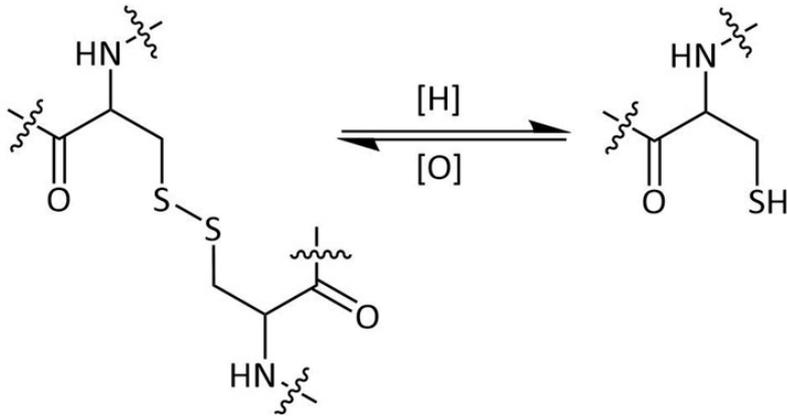


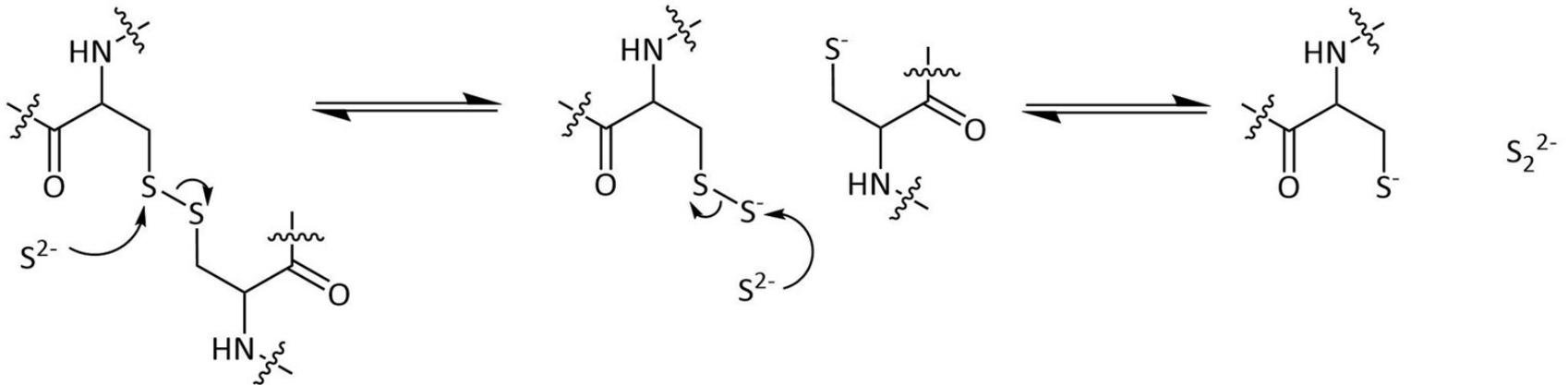
# SULFIDE UNHAIRING: RETHINKING THE RECEIVED WISDOM

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# Previously accepted mechanism

