

NMR Study on Sulfonation of Internal Olefins

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Terminal olefins can be converted into the corresponding sulfonates by sulfonation with SO_3 followed by hydrolysis, the products are used as detergent ingredients. Although internal olefins were also expected to be good feed stocks, it was difficult to convert them into the corresponding sulfonates with as good of a yield as that of terminal olefins under the same synthesis conditions.

Our studies have been carried out in order to clarify the reason for poorer conversion of the internal olefins. It was found by a nuclear magnetic resonance spectroscopic study that the major components of the sulfonated intermediate of internal olefins were β -sultones, the amounts of which were usually very small in sulfonated terminal olefins. A portion of these β -sultones was desulfonated, depending on temperature, to the original olefins and the corresponding sulfate salts during alkaline hydrolysis. The prevention of desulfonation of the β -sultones in the hydrolysis process was one of the most important aspects for the production of internal olefin sulfonates.

Finally, by keeping the hydrolysis temperature below 35°C , the conversion of internal olefins into sulfonates was achieved with the same yield as that of conventional terminal olefins.

KEY WORDS: α -Olefin, α -olefin sulfonate, alkenesulfonate, AOS, β -sultone, carbyl sulfate, desulfonation, γ -sultone, hydroxy-alkanesulfonate, internal olefin sulfonate.

The sulfonation of terminal olefins (α -olefins) on a commercial scale was developed about 20 years ago, and the sulfonated products known as AOS have become widely used ingredients in household detergents (1). Sulfonation of internal olefins was regarded as being difficult when compared with that of terminal olefins, hence, they have not been applied to many commercial uses. Roberts *et al.* (2) suggested that the poor conversion of internal olefins into sulfonates might be due to production of carbyl sulfates (cyclic sulfonate sulfate anhydrides) as intermediates. However, no direct evidence for it has been shown.

A nuclear magnetic resonance (NMR) spectroscopic method has been shown to be a powerful tool for the study of sulfonated intermediates of terminal olefins (3). We tried to identify the sulfonated intermediates of internal olefins by means of NMR and elucidate the reason for their poor conversion to sulfonates.

EXPERIMENTAL PROCEDURES

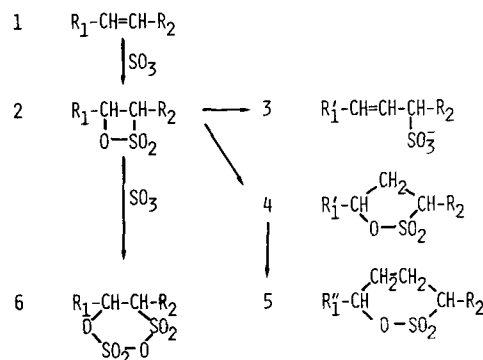
Reagent-grade chemicals and solvents were used without any additional purification except for SO_3 , dioxane and carbon tetrachloride, which were distilled. Internal olefins employed in this study were obtained by isomerization of 1-tetradecene (Mitsubishi Chemical Co. Ltd., Tokyo, Japan) with 5% dodecylbenzenesulfonic acid under a nitrogen

stream at $180\text{--}200^\circ\text{C}$ for 8 hr following distillation. The isomerized olefins were analyzed according to the method given in the literature (4). The *trans/cis* ratio was 2.7 and the distribution of the double bond position was as follows: 1- (2.2%), 2- (16.9%), 3- (17.0%), 4- plus 5- (34.5%) and 6- plus 7- (27.9%). The product also contained tetradecane (1.5%).

The NMR spectra were obtained with a Varian XL-200 spectrometer (Varian Associates, Palo Alto, CA). Tetramethylsilane or 3-(trimethylsilyl)propanesulfonic acid sodium salt was used as standard for chemical shifts. Mass spectra (MS) measurements were performed with a JEOL DX-300 (JEOL Ltd., Tokyo, Japan) spectrometer. The determination of the sulfonates of the tetradecenes was carried out by two-phase cationic titration with methylene blue indicator (5). A high-performance liquid chromatography (HPLC) method (6) was employed for the determination of the sulfonates of *trans*-2-octene. A Shimadzu LC-3A type HPLC pump (Shimadzu, Kyoto, Japan) equipped with refractive index (RI) detector was used and sodium octanesulfonate was employed as the standard on the assumption that RI response factors were the same between the standard and the sulfonate of *trans*-2-octene. Sulfate ion was determined with an ion-chromatograph (Yokogawa IC-500R, Yokogawa Electric Corp., Tokyo, Japan). The amount of olefins in hydrolyzed mixtures was determined by weighing the pentane extracts for the products of tetradecenes and by gas chromatography (GC) for the products of 2-octene with nonane as the internal standard (chromatograph, Hewlett Packard HP-5890A; column, 5% phenylmethylsilicone; temperature, $40\text{--}150^\circ\text{C}$).

