Hydroxy Alkane Sulfonate (HAS), a New Surfactant Based on Olefins[1]

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Mild sulfonation of detergent-range internal olefins in a falling-film reactor results in quantitative conversion to a mixture of β-sultones, alkenesulfonic acids, and larger-ring sultones in a molar ratio of ca. 85:10:5. By direct neutralization and hydrolysis under well-controlled conditions such mixtures can be converted into products that are rich in β-hydroxysulfonates and have low levels of residual sultones, inorganic sulfate, and free oil.

Although α-olefins are readily sulfonated to give a class of well-established, commercially available anionic surfactants (α-olefin sulfonates; AOS), the sulfonation of internal olefins (IO) has always been hampered by low yields and the formation of dark products. The literature provides several explanations for this difference in behavior between α- and internal olefins (1,2), and many practical solutions to these problems have been claimed (3–7). However, we are not yet aware of any commercial application of internal olefin sulfonates in household products and, therefore, we have studied the IO sulfonation chemistry with the aim of identifying the origin(s) of the poor sulfonatability of detergent-range internal olefins and, if possible, delineating a process to make good quality internal olefin sulfonates.

EXPERIMENTAL PROCEDURES

Materials. The internal olefins used in this study were prepared over a basic catalyst from the corresponding α-olefins by isomerization to near thermodynamic equilibrium. The level of branching and the paraffin content in these materials were below 5% and 1%, respectively. Liquid SO_3 was purchased from Aldrich Chemie (Brussels, Belgium).

Sulfonation. Sulfonations were carried out in a falling-film glass reactor (100 × 0.5 cm) with gaseous sulfur trioxide diluted with dry nitrogen; no post-reactor was used. Details of the sulfonation set-up were essentially the same as those described previously (8).

Aging. Aging was performed in a magnetically stirred glass vessel at the temperatures and times indicated for each experiment in the text.

Neutralization. Neutralizations were carried out batchwise by allowing 40-g aliquots from the sulfonation reaction to run into a magnetically stirred aqueous NaOH

solution containing 1.2 eq. NaOH calculated on olefin intake. The concentration was arbitrarily chosen to yield products with an active matter (AM) concentration of 33 wt % at a theoretical conversion of 100%.

Hydrolysis. The neutralization mixtures obtained as described above were hydrolyzed batchwise for one hour at 160°C (excluding warm-up and cool-down periods) in a magnetically stirred autoclave. The autogeneous pressure at 160°C amounted to ca. 6 bar.

Analysis. Gas-liquid chromatography (GLC), high-performance liquid chromatography (HPLC) and ^1H and ^{13}NMR (nuclear magnetic resonance) analyses were performed on a Carlo Erba HRGC 5160 (Carlo Erba, Milano, Italy), Hewlett-Packard HP 1090 M and RI HP 1047 A (Hewlett-Packard, Palo Alto, CA), a Jeol 90 (Jeol Ltd., Japan), and Bruker AM 500 and AC 250 (Bruker Spectrospin, Wormerveer, The Netherlands), respectively. Specific surfactant analyses, such as the determinations of active matter (AM; two-phase titration with hyamine using a mixed acid indicator), unconverted organic matter or free oil (FO; the petroleum ether-extractable material in an aqueous alcoholic solution of the anionic sulfonation products), inorganic sulfate (potentiometric titration with lead nitrate), color (degree Klett in a Klett-Summerson photoelectric colorimeter, equipped with a KS No. 42 color filter, and a 2 × 4 cm glass cell, measured on a non-bleached 5 wt % anionic AM solution), and residual sultones (HPLC/GLC analysis of the FO fraction with C_{18} terminal Δ-sultone as internal standard) are all described elsewhere (9).

