SULFIDE UNHAIRING: RETHINKING THE RECEIVED WISDOM

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Abstract. The removal of hair from a hide or skin by dissolving it with a mixture of lime and sulfide is a fundamentally understood feature of leather technology. Or is it? For a long time, it has been accepted within the leather literature that, in water, sulfide may be present as either hydrogen sulfide (H2S), hydrosulfide (HS-) or sulfide (S2-), depending on the pH.

$$\begin{array}{ccccc} pH < 6 & & 6 < pH < 12 & & pH > 12 \\ H_2S_{(aq)} & \rightleftharpoons & HS^-_{(aq)} & \rightleftharpoons & S^{2-}_{(aq)} \end{array}$$

The generally accepted mechanism of hair burning is sulfide attack at the cystine disulfide linkages in keratin. Also, it is believed that the unhairing reaction only proceeds at an appreciable rate in the presence of the dianionic S2- species, because that fits with the technological observation that unhairing reactions only proceed at pH greater than 12. However, recent publications have provided substantive proof that the S2- species does not exist in aqueous media at any pH: researchers were unable to observe any evidence of the S2- species in a solution of Na2S dissolved in hyper-concentrated NaOH and CsOH using Raman spectroscopy. The assigned second pKa for removal of the second proton has now been estimated to be 19, making the concentration of S2- (see below) vanishingly small.

$$HS^- \leftrightharpoons S^{2-} + H^+$$

There is a clear contradiction between the currently accepted mechanism for sulfide unhairing with the evidenced speciation of sulfide species in aqueous environment. Here the implications for this important process are discussed and possible alternative mechanisms postulated that fit with the new knowledge.

1 Introduction

The subject of Leather Science is relatively young, certainly less than a century old, and has had relatively few practitioners. Consequently, certain myths about the mechanisms of processes fundamental to leather processing have been perpetuated: examples are the underlying principles of chromium(III) tanning and masking.[1] The process of hair burning unhairing with lime and sulfide is such an accepted part of leather technology that it might come as a surprise to be told that the understanding of the chemistry is flawed.

It has long been accepted that, in water, sulfide is speciated as follows (Equation 1).

$$\begin{array}{ccccc} pH < 6 & & 6 < pH < 12 & & pH > 12 \\ H_2S_{(aq)} & \rightleftharpoons & HS^-_{(aq)} & \rightleftharpoons & S^{2-}_{(aq)} \end{array} \qquad \text{Equation 1}$$

Consequently, the previously accepted mechanism for sulfide degradation of keratin at pH>11, presented in Fig. 1, can be summarised as follows, defining what is known unequivocally.[2] At high pH, the reducing nucleophilic sulfide ion attacks the disulfide bond of cystine. The disulfide link is broken, creating cysteine moieties and the sulfide is converted to polysulfide.

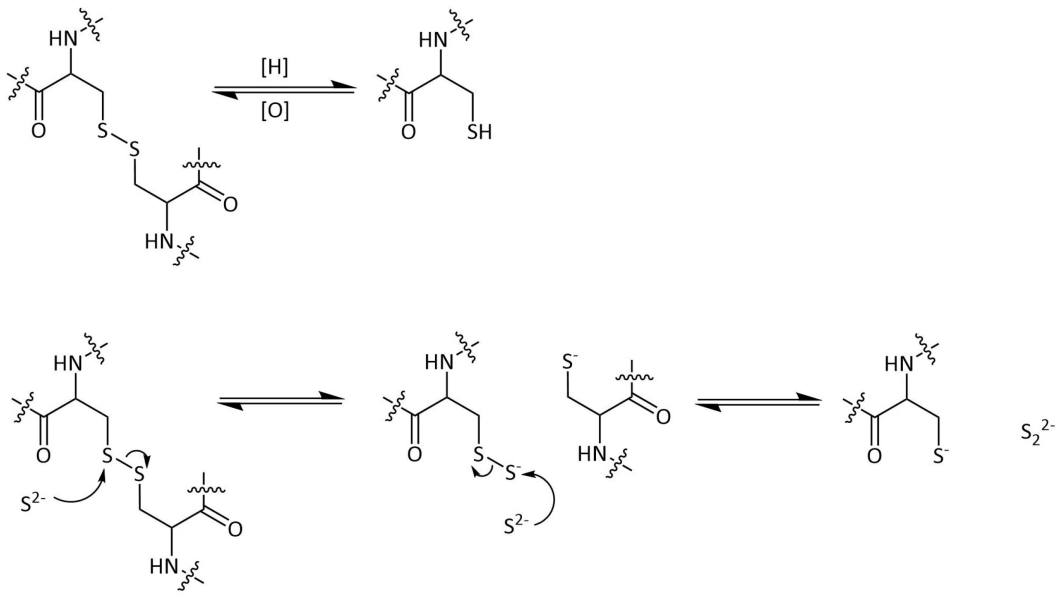

Fig. 1. The previously accepted mechanism of sulfide hair burning.