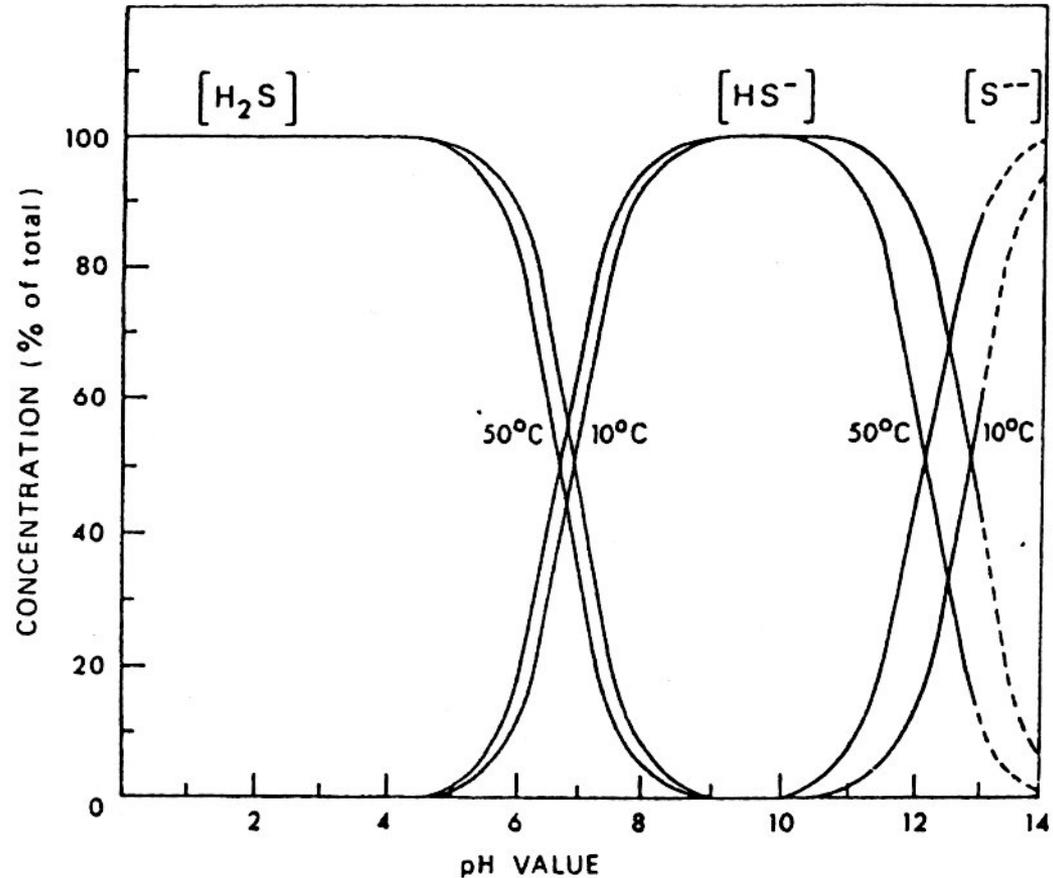


- ▶ Sulfide attacks disulfide bond of cystine
- ▶ Disulfide link is broken
- ▶ Creating cysteine moieties and the sulfide is converted to polysulfide



# Previously accepted mechanism

- ▶ The mechanism presented is based on an assumption.
- ▶ Equilibria between hydrosulfide and sulfide at pH values familiar in lime liquor.
- ▶ Fits with observation



# The problem



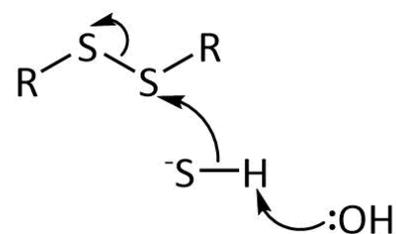
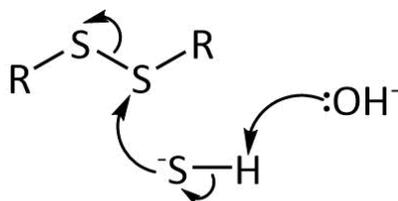
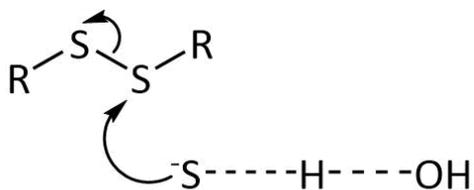
- ▶ The problem lies in the pKa value of HS<sup>-</sup> to S<sup>2-</sup>
  - Long thought to have a low pKa ~13.
- ▶ In 2018 new research revised the pKa value upwards to ~19
  - Could not detect presence of S<sup>2-</sup> in concentrated solutions of KOH/CsOH by Raman spec. pH > 14
- ▶ As a result S<sup>2-</sup> will not be present in lime!
- ▶ So how does unhairing work?