RESULTS AND DISCUSSION

α-Olefins are sulfonated to AOS in four steps—sulfonation, aging, neutralization, and hydrolysis. In the sulfonation step the olefins are contacted with gaseous sulfur trioxide to yield a complex mixture of alkenesulfonic acids and sultones of different ring sizes. This mixture is then aged to allow rearrangement of any four-membered ring β-sultone that has been formed to alkenesulfonic acids and γ-plus δ-sultones, because such terminal β-sultones yield highly insoluble 2-hydroxy-1-sulfonates as products upon neutralization. Subsequently, neutralization of sulfonic acids in the aged mixture is trivial, but leaves the γ- and δ-sultones unaffected. In order to convert the latter compounds also into surface-active material, the neutralization mixture has to be heated, and this is done in the hydrolysis step. In our study of the sulfonation of internal olefins described below, we will discuss the results obtained by following the same four steps as in the case of AOS.
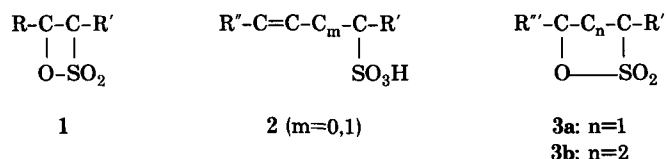
Sulfonation. Starting with the falling-film sulfonation step and using C_{16} IO as a model olefin, we first tried to optimize the sulfonation conditions on the basis of analysis of the final products, i.e., after aging (either 24 hr at 20°C or 2 hr at 40°C), neutralization, and hydrolysis. However, apart from the fact that very dark products were observed under all sulfonation conditions, we found it

difficult to achieve good reproducibility. Therefore, we decided to analyze the products that were obtained from the falling-film reactor directly by NMR spectroscopy at $-20°C$, *i.e.*, before neutralization.

In this way we made a number of important discoveries. The primary falling-film sulfonation product consisted largely of internal β-sultones 1, together with some alkenesulfonic acids 2 and internal γ-sultones 3a; δ-sultones 3b could not be detected.

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R-C-C-R'              R''-C=C-Cm-C-R'         R'''-C-Cn-C-R'
  |  |                          |                  |      |
  O-SO2                        SO3H               O——SO2

    1                      2 (m=0,1)            3a: n=1
                                                3b: n=2
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The identification of these compounds rests on several facts. First of all, evidence for the possible intermediacy of β-sultones 1 in olefin sulfonation is accumulating in the literature (1,10–19). A concerted [2 + 2] cycloaddition reaction constitutes an elegant explanation for the observed small differences in rate between olefins of different structure, as well as for the observed stereospecificity of the reaction (10,13). Furthermore, comparison of NMR spectral data of model compounds—*e.g.*, 1 and 4 prepared from

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R-C————C-R'
  |        |
  O-SO2-O-SO2

       4
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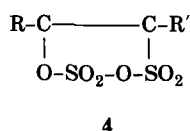
cis- and *trans*-4-octene as well as from *cis-* and *trans*-7-tetradecene according to Bakker and Cerfontain (13)— with those of our NMR mixtures clearly indicated the presence of 1 and the absence of carbyl sulfates 4; in particular, the sets of ^{13}C NMR absorptions at 71 and 75, respectively, 73 and 78 ppm for the sulfur- and oxygen-bearing carbon atoms of the *cis-* and *trans*-1 derivatives, respectively, were very characteristic. After the sulfonation mixtures obtained from the falling-film reactor had been allowed to age for various periods of time at 20–40°C before NMR analysis, it also could be observed that the amounts of 2, 3a, and now 3b increased at the cost of 1 (*cf.* ref. 19). Furthermore, the mixture of 3a plus 3b was isolated from the neutralized product by a standard FO extraction procedure and its spectral data were compared with those of the sulfonation mixtures. In this way, and by applying simple additivity rules to AO-based products to calculate the ^{13}C NMR chemical shifts of the corresponding IO-based materials, we were able to discern the different groups of compounds. Table 1 gives the chemical shifts of the most characteristic carbons for the various compounds. Most interestingly, and in line with similar observations in the literature (11,13), we found that the original 25:75 *cis/trans* ratio of the starting C_{16} IO was retained in the *cis*-1/*trans*-1 ratio observed in the low-temperature NMR spectra.

Finally, conclusive proof of the intermediacy of large quantities of 1 in the sulfonation of internal olefins comes from the isolation of the corresponding amounts of β-hydroxysulfonates (5) upon neutralization, and the fully consistent relation between the proposed chemistry and

TABLE 1

Characteristic ^{13}C NMR Chemical Shifts (ppm) of Various Sulfonation Products in CD_2Cl_2

Compound	C-S	C-O
cis-1 Mixture	71	75
trans-1 Mixture	73	78
3a Mixture (*cis/trans* or *trans/cis*)	55/58	80/82
3b Mixture (*cis/trans* or *trans/cis*)	55/59	87/86
cis-β-2 Mixture	60?	—
trans-β-2 Mixture	66	— (C=C: 120,140)
cis-4 Mixture	64	84
trans-4 Mixture	65	85

the observed analytical data of the end products, as described in detail below.

