the para fraction, **4-nitrotoluene**, Cc1ccc([N+](=O)[O-])cc1:



Oxidize the methyl group to obtain **4-nitrobenzoic acid**, O=C(O)c1ccc([N+](=O)[O-])cc1:



Finally, reduce the nitro group:



This gives 4-aminobenzoic acid without introducing an amino-protecting group.

For completeness, the additional molecular and ionic species used in these equations have the following SMILES:

Species	SMILES
Hydrogen chloride, HCl	<chem>Cl</chem>
Nitric acid, HNO ₃	<chem>O=[N+]([O-])O</chem>
Sulfuric acid, H ₂ SO ₄	<chem>OS(=O)(=O)O</chem>
Water, H ₂ O	<chem>O</chem>
Hydrogen, H ₂	<chem>[H][H]</chem>
Hydrogen ion, H ⁺	<chem>[H+]</chem>
Dichromate ion, Cr ₂ O ₇ ²⁻	<chem>[O-][Cr](=O)(=O)O[Cr](=O)(=O)[O-]</chem>
Chromium(III) ion, Cr ³⁺	<chem>[Cr+3]</chem>
Aluminium chloride, AlCl ₃ , monomeric representation	<chem>Cl[Al](Cl)Cl</chem>

These representations omit aqueous solvation; the aluminium chloride representation also omits its possible dimerization.

The solution was checked against the official solution.

Problem 6: Hydration of a mixture of two homologous hydrocarbons

A gaseous mixture containing two neighbour hydrocarbons of the same homologous series was 14.4 times as dense as hydrogen. This mixture with a volume of 16.8 dm³ was hydrated and 350 g of the solution were obtained when the products of hydration were absorbed in water. Ten grams of this solution were taken and heated in the presence of silver(I) oxide which was prepared from 70 cm³ of a 1 N silver(I) nitrate solution. Unreacted Ag₂O was dissolved in an aqueous ammonia solution and a residual precipitate was filtered off. The filtrate was acidified with nitric acid and addition of an excess of sodium bromide to it resulted in 9.4 g of a precipitate.

When the mixture of the hydrocarbons that remained unreacted, was mixed with a 50 % excess of hydrogen and transmitted above a heated Pt-catalyst, its resulting volume decreased to 11.2 dm³. Volumes of gases were measured in STP conditions.

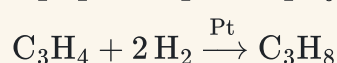
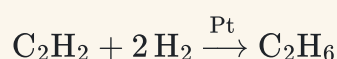
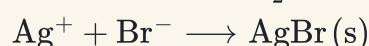
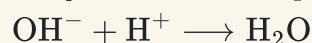
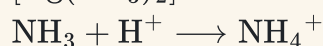
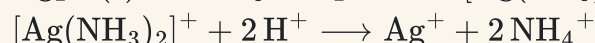
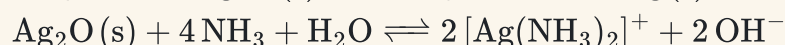
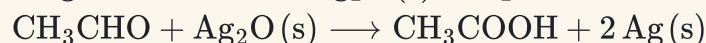
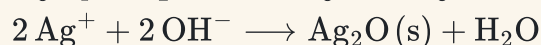
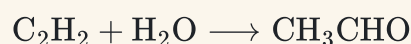
Problems:

- 6.1 What hydrocarbons were in the starting mixture?
- 6.2 Write chemical equations for the above mentioned reactions.
- 6.3 Calculate the composition of the starting mixture in % by volume.
- 6.4 How much (in %) of each hydrocarbon was hydrated?

Official English text of the problem.

Answers

- 6.1 **Ethyne (acetylene)**, C₂H₂, C≡C, and **propyne (methylacetylene)**, C₃H₄, CC≡C.
- 6.2 The balanced equations are listed below; the analytical reactions are written in net ionic form.



- 6.3 The starting mixture contained **80.0% ethyne and 20.0% propyne by volume**.
- 6.4 **58.3% of the ethyne and 100% of the propyne** were hydrated.

Solution

Use the conventional rounded atomic masses appropriate to these data:

$$A_r(\text{H}) = 1, \quad A_r(\text{C}) = 12, \quad A_r(\text{Ag}) = 108, \quad A_r(\text{Br}) = 80,$$

and the STP molar gas volume

$$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}.$$

6.1 Identification of the hydrocarbons

The relative density with respect to hydrogen, $[\text{H}][\text{H}]$, gives the mixture's mean molar mass:

$$\overline{M} = 14.4 M(\text{H}_2) = 14.4(2.00) = 28.8 \text{ g mol}^{-1}.$$

The silver experiment establishes that a hydration product reduces silver(I). Initially there were 0.070 mol of silver(I), whereas the final silver bromide precipitate accounts for only

$$\frac{9.4 \text{ g}}{188 \text{ g mol}^{-1}} = 0.050 \text{ mol}.$$

The difference represents silver reduced to the metal.

Ordinary alkene hydration produces alcohols, which do not give this aldehyde oxidation reaction. In ordinary alkyne hydration, ethyne produces **ethanal (acetaldehyde)**, $\text{CC}=\text{O}$, an aldehyde; higher alkynes produce ketones. Thus ethyne must be present.

Its neighbouring member in the same homologous series is propyne. Their molar masses,

$$M(\text{C}_2\text{H}_2) = 26.0 \text{ g mol}^{-1}, \quad M(\text{C}_3\text{H}_4) = 40.0 \text{ g mol}^{-1},$$

bracket the observed mean of 28.8 g mol^{-1} , as required.

