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 $Ag(NH_3)_2OH$ 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 $Ba(OH)_2$ 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 aldehyde + 2 $Ag^+ \rightarrow$ carboxylic acid + 2 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 g / 2 10^{-3} = 54 g/mol
If the reaction was formaldehyde + 4 $Ag^+ \rightarrow$ carbonic acid + 4 Ag
where the formaldehyde oxidation needs 4 electrons, then 4 mmol of Ag^+ con oxidize 1 mmol of formaldehyde. In this second case PM of compound X is 0,108 g / 10^{-3} = 108 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 CH_3-S-CH_2-S-CH_3 and its PM is exactly 108 g/mol.
The first reaction then is

$$\underset{X}{CH_3\text{-}S\text{-}CH_2\text{-}S\text{-}CH_3} + 3\ H_2O + 2\ Hg^{2+} \rightarrow \underset{A}{2\ CH_3OH} + \underset{Z}{CH_2O} + 2\ HgS\downarrow + 4\ H^+$$

From 0.108 g of X, 1 mmol, we obtain 2 mmol of precipitate Z: mass of 2 mmol of HgS = 0.465 g.
The second reaction is

$$CH_2O + 4\ Ag^+ + 4\ OH^- \rightarrow H_2CO_3 + 4\ Ag + 2\ H_2O$$

For the combustion we have 0.648 g of X, 0.648/108 = 6.0 10^{-3} mol of X (CH_3-S-CH_2-S-CH_3)
Combustion of 3.0 mmol of X (CH_3-S-CH_2-S-CH_3 = $C_3H_8S_2$) gives

$$\underset{3.0\ mmol}{C_3H_8S_2} + 7\ O_2 \rightarrow \underset{9\ mmol}{3\ CO_2} + \underset{6\ mmol}{4\ H_2O} + 2\ SO_2$$

Treatment of this sample with the $Ba(OH)_2$ solution gives

$CO_2 + Ba(OH)_2 \rightarrow BaCO_3 + H_2O$ 9 mmol of $BaCO_3$ 1.773 g
$SO_2 + Ba(OH)_2 \rightarrow BaSO_3 + H_2O$ 6 mmol of $BaSO_3$ 1.302 g

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: CH_3-S-CH_2-S-CH_3

Soluzione proposta da
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