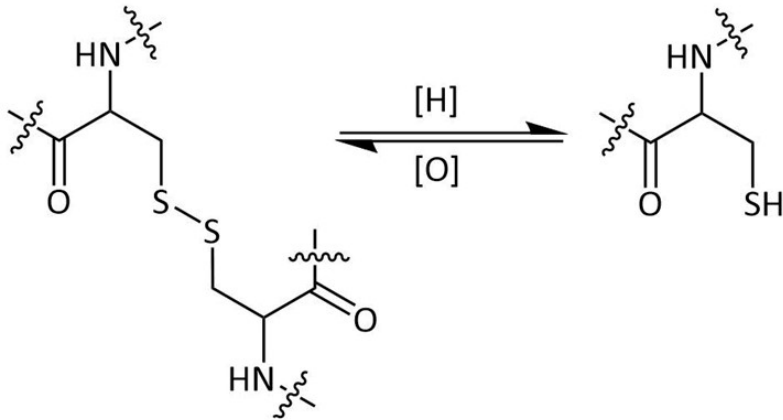


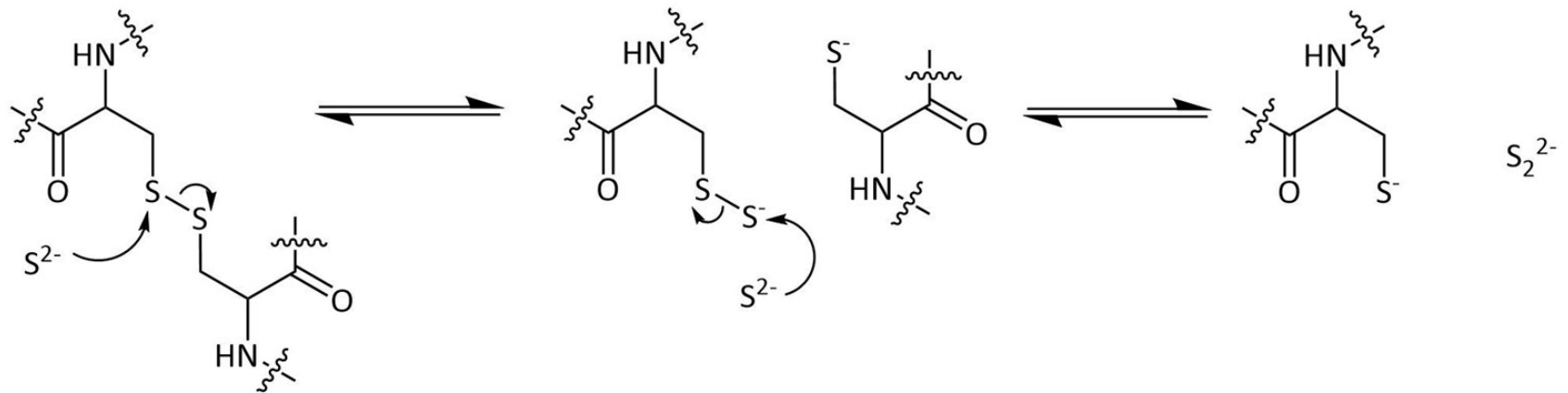
SULFIDE UNHAIRING: RETHINKING THE RECEIVED WISDOM

A. D. Ballantyne, A. D. Covington, W. R. Wise

Previously accepted mechanism

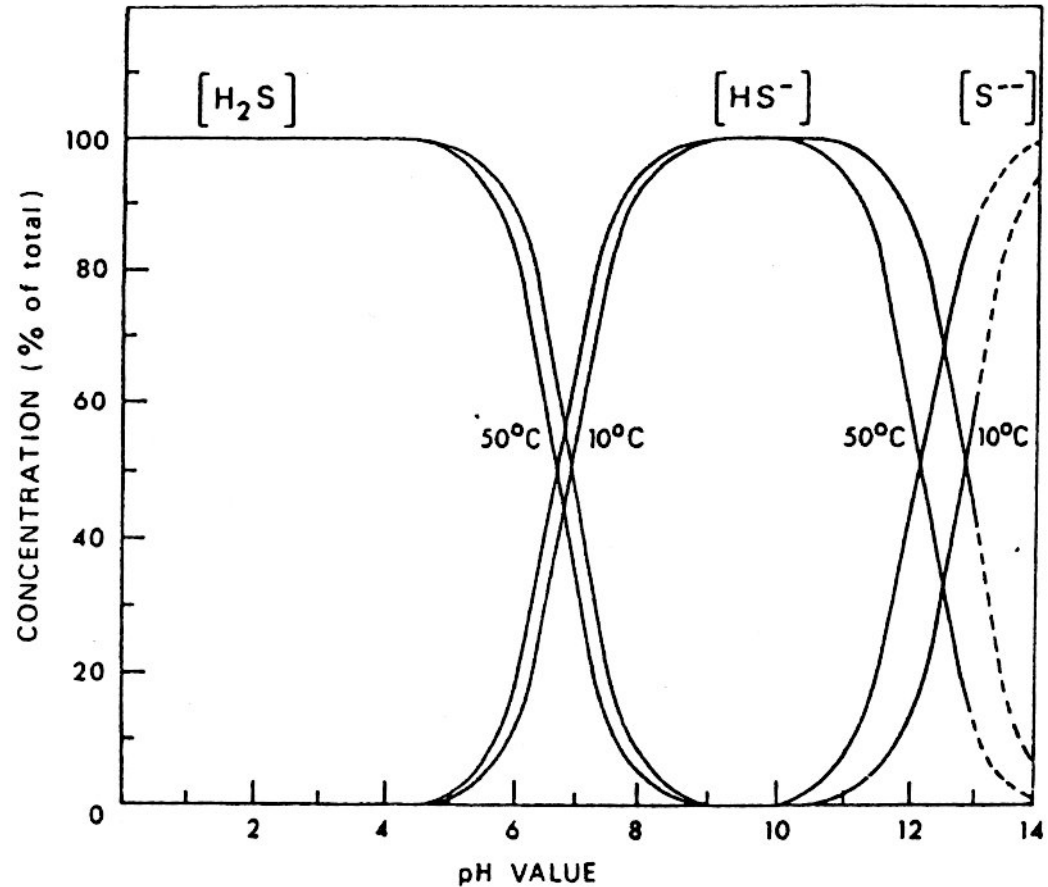


- ▶ Sulfide attacks disulfide bond of cystine
- ▶ Disulfide link is broken
- ▶ Creating cysteine moieties and the sulfide is converted to polysulfide



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