RESULTS AND DISCUSSION

A reaction scheme for the sulfonation of internal olefins with SO_3 is shown in Scheme 1, based on the analogy for terminal olefins (7) as β -sultones (formula 2 in Scheme 1) are considered the primary sulfonation products. The β -sultone is usually unstable and rapidly changes to an alkene-sulfonate (formula 3), a γ -sultone (formula 4) or a δ -sultone (formula 5). In some cases, a β -sultone takes up



SCHEME 1

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a second molecule of SO_3 to give a carbyl sulfate (formula 6).

The isomerized tetradecenes were sulfonated with a molar equivalent of SO_3 to the corresponding olefins in the same way as reported by Nagayama *et al.* (8). The sulfonated product was collected in a vessel cooled by dry ice/methanol (**sample A**). An aliquot of **sample A** was left standing about 24 hr at room temperature (**sample B**). The NMR spectra for **sample A** and **sample B** are shown in Figures 1 and 2, respectively. An aliquot of **sample B** was dissolved in 50% (v/v) ethanolic aqueous solution and neutralized with NaOH. Sulfones and unreacted olefins were separated from their solution by extraction with pentane. It was found that signals a, b, c and h in Figure 2 were due to the residual components in the ethanolic aqueous solution. These components were identified as β -alkenesulfonates, since the adjacent relations of protons were assured between a and b, c and between b, c and h by a two-dimensional correlated (COSY) NMR. The assignment of signals is shown by formula 3 in Scheme 2. The signals l, i, j and k were found to be due to the

components extracted by the pentane. Since these components were soluble in pentane, the signals l and i were supposed to be those of CH-O and CH-S, respectively, of sulfones based on a spectrum in the literature (8). With the aid of its COSY NMR spectrum, in which the off-diagonal signals were observed between j, m and l, between j, m and i, between k and l and between k and i, and its MS spectrum (negative FAB-MS), which suggested the mass number of the components to be 276, they were identified as γ -sulfones. The assignment of signals is shown by formulas 4a and 4b in Scheme 2. We suppose that 4a and 4b originated from the *trans*- and *cis*-tetradecenes, respectively, because the signal intensities were consistent with the *trans/cis* ratio of the original ones. **Sample B** was found to consist of γ -sulfones and β -alkenesulfonates as its major components. This composition was almost within our expectation, though δ -sulfones were not observed.

The main difference in the NMR spectra between **sample A** and **sample B** was that the signals d, e, f and g in Figure 1 disappeared in Figure 2. With the aid of COSY

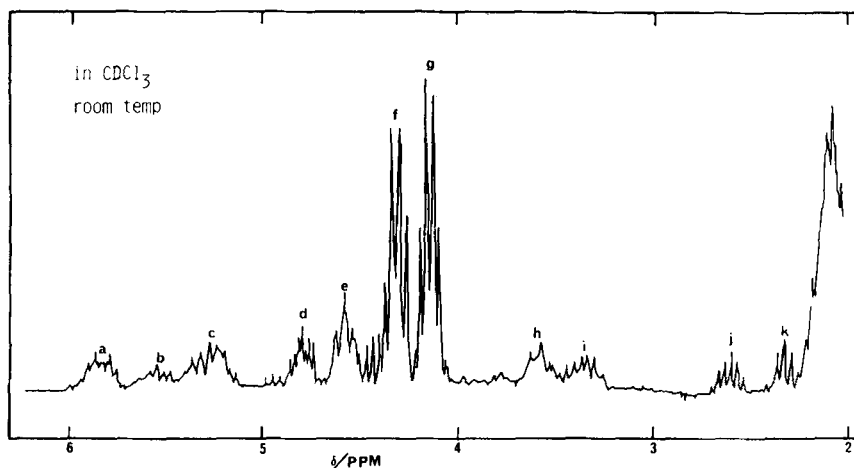


FIG. 1. NMR spectrum of sulfonated tetradecenes (sample A).

