Level and Position of Unsaturation in Alpha Olefin Sulfonates

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ABSTRACT

A comparison of the levels of unsaturation in α-olefin sulfonates (AOS) and related derivatives determined by iodination, bromination and hydrogenation techniques showed that quantitative hydrogenation is the only method having wide applicability. Although halogenation methods frequently give results in agreement with hydrogenation data, they can show variations with reaction time and composition of the sample. Unsaturation in sulfonate methyl esters could not be determined by halogenation. The amount of Δ^1-isomer in alkene sulfonate sodium salts determined by oxidative cleavage with periodate-permanganate was always low compared to that determined by NMR. Oxidative cleavage of the sulfonate methyl esters gave Δ^1-isomer levels in agreement with NMR results.

INTRODUCTION

The sulfonation of α-olefins with uncomplexed sulfur trioxide produces, after hydrolysis, a mixture containing major proportions of alkene monosulfonates and hydroxy alkane monosulfonates (1,2). Smaller amounts of alkene disulfonates and hydroxy alkane disulfonates can also be present in the hydrolyzed product (3,4). Total unsaturation in such α-olefin sulfonates (AOS) or in preparations of some of the individual components has been determined by quantitative hydrogenation (5,6) and halogenation with bromate-bromide (5,7). The position of the unsaturation has been determined by periodate-permanganate oxidation (5,7,8) and NMR (8,9). It is our experience that some of these techniques are not widely applicable to AOS and related compounds, giving spurious results in many cases.

In the present study, levels of unsaturation determined by quantitative hydrogenation, iodination and bromination were compared. The double bond distribution in sulfonate sodium salts and sulfonate methyl esters was determined both by NMR and oxidative cleavage with periodate-permanganate. Formation and chromatographic separation of sulfonate methyl esters was used extensively in our characterization and analysis work, and enabled double bond distributions to be obtained for the alkene monosulfonates and the alkene disulfonates, if present.

EXPERIMENTAL PROCEDURES

Alcohol-Soluble, Alcohol-Insoluble Separation

The aqueous paste resulting from hydrolysis and neutral-

TABLE I

Total Unsaturation (Iodine Value) in Various Sulfonates

Sample	Carbon number and position	Theory Iodine value	Iodine value by H_2[a]	Iodine value by ICl (Wijs) 30 min[b]	Iodine value by ICl (Wijs) 4 hr	Iodine value by BrO_3^- - Br^-[c]
α-Olefin sulfonates						
A	16		49.0	37.6	43.7	
B	16,18		52.9	46.7	51.6	
C	16		50.1	38.9	46.3	
D	16		50.8	44.3	49.9	
E	12		48.6	31.5		49.2
F	16		52.5	40.8		
G	18		46.6		51.7	50.9
H	18		47.5		54.9	51.7
I	16		48.8			38.0
Alkene monosulfonates						
J[d]	18 (Δ^2-Δ^5)	68.5	68.9		65.9	66.8
K	16 (Δ^1-Δ^2)	77.7	51.8			46.1
L	16 (Δ^2)	77.7	69.7	67.4	69.3	71.3
M	16 (Δ^1-Δ^2)	77.7	68.6			57.1
N	16 (Δ^3)	77.7	71.1	71.2		
O	16 (Δ^2)	77.7	73.0	72.4		
Hydroxy monosulfonates						
P	14 (4-OH)	0	2.0			17.1
Q	16 (4-OH)	0	4.8	2.6		20.3
R	16 (4-OH)	0	1.0	0.6		16.4
Sulfonate methyl esters						
S	20 (Δ^1)	67.8	65.2	2.9		1.9
T	16 (Δ^2)	79.7	78.7	46.2		8.9
U	16	45-55[e]				10.7
V	14	50-60[e]				11.1
W	12	45-55[e]				7.2

[a]Standard deviation of the method in the 45-80 iodine value range is ±1.3 based upon 38 replicate determinations on 12 samples in this table.

[b]Standard deviation of the method in the 35-75 iodine value range is ±0.7 based upon 18 replicate determinations on 7 samples in this table.

[c]Standard deviation of the method in the 35-75 iodine value range is ±1.4 based upon 31 replicate determinations on 8 samples in this table.