It is assumed the polymerisation of sulfur will not progress much further, because the bisulfide ion is a weaker nucleophile than sulfide and therefore is less effective in attacking the disulfide link. This can be seen in Table I, setting out the oxidation potentials:[3] note the reducing power of the reactions will depend on the precise chemical conditions, particularly pH.

Table 1. Standard reduction potentials for sulfide species.

Species	Standard reduction potential, E^0 (mV)
$H_2S \leftrightharpoons S + 2H^+ + 2e^-$	-0.142
$HS^- + OH^- \leftrightharpoons S + H_2O + 2e^-$	+0.478
$S^{2-} \leftrightharpoons S + 2e^-$	+0.476
$S_2^{2-} \leftrightharpoons 2S + 2e^-$	+0.428

The relative power of oxidising can be judged because of the following equation, which relates the Gibbs free energy to the standard electrode potential (Equation 2).

$$\Delta G^o = -nFE^o \qquad \text{Equation 2}$$

where: n is the number of faradays (the number of electrons in the reaction) and F is the Faraday constant. A positive electrode potential results in a negative free energy, which means a spontaneous or favoured reaction.

The mechanism presented in Fig. 1 is based in part on the assumption of the relationships between the sulfide species, in particular the low pKa of the second ionisation, long thought to be ~13, which creates equilibria between hydrosulfide and sulfide at pH values familiar in lime buffer.[2]

2 The Problem

A large question mark has been raised over the chemistry of sulfide: the very existence of the S^{2-} species in aqueous solution has been queried.[4]

The problem lies in the value of the pKa of the dissociation of HS^- to S^{2-}: the previously assumed value of 13 has been revised upwards to 19, which means at pH 12.6 the concentration of sulfide ion in water can only be vanishingly small.[3] The latest argument is based on high resolution Raman spectrometry, which could not confirm the presence of sulfide, whilst it was clear that hydrosulfide was still detectable at very high pH.[4] The conclusion is not completely confirmed and accepted, but the evidence is compelling, so the new situation must be addressed and the implications reviewed.[5]

Up to 2014, the literature reported the value for the second dissociation constant of hydrogen sulfide at 12.9. The recent suggestion is that the value is not correct and a more accurate value for pKa2 should be about 17. There is controversy concerning the revised number and there appears to be some agreement that it should be 19: either way, this would in effect eliminate sulfide ion from consideration in aqueous medium. There is supporting evidence for this proposal in the literature; it is not as yet accepted chemistry, although current and recent editions of the 'Rubber Book' quote pKa2 as 19.3.[3] Therefore, the possibility should be recognised and the implications for the leather industry assessed.

In 1946, Bowes assumed, without reference to pKa values, that sulfide was hydrolysed to completion at pH 12 (Equation 3):

$$Na_2S + H_2O \rightleftharpoons 2Na^+ + HS^- + OH^- \qquad \text{Equation 3}$$

and therefore, the unhairing agent is hydrosulfide.[6] It may be noted from Table I that the quoted redox potentials for sulfide and hydrosulfide are the same in older reference sources[2] and in the latest definitive references.[3]

In 1956, Merrill reviewed the literature on unhairing,[7] reporting that some sulfur is lost from degraded keratin and Bienkiewicz states that sulfide-based hair dissolving is negligible below pH 11.2. Sodium hydroxide is ineffective as a pulping agent below pH 13, so there is a clear pH effect on sulfide-based unhairing. The implication is that the rate can be expressed in the following generalised ways:

$$\text{rate } (S^{2-}) = k_s[S^{2-}]^a \qquad \text{Equation 4a}$$

$$\text{rate } (HS^-) = k_{HS}[HS^-]^a[OH^-]^b \qquad \text{Equation 4b}$$

But the order of the reaction has not been defined. If the revised case applies (Equation 4b), the mechanism of attack at the disulfide link and formation of polysulfide will also have to be redefined.