# What do we know?

- ▶ Before postulating a new mechanism consider what we already know:
  - It is a pH dependent process.
  - Unlikely to involve  $S^{2-}$ .
  - Mechanism must still involve breakdown of disulfide bond.
  - ... but that mechanism and formation of polysulfide will have to be redefined
- ▶ What does this suggest?
  - The rate equation and mechanism must involve  $OH^-$

# New reaction mechanism?

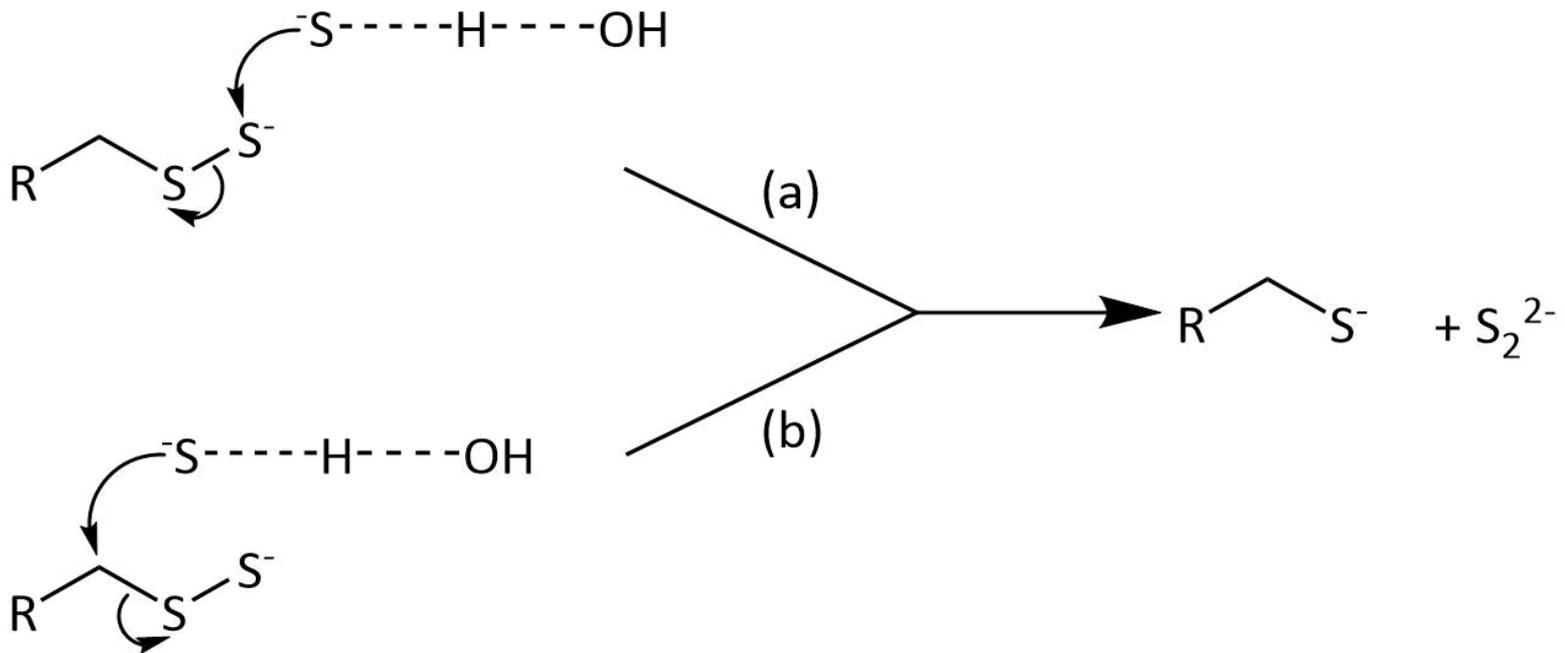
- ▶ Original mechanism was two step: address each step in turn – Step 1 disulfide attack:



- ▶ Analogous to original mechanism.
- ▶ Same result – different way of depicting the mechanism.
- ▶ Uses OH<sup>-</sup> to increase nucleophilicity of HS<sup>-</sup>.
- ▶ No S<sup>2-</sup> actually formed.
- ▶ Concerted reaction mechanism?

# New reaction mechanism?

- ▶ Step 2 - formation of polysulfide.



# Conclusions and implications

- ▶ New mechanisms are postulations only.
- ▶ Research required to determine exactly which route.
- ▶ Better understanding of process may lead to greater potential for innovation
- ▶ By whichever is the cheaper material, hydrosulfide or sulfide:
  - No difference in speciation between the two
  - Makes a minor difference to possible lime loading
- ▶ No change to processing – yet.

Thank you for your  
attention!

Vielen Dank für Ihre  
Aufmerksamkeit!