[d]This sample is a potassium octadecenesulfonate.

[e]Hydrogenation data on the esters were not obtained but results on the original alcohol-soluble material indicated methyl esters should have iodine value in this range.

ization of the acid mix (the initial product of the reaction of sulfur trioxide with olefin) was separated into organic and inorganic constituents based on solubility in 90% ethanol. The aqueous paste was extracted with petroleum ether prior to the alcohol-soluble, alcohol-insoluble separation to remove unsulfonated material and unhydrolyzed sultones. The alcohol-soluble material thus obtained contains the sulfonated actives of interest (usually as sodium salts). All analytical work described herein was carried out on this alcohol-soluble material.

Methyl Esters of Sulfonic Acids

The sulfonate sodium salts were converted to their corresponding sulfonic acids by ion exchange on a column (in a 100 ml buret) of Dowex 50W-X8 100-200 mesh resin. Approximately 750 mg of sample were dissolved or slurried with a small amount of resin and a few milliliters of methanol-water 80:20, and quantitatively transferred to the column with additional solvent. The sulfonic acids were eluted with 175 ml methanol-water 80:20. The eluant was concentrated to a volume of 10-15 ml in a water bath under a nitrogen stream. Residual solvent was removed on a simple nitrogen-vacuum setup described previously (10). Solvent was usually removed from the sulfonic acids until the sample weight was in the 850-950 mg range.

Diazomethane for the esterification was generated in a special 250 ml flask (10) equipped with pouring spout, using a two phase system of diethyl ether (60 ml) and 3.2% potassium hydroxide solution (50 ml), from nitrosomethylurea (1.7 g). The etheral diazomethane was decanted into the cooled (ice bath) flask containing the sulfonic acids dissolved in 15 ml of diethyl ether-methanol 10:1. Two to four such additions of diazomethane (freshly generated each time), with evaporation of the diethyl ether from the sample in between, were frequently required to completely esterify the sulfonic acids. The sample with excess diazomethane was allowed to stand for at least 2 hr in the ice bath with constant stirring to insure complete reaction.

The bulk of the diethyl ether was removed in a water bath under a nitrogen stream as before. Residual solvent was removed and the sulfonate methyl esters taken to constant weight in the nitrogen-vacuum setup. The esters were refrigerated under nitrogen until further processing.

Chromatography of Methyl Esters

Davison grade 923 silica gel 100-200 mesh adjusted to contain 3.0 ± 0.2% moisture was used as adsorbent for the chromatographic separation of the sulfonate methyl esters. The ester preparation from above was dissolved in petroleum ether and transferred to the silica gel column (11). Hydrocarbons in the sample, formed during the esterification, were eluted with 150-200 ml of petroleum ether. The alkene monosulfonate esters were eluted with 500 ml of petroleum ether-diethyl ether 90:10 followed by several 50 ml fractions to insure a proper separation between components. The weight of sample in each 50 ml fraction was determined while the succeeding 50 ml fraction was being eluted. Small fractions were collected until the weight was <1 mg/50 ml. The fraction containing the hydroxy monosulfonate and all the disulfonate esters was eluted with 500 ml diethyl ether followed by a few 50 ml fractions as before. Unesterified material was eluted with 400 ml of diethyl ether-methanol 1:1.

The large fraction and the small tailing fractions for each of the two main components were concentrated and then composited. After evaporation of the bulk of the solvent, residual solvent was removed and the sulfonate esters taken to constant weight in the nitrogen-vacuum setup. Thin layer chromatography (TLC) was used to check the purity of the isolated components.