6.2 Explanation of the reactions

The balanced equations are given in Answers 6.2.

Hydration of ethyne gives ethanal, while hydration of propyne gives **propanone (acetone)**, $\text{CC}(=\text{O})\text{C}$. In the usual acid-catalysed alkyne hydration, addition of water is followed by enol-carbonyl tautomerization.

Ethanal is oxidized to **ethanoic acid (acetic acid)**, $\text{CC}(=\text{O})\text{O}$. Each mole of ethanal reduces one mole of silver(I) oxide, producing **two moles of metallic silver**. Propanone does not undergo this aldehyde oxidation.

Silver(I) oxide can be prepared by adding hydroxide to the silver(I) nitrate solution. After oxidation, ammonia dissolves the remaining oxide by forming the soluble **diamminesilver(I) ion**, $[\text{NH}_3] \rightarrow [\text{Ag}^+] \leftarrow [\text{NH}_3]$. This ion has linear coordination around silver; the SMILES specifies the donor bonds but does not establish that geometry. Metallic silver remains as the precipitate that is filtered off.

Acidification with **nitric acid**, $\text{O}=[\text{N}^+](\text{O}^-)\text{O}$, protonates ammonia and destroys the silver-ammonia complex. Addition of **sodium bromide**, $[\text{Na}^+].[\text{Br}^-]$, then precipitates the remaining silver(I) as silver bromide.

The other molecular and ionic species in the analytical equations are:

Species	SMILES
Water	O

Species	SMILES
Ammonia	N
Silver(I) ion	[Ag+]
Hydroxide ion	[OH-]
Hydrogen ion, used as aqueous acid–base shorthand	[H+]
Ammonium ion	[NH4+]
Bromide ion	[Br-]
Silver(I) oxide, ionic formula unit	[Ag+] . [O-2] . [Ag+]
Silver bromide, ionic formula unit	[Ag+] . [Br-]

The formula-unit SMILES for the solids do not represent their crystal lattices.

Complete hydrogenation over heated platinum gives **ethane**, CC, from ethyne and **propane**, CCC, from propyne. Each alkyne requires two moles of hydrogen per mole. The calculation in 6.4 will show that only ethyne actually remains for this stage.

6.3 Composition of the starting mixture

Let x be the mole fraction of ethyne. For gases measured under the same conditions, mole fraction equals volume fraction. Therefore,

$$26.0x + 40.0(1 - x) = 28.8,$$

so

$$x = \frac{40.0 - 28.8}{40.0 - 26.0} = 0.800.$$

Hence the volume composition is

80.0% ethyne, 20.0% propyne.

The initial total amount was

$$n_0 = \frac{16.8 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.750 \text{ mol}.$$

Thus,

$$n_0(\text{C}_2\text{H}_2) = 0.800(0.750) = 0.600 \text{ mol},$$

$$n_0(\text{C}_3\text{H}_4) = 0.200(0.750) = 0.150 \text{ mol}.$$

6.4 Percentage of each hydrocarbon hydrated

For **silver(I) nitrate**, [Ag+] . [O-] [N+] (=O) [O-], one mole supplies one equivalent of silver(I), so the 1 N solution contains 1 mol dm^{-3} of silver(I). The initial amount of silver in the aliquot experiment was therefore

$$n_{\text{Ag,initial}} = (0.070 \text{ dm}^3)(1 \text{ mol dm}^{-3}) = 0.070 \text{ mol}.$$

The unreduced silver was recovered as silver bromide:

$$n_{\text{Ag,unreduced}} = \frac{9.4 \text{ g}}{188 \text{ g mol}^{-1}} = 0.050 \text{ mol}.$$

Consequently,

$$n_{\text{Ag, reduced}} = 0.070 - 0.050 = 0.020 \text{ mol.}$$

Because one mole of ethanal produces two moles of silver, the 10 g aliquot contained

$$n_{\text{ethanal, aliquot}} = \frac{0.020}{2} = 0.010 \text{ mol.}$$

The full 350 g solution therefore contained

$$n_{\text{ethanal, total}} = 0.010 \left(\frac{350}{10} \right) = 0.350 \text{ mol.}$$

Hydration produces one mole of ethanal per mole of ethyne, giving

$$n_{\text{ethyne, hydrated}} = 0.350 \text{ mol.}$$

Thus the percentage of ethyne hydrated was

$$\boxed{\frac{0.350}{0.600} \times 100 = 58.3\%}$$

The amount of ethyne remaining was

$$0.600 - 0.350 = 0.250 \text{ mol.}$$

To determine propyne conversion, let u be the total number of moles of unhydrated alkynes. Complete hydrogenation requires $2u$ moles of hydrogen. With a 50% excess, the amount added was

$$n_{\text{H}_2, \text{added}} = 1.50(2u) = 3u.$$

After hydrogenation, the gas contains u moles of alkanes and $3u - 2u = u$ moles of excess hydrogen. Its total amount is therefore $2u$:

$$2u = \frac{11.2 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.500 \text{ mol,}$$

giving

$$u = 0.250 \text{ mol.}$$

This equals the amount of ethyne already known to remain. Therefore no propyne remained:

$$n_{\text{propyne, unhydrated}} = 0.250 - 0.250 = 0.$$

All 0.150 mol of the original propyne was hydrated:

$$\boxed{\text{Propyne hydrated} = 100\%}$$

As a volume check, the final gas consists of 0.250 mol of ethane and 0.250 mol of hydrogen, occupying $5.60 + 5.60 = 11.2 \text{ dm}^3$ at STP.

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.