Subsequently, the reaction conditions of the sulfonation step were optimized by minimizing the level of unreacted C_{16} olefin and maximizing the yield of 1. Interestingly, it was observed that conversions were optimal at very mild conditions, *viz.*, a low reactor temperature (<20°C), near stoichiometric SO_3/IO ratios (1.05–1.10; feedstocks such as alcohol ethoxylates and linear alkylbenzenes are processed at similar ratios in this reactor), and moderate SO_3 dilutions (*ca.* 3 v%) and reactor throughputs (1.5 mol/hr). At the optimum (15°C; SO_3/IO = 1.08; 2.8 v% SO_3) we were able to obtain sulfonation mixtures containing as much as 85% β-sultones 1, together with 10% alkenesulfonic acids 2 and 5% γ-sultones 3a (no 3b detectable); the level of unreacted olefin was below 5%.

These findings are important in several respects. First of all, the reaction has already proceeded to an extent of more than 95% at the outlet of the falling-film reactor, implying that the incomplete conversions described in the literature (1) must be due to some phenomenon that occurs after the sulfonation step (see below). Secondly, the mild conditions that suffice to complete the sulfonation reaction demonstrate that linear internal olefins have a reactivity towards gaseous SO_3 that is similar to that of α-olefins; this finding is in line with recent reports in the literature concerning the influence of the olefin structure on the reactivity towards complexed SO_3 in solution (10–12).
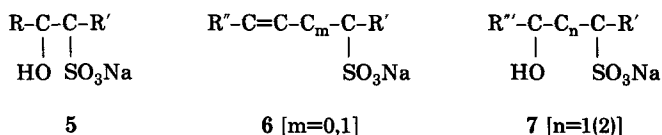
The third important conclusion to be drawn from our findings is that β-sultones 1 are by far the main intermediates in the falling-film sulfonation of internal olefins with gaseous SO_3 under mild conditions. Evidence in favor of the involvement of such products has been accumulating in the literature (1,10–19), but the involvement of β-sultones has never been demonstrated for detergent-range internal olefins under these conditions to such an extent. In addition to the main β-sultones, we always observe small quantities of alkenesulfonic acids 2 and γ-sultones 3a. Presently, it is not clear whether these products are formed *via* a parallel mechanistic pathway involving dipolar intermediates or, in the case of 2, an "ene" reaction (11,12,20), or whether they constitute only secondary intermediates derived from 1.

The last conclusion that can be drawn from our low temperature NMR studies is that carbyl sulfates 4—or

cyclic pyrosulfate esters, the insertion products of a second equivalent of SO_3 into the β-sultone rings of 1—are not detectable in the sulfonation mixtures. Recently, carbyl sulfate formation has been put forward to explain the incomplete sulfonation of internal olefins both at low and high SO_3/olefin ratios under falling-film conditions (1). Additional proof of their absence in our reaction mixtures comes from the near-stoichiometric SO_3/IO ratio used and yet almost complete conversion of the olefin into sulfonated products. In addition, as described in more detail below, the inorganic sulfate levels in the final products are not in line with a significant contribution of carbyl sulfates. Recently, it has also been found that the reaction of β-sultones 1 with excess sulfur trioxide to form carbyl sulfates 4 is slow (11,21).

Aging. Subsequently, we turned our attention to the aging step. As already indicated above, in AOS manufacturing this step is introduced to avoid the poorly water-soluble 1,2-sultone-derived 2-hydroxy-1-sulfonates. However, in contrast with AOS, the end products derived from internal olefins obtained after direct neutralization (*i.e.*, without any aging) showed good solubilities in water; yet, these products were unprecedentedly rich in β-hydroxysulfonates 5 and contained up to 85% (sometimes even 90%) of this material. As expected, the remainder of the material contained *ca.* 10% of alkenesulfonates 6 and 5% γ-hydroxy-sulfonates 7. As with 1 (*vide supra*), the

R-C-C-R′ R″-C=C-C$_m$-C-R′ R‴-C-C$_n$-C-R′
| | | | |
HO SO$_3$Na   SO$_3$Na   HO SO$_3$Na

5   6 [m=0,1]   7 [n=1(2)]

identification of the 5 mixture rests on the combination of spectral analysis, the application of NMR additivity rules, comparison with model β-hydroxysulfonates prepared according to Bakker and Cerfontain (13), and literature reports describing β-hydroxysulfonate formation from β-sultones (12,18,22). Moreover, in this way a fully consistent picture is obtained with respect to the chemistry involved. Table 2 lists the most characteristic ^{13}C NMR chemical shifts.