Halogenation Methods

Iodine values were obtained by modifications of the

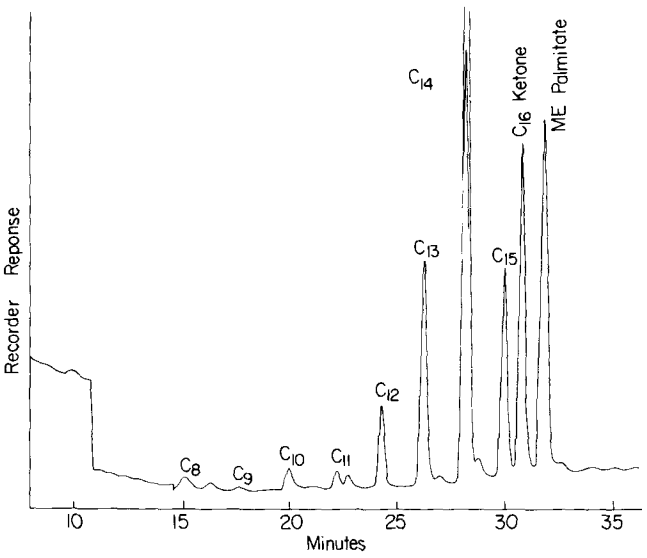

FIG. 1. Gas chromatogram of carboxylic acid fragments (as their methyl esters) from cleavage of C_{16} α-olefin sulfonates. Instrument conditions as in Reference 17. Distribution of $C_{16}H_{31}SO_3Na$ calculated from this run: Δ^1 = 13.2, Δ^2 = 59.4, Δ^3 = 16.1, Δ^4 = 5.3, Δ^5 = 1.7, Δ^6 = 2.2, Δ^7 = 0.4, Δ^8 = 1.7.

standard Wijs method (12). A semimicromethod involved 40-70 mg samples, 5 ml chloroform, 5 ml Wijs solution and 0.05 N sodium thiosulfate as titrant. A somewhat scaled down macromethod involved 200-300 mg samples, 15 ml chloroform and 25 ml Wijs solution. Reaction times of 30 min and 4 hr were used. The sulfonate sodium salts are not soluble in chloroform or other halogenated solvents; the reaction thus occurs under heterogeneous conditions.

Total unsaturation was also determined by bromination using the bromate-bromide reagent (13). Application of this halogenation method to alkene sulfonates was first described by Bordwell and Osborne (14). The macromethod involved 200-300 mg samples dissolved in water; other conditions were similar to those described by Siggia (13). The semimicromethod was a scaled-down (one-fifth) version of the macromethod using 30-60 mg samples in 5 ml of either chloroform or water and titration with 0.01 N sodium thiosulfate. Reaction time was 7-10 min in both methods. No mercuric salt catalyst was used in the brominations.

Quantitative Hydrogenation

Catalytic hydrogenation with 5% palladium on alumina was used extensively for both sulfonate sodium salts and methyl esters, with acetic acid and occasionally water as solvents. Early results were obtained with a simple classical hydrogenation apparatus consisting of a reaction flask connected to a manometer for adjustment to atmospheric pressure and to a jacketed buret (50 or 10 ml) with its appropriate leveling reservoir of mercury. Sample sizes of 200-700 mg were used with the 50 ml buret and 30-60 mg with the 10 ml buret. More recently, hydrogenations have been carried out in a thermostated (± 0.02 C) semimicroapparatus (10 ml buret for 40-70 mg samples) designed to eliminate effects from external pressure and temperature changes. A compensating reservoir (constructed by sealing the bulb from a 25 ml pipet to the nonsystem side of the manometer), placed in the bath near the reaction flask, maintains a constant enclosed pressure in the system, and thus adjustment to outside atmospheric pressure is unnecessary during or after the hydrogenation. A similar compensating principle was described by Vilbrandt (15) many years ago. Vandenheuvel (16) has discussed the advantages and disadvantages of both the simple classical apparatus and the more complicated designs involving constant temperature and pressure.

TABLE II

Δ^1-Isomer Levels by NMR and Oxidative Cleavage

Sample	Carbon no.	Method	Per cent Δ^1-isomer content[a]		
			Original Na salt	Mixed Me esters	Unsaturated[b] Me esters
E	12	NMR	28		
		Oxid.	17		24
AA[c]	14	NMR	33		29
		Oxid.	20		33
BB	14	NMR	0		0
		Oxid.	2		3
I	16	NMR	37		32
		Oxid.	18	23	25
CC	16	NMR		20	
		Oxid.	12	17	19
DD	16	NMR	18		
		Oxid.	13	18	19
D	16	NMR		17	
		Oxid.	10	14	15
EE	16	NMR	100		100
		Oxid.	87		98
K	16	NMR	45		
		Oxid.	28		43

[a]All results expressed as the percentage of the total alkene monosulfonate isomers present.