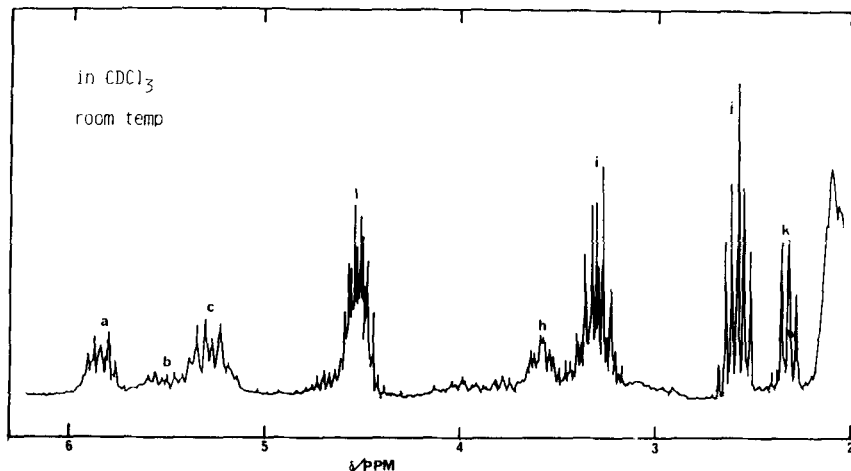
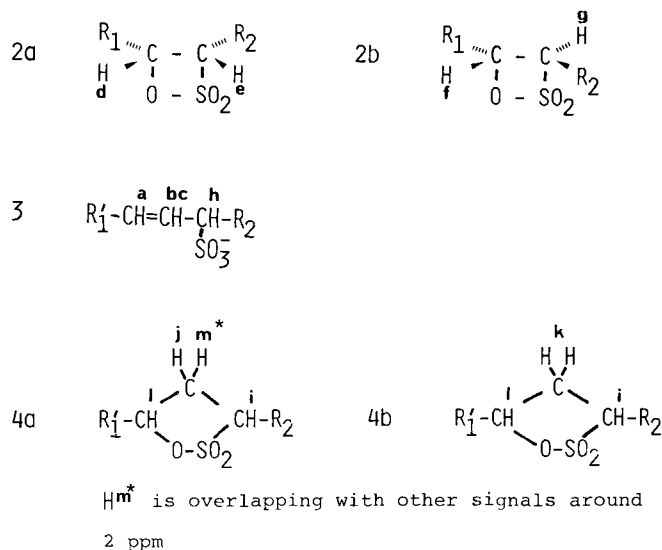


FIG. 2. NMR spectrum of sulfonated tetradecenes (sample B).

SURFACTANTS & DETERGENTS



SCHEME 2

NMR it was also proved that d and e were adjacent protons, as were f and g. Bakkar *et al.* (6,7) reported NMR chemical shifts for some β -sultones and carbyl sulfates. Each of the signals for d, e, f and g was assigned to a β -sultone on the basis of their data. The relationship of signal intensities among them rationalized the existence of two kinds of β -sultones, which originated from the *cis*- or *trans*-olefins (see formulas 2a and 2b in Scheme 2). Since the signal of the double bond protons of unsulfonated olefins would have appeared around 5.3 ppm in Figures 1 or 2, their amount was supposed to be very small. These results also indicated that both samples A and B consisted not of carbyl sulfate but mainly of sultones and alkenesulfonates, because the production of a carbyl sulfate would have been accompanied with a shortage of SO_3 available to the olefins and, consequently, a considerable amount of olefin would have remained unsulfonated.

Hydrolysis of sample A was carried out as follows: 100 g of sample A was put in a 500-mL, round-bottom flask equipped with a water cooler in a water bath. Ten percent aqueous NaOH solution was introduced with stirring and monitored with phenolphthalein indicator. The unsulfonated olefins and unhydrolyzed sultones were removed from the solution with pentane. The major components after the hydrolysis were identified as β -hydroxyalkanesulfonates and β -alkenesulfonates from the NMR spectrum shown in Figure 3, together with its signal assignments.

