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Primary Alkane Sulfonates¹

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ABSTRACT

The purpose of this paper is to draw attention to two neglected subjects in the field of surfactants: one is the class of compounds of primary alkane sulfonates (PAS), which have so far found no commercial success; the other is the process of sulfitation by which they are made, for which the state of the art has no satisfactory mechanism.

Primary alkane sulfonates (PAS) have been around for quite some time. In fact, they are the oldest properly identified synthetic detergent, dating back to 1913 when Reychler (1), who was at that time investigating the properties of palmitates, synthesized the equivalent hexadecane sulfonate by oxidizing cetyl mercaptan. The significance of this synthesis is not in its practicality, but in its historic importance: it stands to synthetic detergents as Wohler's synthesis of urea in 1828 stands to organic chemistry. Reychler's historic synthesis is shown below:

 $RI + NaSH \longrightarrow RSH + NaI$ $RSH + 2 KMnO_4 \longrightarrow RSO_3 K + 2 MnO_2 + KOH$ $RSO_3 K + Pb(AcO)_2 \longrightarrow (RSO_3)_2 Pb$ $(RSO_3)_2 Pb + H_2 S \longrightarrow RSO_3 H$ yield: 30-50%

Between 1913 and the early 1930s, there were quite a number of prominent chemists with an interest in this subject (2-9), but Reychler's synthesis remained the state of the art until Reed and Tartar (10,11) applied the Strecker reaction to obtain PAS in good yield. This reaction is shown below:

$$RBr + Na_2 SO_3 \xrightarrow{200 C} RSO_3 Na + NaBr$$
$$RBr + H_2 O \longrightarrow ROH by product$$

yield: 70%

Another Strecker-type reaction is shown below, in which alkyl halide was replaced with a more accessible alkyl sulfate, as first reported by Schrauth (7).

$$ROSO_3 Na + Na_2 SO_3 \xrightarrow{160 C} RSO_3 Na + Na_2 SO_4$$

Some years later, Weil et al. (12) obtained PAS in fair yield by decarboxylating salts of α -sulfo-acids in strong alkali medium. They reported ca. 30% desulfonation, so that the product contained that much soap.



All these processes had only academic value, having been designed solely for investigating the end product. However, with the advent of commercially available α -olefins, there followed a large number of patents concerning the process of sulfitation of 1-olefins (13-30). The process for making PAS consists essentially of bringing together a solution of sulfite and bisulfite with the desired olefin with the aid of a suitable cosolvent. The initiator can be an organic peroxide of suitable half-life, or some other convenient oxidizing agent, like nitrates, air or inorganic peroxides (15,24,26,29, 31-36). Yields are high, and the product so obtained is colorless.

$$RCH=CH_2 + N_2HSO_3 \xrightarrow[cosolvent]{} RCH_2CH_2SO_3N_2$$
yield: 85-98%

This process has its roots in Kolker and Lapworth's work with the addition of HSO_3 to short-chain olefins and cyclohexene (6), and Kharasch's discovery of the peroxide effect (37) and discussed at length by his coworker Mayo in 1940 (38). That dissertation by Mayo is the most comprehensive article on the theoretical aspects of the peroxide effect in general, and the sulfitation of olefins in particular, and every publication since has lamented the absence of additional work to elucidate the reaction mechanism.

The facts known about this reaction are as follows.

Position of double bond. There is a qualitative difference between terminal and internal olefins. With long-chain terminal olefins there is practically complete conversion, but with long-chain internal olefins there is no reaction. As shown by Kolker and Lapworth, and 40 years later by Norton and others, there is partial conversion with internal olefins that are in a *cis* configuration, or that have the double bond exposed, as in cyclohexene, which suggests a steric effect.

Position of sulfonic group. The sulfonic group always goes to the terminal position in an anti-Markownikoff way. There is no evidence whatever for any other positioning of the sulfonic group, except perhaps in the case of disulfonates, the formation of which is likely, but which have not yet been isolated and idenified.

Rate of reaction. The effect of peroxide (or of any oxidant used in this reaction) is not in directing the position of the sulfonic group, but in generating and speeding up the reaction. We were able to obtain good yields of PAS without addition of peroxide, and these sulfonates were identical with the ones obtained in presence of peroxides, as proven

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by physical properties and by NMR. However, the reaction took ca. 35-40 hr, compared to ca. 4-6 hr with catalytic amounts of peroxide. (It must be noted that no attempt was made to exclude contact with air, so that some peroxide may have been present.)

Additional evidence in favor of the free radical nature of this reaction is that presence of an antioxidant stops it (37,38).

Yield. Yield is affected by pH, which is understandable in the light of relative concentration of sulfite and bisulfite ions. Various authors, including ourselves, have different opinions about what that preferred pH range is (20,21, 23-25,28,39).

A rather puzzling effect is the dependence of conversion on the nature of the cosolvent in the reaction medium. Thus Norton, who has given the matter close attention (40), reported that the yield can vary by as much as between 6 and 90% with the kind of cosolvent used, everything else being equal. This suggests a specific role of cosolvent as a chain transfer agent.

Other aspects. The net effect of sulfitation is the abstraction of a proton from bisulfite, which causes the pH to rise; a side reaction is the oxidation of bisulfite to sulfate, which, of course, causes the pH to drop.