[b]Alkene monosulfonate methyl esters isolated by silica gel chromatography.

[c]Gas chromatographic analysis (2 ft x .25 in. OD, 20% DC 200 silicone column, programed 125-200 C at 4.0 C/min) of the unsaturated methyl esters from this sample gave a level of 31% Δ^1-isomer.

The 125 ml reaction flask used with the more recent semimicroapparatus was constructed with four sample chambers spaced evenly around the shoulder of the flask, thus permitting up to four samples to be run consecutively after one equilibration of the system. Most samples of sulfonate methyl esters were completely hydrogenated in 15-30 min. Sulfonate sodium salts frequently required 50-70 min for a constant (± 0.02 ml in 15 min) buret reading to be obtained.

Oxidative Cleavage

The periodate-permanganate method used has been described previously (17), but three changes (see below) from the published procedure were involved in the present work. A sample size of 50 mg was taken for all oxidations. The same quantities of oxidant, potassium carbonate and sodium bisulfite (26 ml, 45 mg, 1.06 g, respectively) were used for all samples. An inert marker (5 mg) of methyl palmitate or stearate was added to all samples prior to oxidation to serve as a rough check on the completeness of oxidation and the recovery of fragments.

Nuclear Magnetic Resonance

NMR spectra were obtained on Varian A-60 or HA-100 spectrometers. Chemical shifts were measured in τ units (ppm) from internal or external (depending upon the solvent) reference tetramethylsilane at 10.0 τ. Sulfonate sodium salts were dissolved in deuterated water and sulfonate methyl esters in either carbon tetrachloride or deuterated chloroform to give 5-10% w/v solutions. Vinyl protons from the Δ^1-isomer in salts gave peaks in the 3.0-4.0 τ region while protons from more internal unsaturated isomers absorbed at 4.0-5.0 τ. Corresponding regions for esters were 2.8-3.9 and 3.9-4.9 τ, respectively. Vertical scale expansion of the olefinic proton region was applied routinely, and signal averaging with a computer of average transients was used in a few select cases. The area obtained from the average of two to six integrals was used in the calculations.

RESULTS AND DISCUSSION

Separations

The yields of sulfonate methyl esters recovered after esterification were 96-101% of theory, theory being calculated assuming for simplicity that the original alcohol-soluble sample was entirely alkene monosulfonate. Recovery of the ester sample in the silica gel chromatography was 98-101% of the material placed on the column. The hydrocarbons eluted from the silica gel column amounted to 0.1-0.4% of the sample. The unesterified fraction was typically 3-6% of the material recovered from the column. This unesterified material represents both sulfonic acids not esterified by diazomethane and esters hydrolyzed during chromatography. TLC of this fraction usually indicated the presence of the same sulfonates that were in the original sample. The weight percentages of the second and third fractions were normalized to give the levels of alkene monosulfonate and other sulfonates in the sample. Quantitative hydrogenation of the third fraction enabled the alkene disulfonate level to be calculated.

Level of Unsaturation

Table I compares iodine values obtained on a variety of sulfonates by hydrogenation and by halogenation methods. No attempt was made to distinguish between results obtained by semimicro- and macro- variations of the various methods, since the intent of the study was to compare the different approaches to determining unsaturation. Results by the two variations were generally in good agreement.

The AOS samples in Table I contained alkene monosulfonate, hydroxy monosulfonate and disulfonate (by TLC). For this group, the normal 30 min Wijs iodine value almost always gave a significantly lower level of unsaturation than hydrogenation. Increasing the reaction time to 4 hr resulted in better agreement with hydrogenation iodine values, but occasional high values were obtained. The bromate-bromide method presented a similar picture in that results were lower, higher or sometimes in agreement with hydrogenation data.

Table I also gives results on purified samples of alkene monosulfonates, hydroxy monosulfonates and a few sulfonate methyl esters. Some of these samples were isolated or prepared from AOS; others were synthesized by alternate routes. Moisture or other sulfonates, or both, in these samples accounts for the hydrogenation iodine values being

lower or higher than theory. Results on alkene monosulfonates by halogenation methods were generally in agreement with hydrogenation data although an occasional low bias was again seen. The bromate-bromide method gave spuriously high results with monosulfonates having a hydroxyl group in the 4 position. Neither halogenation method was applicable to sulfonate methyl esters.