Based on the material balance of the sulfur and the organic moiety, the hydrolysis reaction is summarized in Table 1. Two different conditions were employed for sample A: A-1 had its temperature controlled below 35°C for 2 hr from the beginning and then raised to 90–95°C, for A-2 it was kept at 90–95°C throughout the reaction. Sample B was hydrolyzed under a different set of conditions from the other two, since a temperature of over 100°C was required for the hydrolysis of the γ -sultones. One hundred grams of sample B was put into an autoclave vessel, 174 g of 10% NaOH aqueous solution (20% excess to the

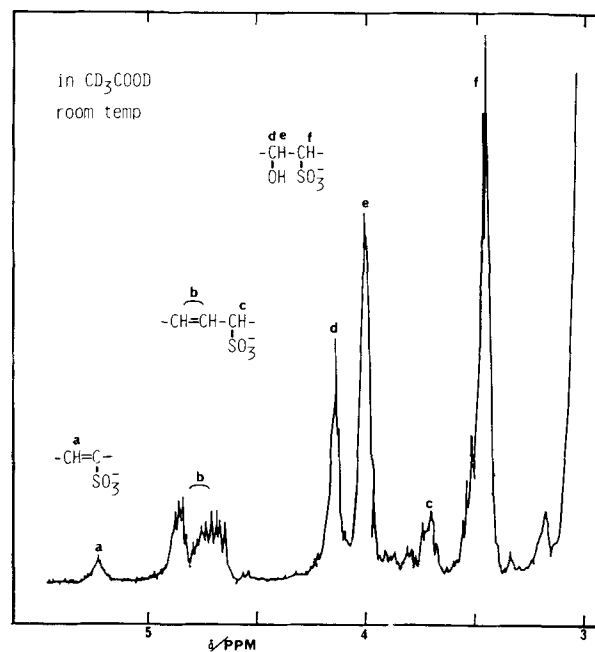


FIG. 3. NMR spectrum of hydrolyzed sample A.

calculated equivalence) was added, and hydrolyzed at about 130°C for 30 min. The amount of olefins and Na_2SO_4 were expected to be the same within experimental error between A-1 and A-2, because they would have been independent of the hydrolysis conditions. However, we found that they were considerably different from each other. The sulfonate yield of A-1 was clearly higher than that of A-2 and almost the same as that of B-1. The experimental results in Table 1 suggest to us that thermal desulfonation should occur for the β -sultones during their hydrolyses.

Study of β -sultones from trans-2-octene. Concerning the ring opening reaction of β -sultones under alkaline conditions, it has been reported that S-O and/or C-O cleavage occurs (7,9,10), but we have not found any precedent for S-C cleavage. Therefore, we thought it necessary to get more confirming evidence for the desulfonation of a β -sultone. For this purpose, we obtained a mixture (sample C) involving more than 80% β -sultones as follows. Nine grams of dioxane was put in a 500-mL round-bottom flask. Carbon tetrachloride (120 g) was added and then cooled to below 5°C in an ice-water bath. The solution was stirred with a magnetic stirrer, and 0.025M of SO_3 was introduced to form the SO_3 -dioxane complex. Then 0.05M of *trans*-2-octene was introduced dropwise into the flask for 30 min. The mixture was stirred for another 3 hr. To 20 g of this reaction solution was added 50 mL of pentane. This solution was treated with 20 mL of water five times so as to remove all dioxane, SO_3 and alkenesulfonates. Pentane and carbon tetrachloride were then removed under vacuum at room temperature.