We also addressed the effects of (partial) aging on the composition and properties of the final product mixture.

During the NMR studies of (partially) aged sulfonation mixtures, we had already noticed that IO-derived β-sultones 1 possessed higher thermal stabilities than AO-derived ones, and that longer aging times were required for the complete disappearance of 1, *i.e.*, of the order of 2 hr at 35–40°C; similar observations have been reported by others (13). Tables 3 and 4 show trends with respect to product quality and product composition as a function of aging time, observed for the end products after sulfonation under optimum conditions, standard neutralization, and hydrolytic work-up. Note that a 120-min aging time at 35–40°C leads to complete disappearance of 1.

From Table 4 it is clear that a wide product spectrum becomes accessible by aging, partial aging or not aging at all. In the case of complete aging, the final product composition closely resembles that of AOS, whereas direct neutralization without any aging yields products that contain high levels of β-hydroxysulfonates 5; for this reason we refer to the material that is not aged as hydroxy alkane sulfonate (HAS) and we use the term internal olefin sulfonate (IOS) for the aged materials.

The easy access to a wide product spectrum in the sulfonation of internal olefins may be advantageous from the point of view of ability to handle and formulate, etc. However, from a process point of view it is clear that direct neutralization to HAS, *i.e.*, without any aging step, is clearly preferred, as this simplifies the overall process. Moreover, the trends that are apparent from Table 3 support this because product quality, particularly the color of the final products, deteriorates with aging.

The finding that the free oil and the inorganic sulfate level increase simultaneously upon aging is due to the fact that the formation of β-sultones from olefins is a reversible reaction. This surprising reaction has recently been reported for the first time (12). It competes with the desired thermal rearrangement (aging) of the β-sultones

TABLE 2

Characteristic ^{13}C NMR Chemical Shifts (ppm) of Various Sulfonated End Products in D$_2$O

Compound	C-S	C-O
R-C(OH)-C$_m$-C(SO$_3$Na)-C$_n$-C		
(*threo/erythro* or *erythro/threo* Mixture)		
m = 0, n = 0	59.8/61.2	72.3/73.1
m = 0, n = 1	66.9/68.0	71
m = 0, n = 2 and higher	65.0-65.5	71
m = 1, n = 2 and higher	56.8/57.7	68.1/70.0
6	65/66	C=C: 125-140 (max. at 126/139)

TABLE 3

Quality of C$_{13,14}$ IO Sulfonation Products as a Function of Aging Time at 35–40°C

Aging time (min)	FO (wt % on AM)	Na$_2$SO$_4$ (wt % on AM)	Color Klett
0	2.8	3.0	280
30	4.2	3.3	520
45	4.7	3.5	960
120	5.4	3.4	1500

TABLE 4

Composition of C$_{13,14}$ IO Sulfonation Products as a Function of Aging Time at 35–40°C

Aging time (min)	5 (% mol)	6 (% mol)	7 (% mol)	Residual sultones (ppmw on AM)
0	85	10	5	30
30	60	30	10	380
45	35	45	20	660
120	<10	60	>30	1800
cf. AOS	—	65	35	

to alkenesulfonic acid and γ-sultones. This side-reaction regenerates the starting olefin and, after neutralization, forms inorganic sulfate in the final products; therefore, upon analysis of the final products it would appear as if the conversion were not complete. We think that the same situation (*i.e.*, competition between the reversal of β-sultone formation and the desired unimolecular rearrangement) also applies for AOS, but that the detrimental contribution of the reversibility of the reaction is much less in this case, due to the higher rearrangement rate of AO-derived β-sultones (13,19). We have found that for detergent-range internal olefins the contribution of the undesired reverse reaction becomes clearly apparent above 35–40°C.