3 The solution?

The revised mechanism must incorporate the hydroxide ion and generate a polysulfide species as is observed practically. Assuming that the mechanism still involves a two-step process then addressing each step in isolation simplifies the issue. It is possible that the first step is analogous to the previously accepted sulfide mechanism but, instead, involves the attack of an activated hydrosulfide ion where the activity is increased by simultaneous abstraction of the proton as illustrated in Fig. 2.

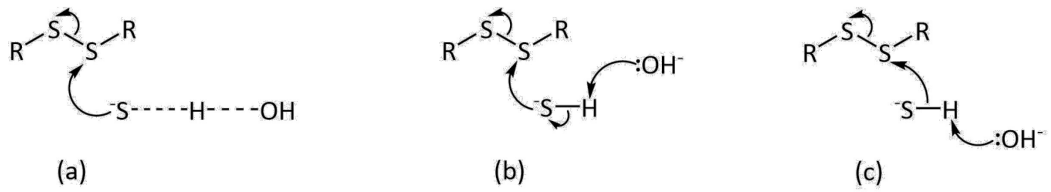

Fig. 2. Initial attack of the disulfide bond by the activated hydrosulfide species – a, b and c all illustrate subtle variations in way in which hydrosulfide activation could be imagined but lead to the same end result.

The second step involves conversion of the intermediate species to a cysteine residue generating the polysulfide species. This step too must be rethought due to the elimination of sulfide from the originally accepted mechanism; the authors of this paper propose two possible mechanisms by which this might be achieved shown in Fig. 3.

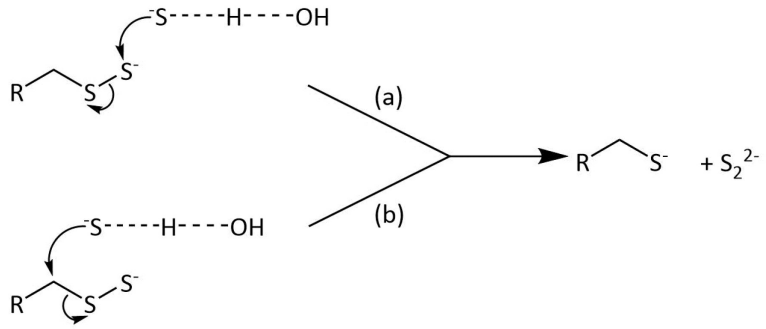

Fig. 3. Two proposed mechanisms (a – top and b – bottom) for conversion of the intermediate species to the cysteine residue.

The first of these mechanisms (Fig. 3a.) is analogous to step 1 where by the hydrosulfide ion undergoes some sort of activation by the hydroxide ion and subsequently attacks the primary sulfide in the intermediate species. However, studies would have to demonstrate that the activated ion is a strong enough nucleophile to attack an already negatively charged moiety.

Alternatively, the authors propose a different mechanism (Fig. 3b) where the hydrosulfide ion might attack the carbon adjacent to the disulfide. As illustrated this mechanism still produces the observed products (polysulfide and cysteine) but might be energetically favoured as it does not involve direct nucleophilic attack on an already negatively charged moiety.

4 The Consequences

The theoretically required amount of sulfide can be calculated to be 0.8% Na_2S or 0.6% NaHS ≡ 1.1 or 0.8% sulfide flake: where 'flake' is industrial sodium sulfide or sodium hydrosulfide, both quoted by the manufacturer as 70% Na_2S or NaHS respectively.[5] The typical industrial offer is 2-3% 'sulfide' flake i.e. at least double the theoretical requirement and since this is considerably higher than the range quoted for calculated amounts, the doubt concerning the sulfide species does not affect the unhairing technology.

Regarding the relationship between hydrosulfide and hydrogen sulfide, there is no suggestion in the literature that there is any error in pKa1 (accepted to be 7). The accepted conditions for hydrogen sulfide gas formation remain and are critical for safety.

5 Conclusion

This paper highlights the issues of preserved wisdom and the impact that this has on control of developments and improvements. In this case however whilst the new view of sulfide speciation does change the science and the mechanism of hair degradation, it does not change the observations made about the reaction nor does it change the current technology of the processing step. It was always an option to combine lime with hydrosulfide, since the equilibrium pH is 12.6, so there need be no process change there. However, it begs the question, what is the difference between reagents labelled NaSH and Na_2S? If the new findings are accepted, once dissolved in an aqueous medium the reagent labelled sodium sulfide is merely sodium hydrosulfide plus some sodium hydroxide.

The commercial consequence is: buy the cheaper version and carry on regardless!

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