The NMR spectrum of sample C is shown in Figure 4. The two significant signals, b and c, were assigned to be S-CH and O-CH, respectively, of 2,3-octanesultone. A carbyl sulfate was also observed, the characteristic signals being a and d, and 6,7-octanesultone, with the signals of e and f which are very close to each other and supposed to

TABLE 1

Composition of the Hydrolyzed Products of Sulfonated Tetradecene

Exp. no.	Sample	Hydrolysis temperature	Products ^a				Total
			HAS-Na ^b ANS-Na ^c	γ -Sultone	Na ₂ SO ₄	Olefin	
A-1	A	Below 35°C for 2 hr then 90–95°C for 2 hr	89.0 (89.0)	3.0 (3.0)	0 (5.2)	4.1 (0)	96.1 (97.2)
A-2	A	90–95°C for 2 hr	78.0 (78.0)	1.9 (1.9)	0 (20.4)	17.6 (0)	97.5 (100.3)
B-1	B	130–135°C for 0.5 hr	90.6 (90.6)	ND (ND) ^d	0 (6.3)	7.7 (0)	98.3 (96.9)

^a Each Figure gives conversion ratio from olefin or SO₃ (Figure in parenthesis) by molar percent.

^b Sodium hydroxyalkanesulfonate.

^c Sodium alkenesulfonate.

^d Not detected.

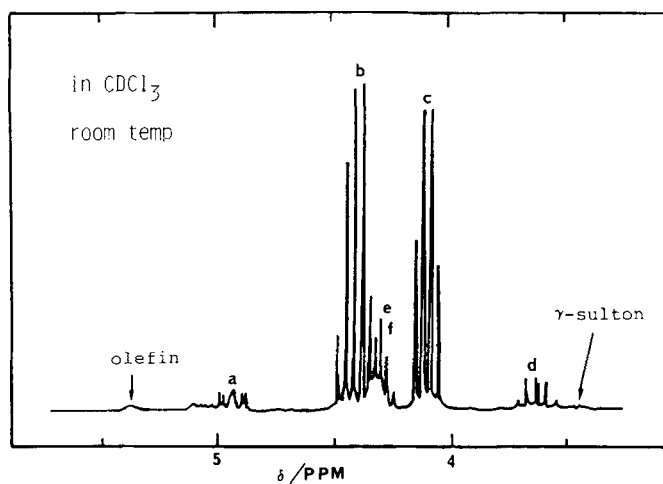


FIG. 4. NMR spectrum of sulfonated 2-*trans*-octene (sample C). Composition of sample C was estimated from the signal intensities as follows: 2,3-octanesultone, 73%; 6,7-octanesultone, 13%; carbyl sulfates, 9%; γ -sultones, 4%; and olefin, less than 1%.

be S-CH and O-CH, respectively. The identification of 6,7-octanesultone was based on the fact that the component showing the signals e and f changed to sodium 2-hydroxy-3-octanesulfonate after NaOH hydrolysis.

An aliquot of sample C was put in an NMR tube and dispersed in D₂O at 4°C. Its NMR spectrum was then measured. The spectrum showed broad signals as shown in Figure 5(a), though the characteristic signals due to CH-O and CH-S of β -sultones could be observed. When NaOD was added to the solution, the spectrum changed to the one shown in Figure 5(b). When successive changes in the NMR spectra were measured with an increase in the temperature up to 70°C, it seemed that no further change occurred [see Fig. 5(c)]. The signals b and c in Figure 5(b) or (c) were assigned to be O-CH and S-CH, respectively, of 3-hydroxy-2-octanesulfonate, and a and d appeared to be those of 2-hydroxy-3-octanesulfonate.

From the relationship of signal intensities among the spectra in Figure 5, it seemed that the β -sultones were completely converted into the corresponding hydroxyalkanesulfonates and that no S-C cleavage took place.