None of the mechanisms proposed so far for this reaction agrees with all these facts. Actually, only one such mechanism is generally accepted as valid in articles and textbooks, and that is the mechanism postulated by Kharasch in 1938 (37):

Initiation:

$$SO_3^{2-}$$
 + oxidant \longrightarrow SO_3^{-} + oxidant

Propagation:

 $SO_3 + RCH=CH_2 \longrightarrow RCHCH_2 SO_3^-$ RCHCH_2 $SO_3^- + HSO_3^- \longrightarrow RCH_2 CH_2 SO_3^- + SO_3^-$

Kharasch, who discovered the so-called "peroxide effect" in the addition of HBr to olefins, tried to translate that mechanism to the addition of bisulfite to olefins (37, 38,41). However, that translation does not work smoothly, for the following reasons:

- (1) Peroxide does not have the same effect with bisulfite as it has with HBr. In the latter case, for which this effect is specific, presence or absence of peroxide determines the nature of the addition. Without peroxide, there is an ionic reaction resulting in normal (or Markownikoff) addition. With peroxide, there is free radical addition resulting in abnormal (or anti-Markownikoff) addition. This is not the case with bisulfite. There is no evidence of any normal addition of bisulfite to α olefins. In sulfitation reactions, peroxide determines whether reaction would take place at all, and how fast it would go, not how it would go.
- (2) The Kharasch mechanism does not explain why sulfitation does not work with internal olefins.
- (3) Other difficulties with the Kharasch mechanism are:
 - (a) it assumes prolonged coexistence of a strong oxidant with a strong reducing agent, and that the main reaction between the two would be the abstraction of only one electron;
 - (b) it implies absence of interaction between peroxide and olefin; and
 - (c) it postulates that the sulfite ion radical is the only

protagonist, yet there seems to be no compelling reason for that radical to react with olefin rather than other electron donors, like water or cosolvent, unless the olefin is in some way excited.

Note that other authors (39) prefer the bisulfite ion radical as opposed to the sulfite ion radical.

We submit that the Kharasch mechanism for sulfitation is an oversimplication of what takes place, and that the reaction is more complex than it was believed to be. It is likely that more than one mechanism is involved, and we propose one such possible mechanism, designed to be closer to the facts known about this reaction, but which also does not address itself to *all* these facts:

Initiation:

Propagation:

 $RCHCH=CH_2 + HSO_3^- \longrightarrow RCHCH_2CH_2SO_3^-$

 $RCHCH_2CH_2SO_3^{-} + RCH_2CH=CH_2 \longrightarrow$

 $RCH_2CH_2CH_2SO_3 + RCHCH=CH_2$

$$\operatorname{RCHCH}_2\operatorname{CH}_2\operatorname{SO}_3^- + \operatorname{HSO}_3^- \longrightarrow \operatorname{RCH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{SO}_3^- + \operatorname{SO}_3^-$$

Termination:

$$\begin{array}{c} \operatorname{RCHCH}_{2}\operatorname{CH}_{2}\operatorname{SO}_{3}^{-} + \operatorname{SO}_{3}^{-} & \longrightarrow & \operatorname{RCHCH}_{2}\operatorname{CH}_{2}\operatorname{SO}_{3}^{-} \\ & & | \\ & & & \\ &$$

 $\operatorname{oxidant}^{-} + \operatorname{SO}_{3}^{-} \longrightarrow \operatorname{SO}_{4}^{2^{-}} + \operatorname{reduced oxidant}^{2^{-}}$

In this mechanism, the protagonist is an olefin radical in an allylic configuration, which would be its most stable form from a thermodynamic point of view. This mechanism agrees with the following hypotheses:

- -that it is more likely for a one-electron transaction to take place between peroxide and olefin, rather than between peroxide and bisulfite; and
- -that such an allylic radical is a necessary and sufficient incentive for a bisulfite ion to react with it.

Note also that this mechanism provides for the formation of a sulfite ion radical which can generate a Kharasch-type chain, and it also provides for the formation of disulfonates, either in the way shown, or by chain termination between two sulfonate radicals.

Further evidence in favor of an allylic radical as chain propagator is the reluctance of bisulfite to react with a vinylidene olefin. This is also a terminal olefin, but the adjacent carbon is substituted, which makes it difficult to obtain an allylic radical or similar stability. Thus, one olefin containing 15% vinylidene produced exactly 85% conversion, as compared to 98% conversion for nonbranched olefins.

Primary alkane sulfonates are true sulfonic equivalents of corresponding fatty soaps, and share some of their properties (Table I).

Solubility. Just like soap, PAS of chain lengths exceeding C_{12} has very low solubility at room temperature, and the solubility increases steeply with temperature. Since it is

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difficult to obtain the solubility of soaps because of their proclivity to hydrolyze, we had recourse to the corresponding Krafft point data (Table II).

Surfactancy. Again, like soap, PAS has no hard water tolerance, and does not excel in any single facet of surfactancy, unless the measurements are carried out above the Krafft point, as shown in Table III.

Biodegradability. Also like soap. PAS is completely biodegradable (12,15,17,42).

Detergency. Another property PAS shares with soap is that it is an excellent detergent. The data shown in Table IV are based on measurements published by Rubinfeld and Cross (42). The standard detergent was tridecyl benzene sulfonate.

PAS also has some advantages over soaps and some other surfactants:

- -unlike soap, PAS is a strong electrolyte, and can be formulated at any desired pH;
- -unlike alkyl sulfates, PAS is stable at low pH;
- -unlike most sulfonates, PAS is colorless;
- -it can be obtained in a state of high purity at low cost; and
- -PAS is competitive in price with heavy-duty surfactants.

PAS is the missing link in the evolution of detergents from soap to syndets. It has failed to gain commercial success mostly because specialists tried to use it for what it is not, and, of course, found it wanting. If regarded as a unique hybrid having unique properties, it is likely to find a niche among commercial surfactants.

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