Neutralization. The latter finding is of particular relevance in the neutralization step, which largely involves the conversion of β-sultones (1) with aqueous caustic besides the trivial acid/base neutralization of the small amounts of 2 that are also present; the γ-sultones 3a are not affected under these conditions. In the neutralization step, it will be clear that the exposure of 1-containing sulfonation mixtures to temperatures above 40°C for extented periods of time should be avoided. We observed that at the conditions indicated in the experimental part (1.2 eq. NaOH on olefin intake; target AM of the end products: 33 wt %; slow magnetic stirring), β-sultones derived from linear IO with a chainlength of up to *ca.* C_{15} reacted sufficiently rapidly with aqueous caustic to prevent significant deterioration of the product due to the reversibility of the reaction. By external cooling, the exothermic reaction was controlled to a maximum temperature of 40°C. However, in the case of starting IO with longer carbon chainlengths we noticed that efficient mixing was required to obtain high enough reaction rates and to avoid extended exposure of 1 to temperatures of 35–40°C. These observations are likely to be correlated with the poor solubility of the relatively apolar β-sultones in the aqueous caustic under the neutralization conditions employed.

Finally, these problems are most pronounced in the case of the *trans*-derivatives because such β-sultones react particularly slowly in bimolecular reactions, resulting in a much larger tendency to lose SO_3 than their *cis*-counterparts (12).

Hydrolysis. In the last step of the process, the hydrolysis, the neutralized mixture obtained above, is heated to convert the γ-sultones 3a (and δ-sultones 3b, if present) into active matter, *viz.*, alkenesulfonates 6 and hydroxysulfonates 7. As in the past, residual sultones in AOS had been associated with skin irritation, an effect later shown to occur only in combination with hypochlorite bleach (23), it is considered important to lower the final sultone level as much as possible. According to the literature (19,22), the hydrolytic stability of sultones increases in the following order: i) δ > γ > β; ii) IO-based > AO-based, with rule (i) dominating rule (ii). Thus it is again evident that omission of an aging step, *i.e.*, aiming for HAS rather than IOS, is advantageous because such sulfonation mixtures contain the smallest amount of the hydrolytically more persistent sultones—the vast majority has already reacted away in the neutralization step, and the remainder (*ca.* 5%) consists almost exclusively of γ-sultones 3a. Aging leads to the formation of more, as well as more persistent, sultones. In other words, HAS has an intrinsically low content of residual sultones. This is clearly reflected in

TABLE 5

Comparison of Typical Product Properties of Laboratory-Produced[a] HAS with Those of Commercial AOS

	HAS[b]	AOS[b]
FO (wt % on AM)	1.5–3.0	1.5–3.0
Na$_2$SO$_4$ (wt % on AM)	1.0–2.5	1.0–2.5
Color (Klett)	100–135	30–80
β-Hydroxysulfonates (wt %)	85	<1
Alkenesulfonates (wt %)	10	65
γ/δ-Hydroxysulfonates (wt %)	5	30
Di-sulfonates (wt %)	—	5
Total residual sultones (ppmw on AM)	6 max.	<100

[a]1.5 mol IO/hr; SO_3/IO = 1.08 mol/mol; 2.8 v% SO_3 in N_2; 15°C cooling water temperature.
[b]Both $C_{14/16}$ (1/2 w/w).

the last column of Table 4; these values were obtained after hydrolysis of mixtures under the same set of conditions. Further reduction of the residual sultone level is, of course, possible by applying more stringent conditions.

The origin of the poor sulfonatability of detergent-range internal olefins is now understood and the solution to this problem has been identified. Film sulfonation under mild conditions is virtually complete in seconds. The most important products by far are β-sultones 1, which have a thermal stability with respect to unimolecular rearrangement to alkenesulfonic acids and γ-sultones that is significantly higher than that of AO-derived β-sultones. Consequently, with IO the reversibility of β-sultone formation—a reaction that was recently reported for the first time—becomes competitive, leading to regeneration of olefin and thus to seemingly incomplete conversions. The reversibility always plays a role when aging is applied, which should therefore be avoided; elimination of aging is also advantageous for reasons of process simplicity and product quality. In the subsequent neutralization step it is then crucial to maintain high rates of reaction with aqueous caustic and yet to avoid high temperatures, which favor the undesired reverse reaction to olefin and SO_3—this requires efficient mixing in the case of starting internal olefins, particularly the *trans* ones, with carbon chainlengths from about C_{15} onwards, because mass transfer limitation then starts to play a role. In this way, end products are obtained that are unprecedentedly rich in β-hydroxysulfonates 5 and are soluble in water; their analytical data are as exemplified in Table 5. The novel hydroxy alkane sulfonates (HAS) also have an intrinsically low content of residual sultones.

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