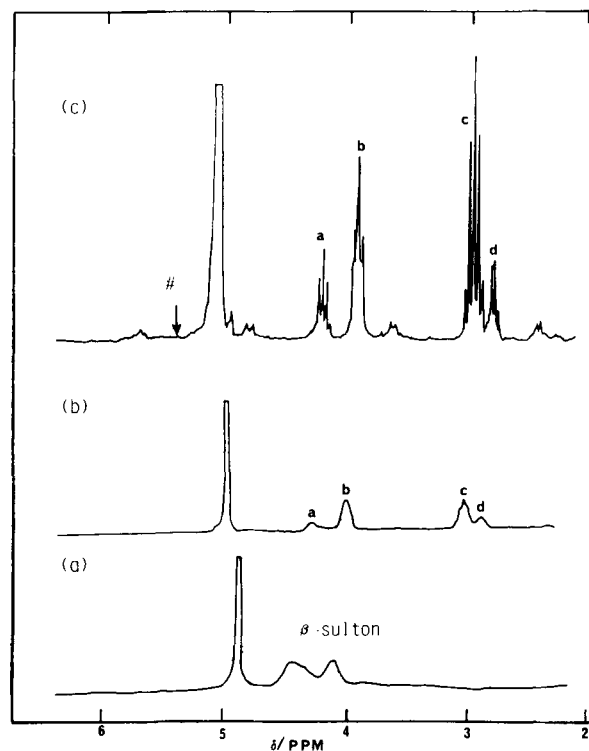


FIG. 5. Successive change in NMR spectrum of sample C in NaOD/D₂O. (a), Dispersed in D₂O at 4°C; (b), at 4°C, after NaOD being added; (c), at 70°C, after being diluted with deuterated acetic acid so as to dissolve any olefin which might have been produced; and #, signal position for the olefin.

Two other aliquots of sample C were put into different NMR tubes and dissolved in deuterated acetonitrile (CD₃CN). When sodium alkoxides were added instead of NaOD, changes in the NMR spectra were observed. In the case of CH₃ONa, most of the β -sultones changed to the corresponding β -hydroxyalkanesulfonic acid methyl esters at low temperature. In addition to that, a small amount of an olefin was also observed to be produced with increasing temperature. When sodium *tert*-butoxide was used, the sultones did not change around room temperature. However, with an increase in temperature, most of them seemed to convert back to an olefin (see Fig. 6).

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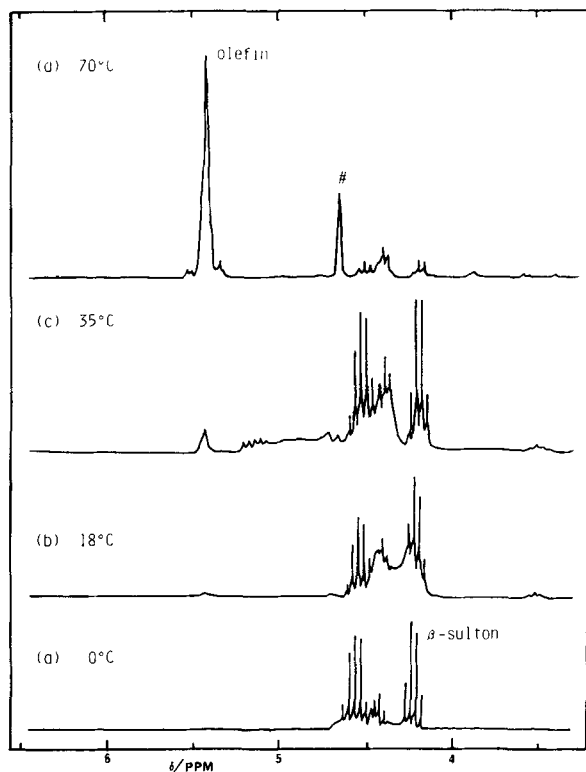


FIG. 6. Successive change in NMR spectrum of sample C in the presence of *t*-butoxide with increase in temperature. #, This signal was supposed to be due to isobutylene.

We think this is fairly convincing evidence for the S-C cleavage of some β -sulfones. The hydrolyses of sample C were carried out under two different temperature controls. About 50 mg of sample C was put into a glass tube (internal diameter, 8 mm), dispersed in 2 mL of 5% NaOH aqueous solution and then sealed. The glass tube was dipped in a water bath with occasional shaking. The products of the hydrolyses were analyzed and the data obtained are listed in Table 2. Based on the material balances, the products obtained under the higher temperature at the beginning involved considerable amounts of olefin (which proved to be *trans*-2-octene by GC-MS), whereas only a trace of it was detected in the other reaction. Both amounts of olefin and sulfate in Table 2 rationalized the desulfonation of the sulfones during their hydrolyses

TABLE 2

Composition of the Hydrolyzed Products of Sulfonated 2-Octene

Exp. no.	Hydrolysis temperature	HAS-Na ^b ANS-Na ^c	Olefin	Products ^a			Total
				Na ₂ SO ₄			
				Total (A)	B ^d	A-B	
1	90–95°C for 3 hr	42.0 (38.6)	51.0 (0)	(53.5)	(8.4)	(45.1)	93.2 (91.2)
2	Below 35°C for 3 hr then 90–95°C for 1 hr	90.7 (83.5)	trace (–)	(8.4)	(8.4)	(0)	90.7 (91.9)

^{a, b, c}See Table 1.

