

Problema 22 **Delightful odor of truffle**

The compound X is responsible for the divine smell of the black truffle. The treatment of 0.108 g of compound X with the acidified solution of HgSO_4 leads to the formation of some precipitate Z. The treatment of the formed organic compound A with the excess of $\text{Ag}(\text{NH}_3)_2\text{OH}$ afforded 0.432 g of metallic silver. Gas formed as a result of the burning of 0.648 g of compound X was divided into two equal parts. One part was passed through the $\text{Ba}(\text{OH})_2$ solution, 3.075 g of precipitate was formed. Another part was passed through NaOH solution. After some time the excess of BaCl_2 solution was added. It led to the formation of 3.171 g of precipitate

Write down the structural formulae of compounds X, Z, A. Determine the weight of the precipitate Z. Assume that all reactions proceed with 100% yield.

Solution:

The treatment of compound X with the acidified solution of HgSO_4 leads to the formation of some precipitate Z, then Z must be HgS . The organic compounds formed after the precipitation of sulphur may be alcohol or aldehyde. Only the aldehyde can react with the Tollens solution.

The Tollens reaction produced 0.432 g of Ag, that is 4 mmol of Ag.

If the reaction was $\text{aldehyde} + 2 \text{Ag}^+ \rightarrow \text{carboxylic acid} + 2 \text{Ag}$

where the aldehyde oxidation needs 2 electrons, then 4 mmol of Ag^+ can oxidize 2 mmol of aldehyde.

In this case PM of compound X is $0,108 \text{ g} / 2 \cdot 10^{-3} = 54 \text{ g/mol}$

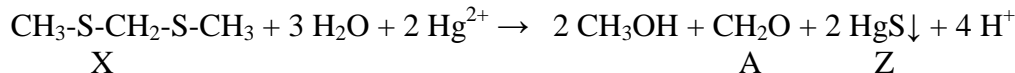
If the reaction was $\text{formaldehyde} + 4 \text{Ag}^+ \rightarrow \text{carbonic acid} + 4 \text{Ag}$

where the formaldehyde oxidation needs 4 electrons, then 4 mmol of Ag^+ can oxidize 1 mmol of formaldehyde. In this second case PM of compound X is $0,108 \text{ g} / 10^{-3} = 108 \text{ g/mol}$

The correct PM is 108 g/mol because two S are 64 g/mol a value that exceeds 54 g/mol.

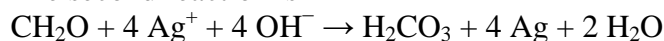
A possible structure that produces formaldehyde is $\text{CH}_3\text{-S-CH}_2\text{-S-CH}_3$ and its PM is exactly 108 g/mol.

The first reaction then is



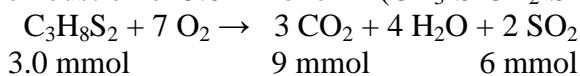
From 0.108 g of X, 1 mmol, we obtain 2 mmol of precipitate Z: mass of 2 mmol of $\text{HgS} = 0.465 \text{ g}$.

The second reaction is

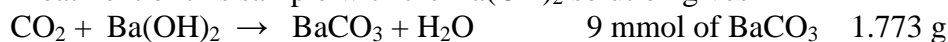


For the combustion we have 0.648 g of X, $0.648/108 = 6.0 \cdot 10^{-3} \text{ mol}$ of X ($\text{CH}_3\text{-S-CH}_2\text{-S-CH}_3$)

Combustion of 3.0 mmol of X ($\text{CH}_3\text{-S-CH}_2\text{-S-CH}_3 = \text{C}_3\text{H}_8\text{S}_2$) gives



Treatment of this sample with the $\text{Ba}(\text{OH})_2$ solution gives



That is 3.075 g of precipitate.

The second treatment of an identical sample at first with NaOH and, after some time, with an excess of BaCl_2 , lets SO_3^{2-} to be oxidized to SO_4^{2-} , then the precipitate is BaCO_3 and BaSO_4 .

9 mmol of BaCO_3 1.773 g

6 mmol of BaSO_4 1.398 g

That is 3.171 g of precipitate.

This confirms the identity of compound X: $\text{CH}_3\text{-S-CH}_2\text{-S-CH}_3$

Soluzione proposta da

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