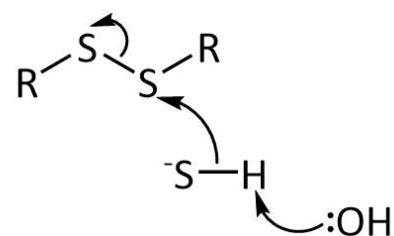
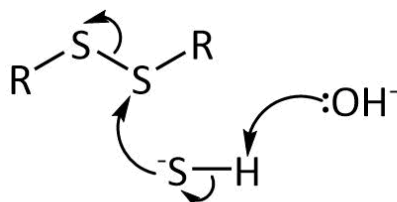
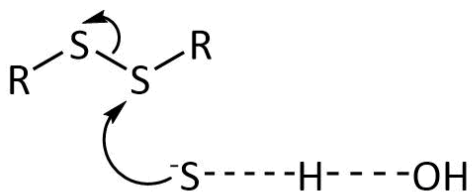
- ▶ The problem lies in the pKa value of HS⁻ to S²⁻
 - Long thought to have a low pKa ~13.
- ▶ In 2018 new research revised the pKa value upwards to ~19
 - Could not detect presence of S²⁻ in concentrated solutions of KOH/CsOH by Raman spec. pH > 14
- ▶ As a result S²⁻ will not be present in lime!
- ▶ 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?