^dCalculated amount being produced from the carbyl sulfate in sample C.

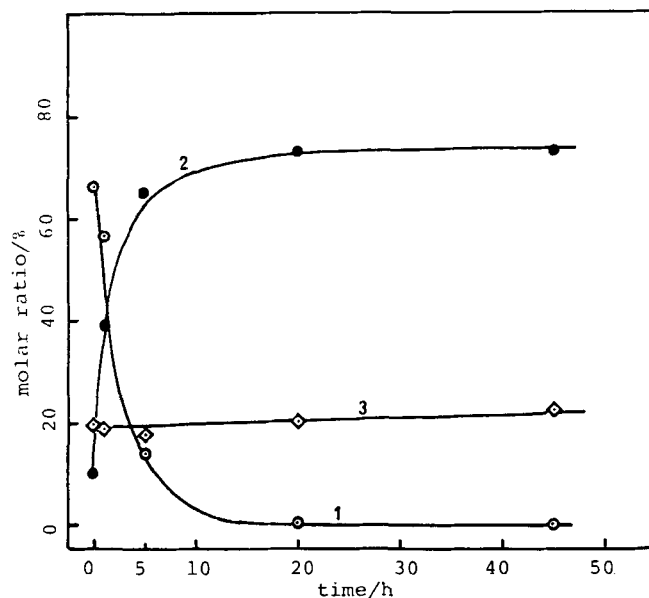


FIG. 7. Change in composition of sulfonated tetradecenes at room temperature. β -Sulfones (1), γ -sulfones (2), alkenesulfonates (3). Each composition was determined by NMR.

depending on temperature. We are now currently studying the mechanism of S-C cleavage of the sulfones.

A β -sulfone is also produced by sulfonation of a terminal olefin with SO₃. However, it is usually so unstable (rapidly changing to a γ , a δ -sulfone or alkenesulfonates) that it is hardly involved even in the very immediate sulfonated product of a terminal olefin (7). Therefore, the desulfonation of a β -sulfone may not be important in the case of a terminal olefin. On the other hand, it was found that the β -sulfones from internal olefins were fairly stable and took a few hours to change into γ -sulfones (any further change to δ -sulfones has not been observed in this study) at room temperature, as shown in Figure 7. This would be the reason for the poorer conversion to the sulfonates of the internal olefins.

We then expected that the desulfonation of the β -sulfones would be reduced by setting their hydrolysis temperature below 35°C. However, a certain amount of γ -sulfones, which were always involved, would require a temperature above 100°C for their hydrolyses. We surmised two possible ways for converting internal olefins into the corresponding sulfonates with high yield. One is to carry out the hydrolysis after allowing the sulfonated intermediates to stand for a few hours, so as to change

TABLE 3

Composition of Sodium Internal Olefin Sulfonates Obtained by Two-Step Hydrolysis

Component	Molar ratio ^a (%)		Analytical method
	1	2	
HAS-Na			
ANS-Na ^{b,c}	95.1 (95.1)	94.4 (94.4)	Two-phase titration
Olefin	4.4 (0)	4.6 (0)	Weighing of pentane extract
Na ₂ SO ₄	0 (5.4)	0 (5.4)	Ion chromatography
Total	99.5 (100.5)	99.0 (99.8)	

Hydrolysis conditions: 100 g of sample A. 10%(W/V) NaOH aq. solution; 159 g (10% excess to the theoretical equivalence based on the assumption of 100% conversion of olefins into the sulfonates). Temperature, 1st, 30–35°C for 2 hr; 2nd, 130–135°C for 0.5 hr.

^{a, b, c}Same as in Table 1.

the β -sulfones to the γ -sulfones. The other is to apply a stepwise hydrolysis, the first step keeping the temperature below 35°C and the second step keeping it above 100°C. According to the latter, we succeeded in getting the sulfonates from internal olefins with a yield about 95% (see Table 3).

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