Position of Unsaturation

Oxidative cleavage with periodate-permanganate was applied at various stages of our investigation to the sulfonate sodium salts (alcohol-soluble material), the mixed sulfonate methyl esters and the methyl ester fractions isolated by silica gel chromatography. Figure 1 shows a typical gas chromatographic (GC) analysis of the carboxylic acid fragments (as their methyl esters) obtained upon cleavage of the sodium salts from a C_{16} AOS. The distribution of alkene monosulfonates was calculated from the uncorrected weight percentages of the fragments assuming all terminal unsaturation. It was also assumed for simplicity that all cleavage fragments came from monosulfonates although disulfonates, when present, contribute minor amounts of a number of fragments. For the sample giving the pattern of Figure 1, an alkene monosulfonate level of ca. 59% was calculated from the methyl palmitate marker percentage compared to 61% obtained from the hydrogenation data on the original sample. The cleavage patterns of fractions containing disulfonate methyl esters gave fragment peaks of much lower intensity because of the low levels (10-25%) of alkene disulfonate present, but were otherwise similar to Figure 1 and gave reproducible cleavage data for calculation of the alkene disulfonate distribution. The assumption made for this calculation is that all the unsaturation is more internal than the two sulfonate groups.

When comparing double bond distributions obtained by oxidative cleavage on the sulfonate sodium salts and their corresponding methyl esters, it was apparent that in many cases the distributions did not agree, particularly in the Δ^1-isomer content. To resolve this discrepancy, the amount of Δ^1-isomer in various samples was also determined by NMR. Table II compares results obtained by the two methods. It is obvious that the methods are in agreement only when cleavage data on the sulfonate methyl esters are considered. Cleavage results on the sulfonate salts could be low due to incomplete oxidation of the Δ^1-isomer, isomerization of this isomer during the oxidation, or degradation of an intermediate oxidation product to nonacidic fragments. Because of this problem with sulfonate salts, all double bond distributions were obtained routinely by oxidative cleavage of the sulfonate methyl ester fractions isolated by silica gel chromatography.

The possible contribution of alkene disulfonates to the above discrepancy was considered. A double bond adjacent to the secondary sulfonate group in disulfonates would probably contribute to the NMR Δ^1-isomer level but would not be included in the level determined by oxidative cleavage (from the n-1 fragment). However the contribution would be small compared to most of the differences seen in Table II. Also, if there is a disulfonate effect, it should be operative in the mixed methyl esters as well; yet cleavage results on these esters generally agreed with other data.

Alul (8) has reported agreement between NMR and oxidative cleavage data on two sodium hexadecenesulfonate samples containing 8 and 40% Δ^1-isomer. Such agreement, particularly for the sample containing the high level of this isomer, is contrary to our experience. The oxidation method used was reported to be essentially the same as ours, but the isolation of the carboxylic acid fragments, their esterification and subsequent GC analysis were entirely different. Errors can occur in analyzing cleavage fragments due to incomplete extraction of the carboxylic acids, incomplete esterification (Alul used a 2 min boiling with boron trifluroride in methanol), improper GC calibration, and interference from extraneous materials (see below.

The ketone peak shown in Figure 1 appeared in all cleavage runs made on samples containing significant amounts of hydroxy sulfonates, such as the alcohol-soluble material, the mixed methyl esters and the hydroxy monosulfonate-disulfonate ester fraction from silica gel chromatography. The hydroxy sulfonates are not affected by the oxidation but are carried along with the carboxylic acid fragments during workup of the samples. It was eventually determined (by preparative GC followed by various spectroscopic techniques) that this component was a vinyl ketone resulting from decomposition of 3-hydroxy monosulfonate in the inlet port (260 C) of the gas chromatograph. Thus both sodium and methyl 3-hydroxyhexadecanesulfonate gave 3-hexadecen-1-one upon injection of their methanol and diethyl ether solutions, respectively, into the GC unit.

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