

# Technical News Features

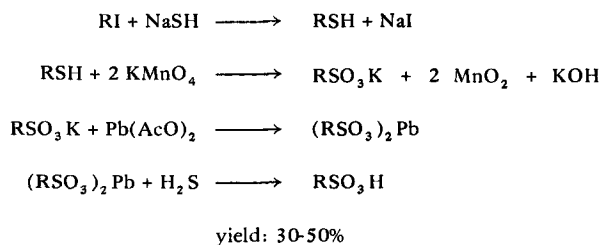
## Primary Alkane Sulfonates<sup>1</sup>

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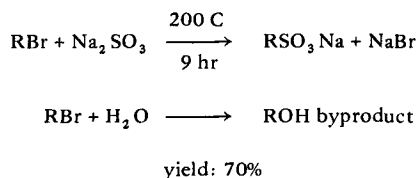
### ABSTRACT

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.

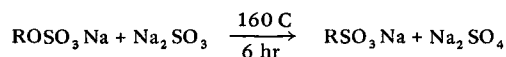
Primary alkane sulfonates (PAS) have been around for quite some time. In fact, they are the oldest properly identified synthetic detergent, dating back to 1913 when Reychler (1), who was at that time investigating the properties of palmitates, synthesized the equivalent hexadecane sulfonate by oxidizing 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:



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:

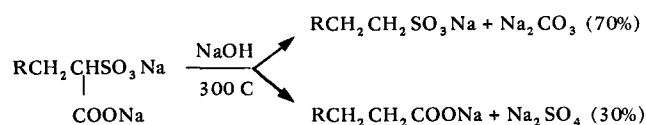


Another Strecker-type reaction is shown below, in which alkyl halide was replaced with a more accessible alkyl sulfide, as first reported by Schrauth (7).

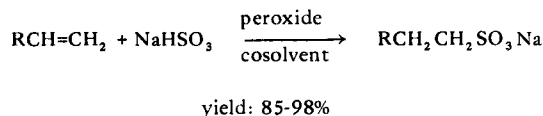


Some years later, Weil et al. (12) obtained PAS in fair yield by decarboxylating salts of  $\alpha$ -sulfo-acids in strong alkali medium. They reported ca. 30% desulfonation, so that the product contained that much soap.

<sup>1</sup> Presented at the 74th annual AOCS meeting, Chicago, 1983.



All these processes had only academic value, having been designed solely for investigating the end product. However, with the advent of commercially available  $\alpha$ -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.



This process has its roots in Kolker and Lapworth's work with the addition of  $\text{HSO}_3^-$  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 identified.

*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



## Technical News Feature

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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