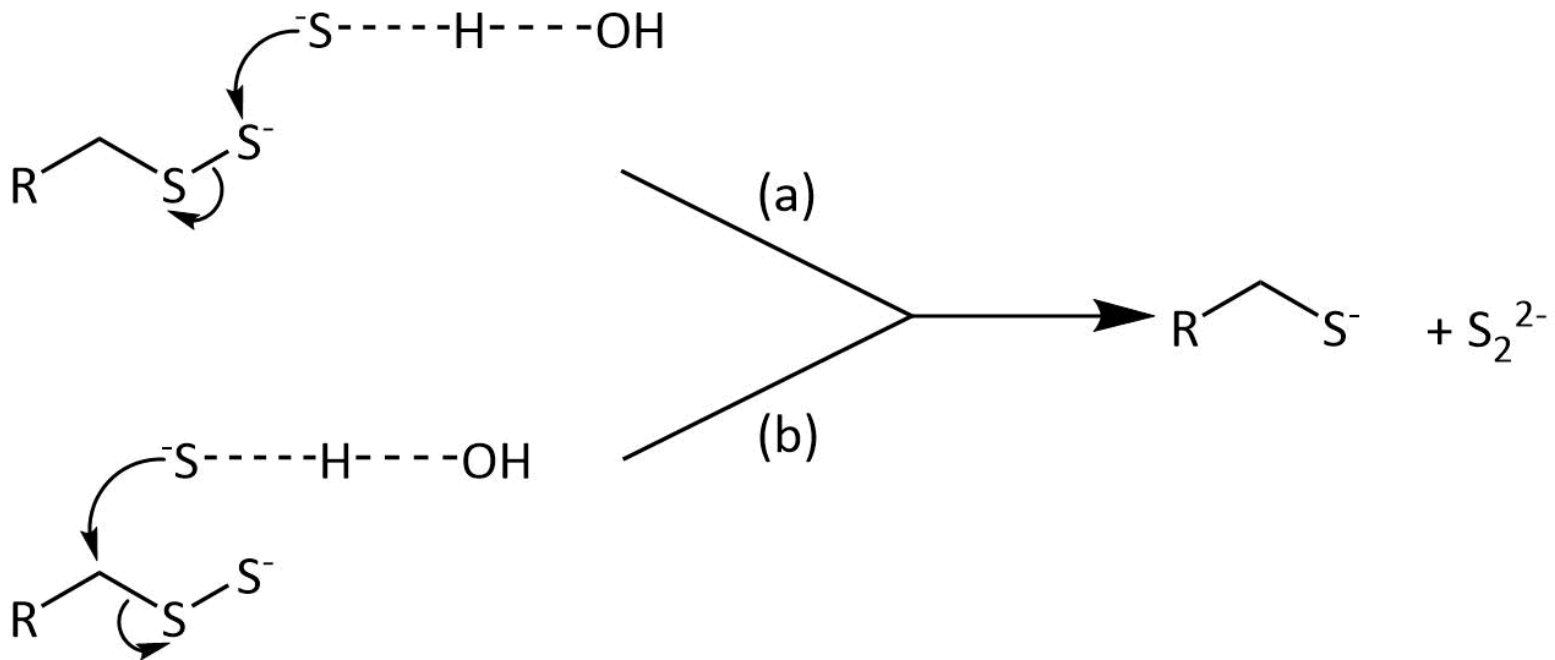
- ▶ Original mechanism was two step: address each step in turn – Step 1 disulfide attack:



- ▶ Analogous to original mechanism.
- ▶ Same result – different way of depicting the mechanism.
- ▶ Uses OH⁻ to increase nucleophilicity of HS⁻.
- ▶ No S²⁻ 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!

