Sulfonation Studies of Monoisomeric Di- and Trialkylbenzenes

Roger A. Grey[a,*] and **Albert F. Chan**[b]
[a]ARCO Chemical Company, 3801 West Chester Pike, Newton Square, PA 19073, and [b]ARCO Oil and Gas Company, 2300 West Plano Parkway, Plano, TX 75075

Sulfonation studies were conducted on a series of monoisomerically pure di- and trialkylbenzenes in order to determine the regioselectivity of sulfonation and how the selectivity varies with structural changes. Sulfur trioxide, because of its commercial significance, was investigated as the primary sulfonating agent. Lewis base adducts of sulfur trioxide and other sulfonating agents were also investigated for comparison. The studies demonstrated, in a quantitative manner, the tendency of the sulfonation to occur para to alkyl substituents. In one class of the alkylbenzenes investigated, 1,3,4-alkyl dimethylbenzene, the sulfonation which occurred at the position para to the 3-methyl group ranged in selectivity from 87–99%, even though this position, which is ortho to the larger alkyl group, was much less favorable from steric considerations than the position ortho to the 4-methyl group. The determination of the position of sulfonation by a combination of nuclear magnetic resonance and high pressure liquid chromatographic techniques is discussed.

Recently, considerable research effort has been directed toward the use of synthetically tailored alkyl aryl sulfonates as surfactants for micellar/polymer enhanced oil recovery (EOR) processes (1–10). Structural changes in these sulfonates can substantially affect their phase behavior properties, which determine their micellar process performance. It is known that the structure of the hydrocarbon lipophile has a large influence on the optimum conditions of surfactancy for EOR applications. However the significant effect of the sulfonate position on the aromatic ring has been only recently unequivocally established during a phase behavior study (11). In order to better understand how the alkylbenzene sulfonate structure affects the ability of the surfactant to recover residual oil, numerous model compounds with monoisomeric hydrocarbon moieties have been prepared and evaluated for their relative effectiveness as surfactants.

In this paper, the selectivity of sulfonate attachment on the benzene ring during sulfonation using a series of monoisomeric di- and trialkylbenzenes is reported. The structures of the di- and trialkylbenzenes investigated in this study are depicted in Appendix 1. The distributions of sulfonate isomers, which are obtained by the sulfonation of these monoisomeric alkylbenzenes under varying conditions, are described. Most of the sulfonations were performed using sulfur trioxide because of its commercial utility. However, for comparative purposes, other sulfonating agents were also examined.

EXPERIMENTAL PROCEDURES

The general procedure for the synthesis of di- and trialkylbenzenes was reported previously (12). Spectroscopically pure hydrocarbons were obtained by distillation using a 10 plate fractionating column. A combination of gas chromatography, mass spectrometry and carbon nuclear magnetic resonance (^{13}C NMR) showed the purified hydrocarbons to be of high purity (99% or greater) and having monoisomeric structures.

The following procedure represents a typical sulfonation of an alkylbenzene. A three-neck, 25-ml, round-bottom flask equipped with a magnetic stirring bar, reflux condenser with argon inlet valve, thermometer and addition funnel is charged with 4 ml of 1,2-dichloroethane, 4-(4-ethylphenyl) undecane (1.1g, 4.2 mmol) and cooled to −20°C. Sulfur trioxide (0.4g, 5.0 mmol) in 4 ml of 1,2-dichloroethane, is added to this over a 10 min period, and the reaction mixture allowed to stir an additional 50 min at −20°C. The reaction mixture is quenched with 2 ml of water and the pH adjusted to 10 with 40% aqueous sodium hydroxide. The solvent is removed by rotoevaporation and the water removed by repeated treatments with isopropanol and rotoevaporation. The recovered solids were dissolved in chloroform, filtered through a 0.5 micron filter and the chloroform removed by rotoevaporation followed by high vacuum to give 1.4 grams of solids. One gram of the solids was purified by silica gel chromatography for NMR analysis. Ten grams of silica gel was packed in a slurry of chloroform, and the solids were dissolved in chloroform and loaded onto the column. Neutrals were eluted off the column first with chloroform. The sulfonate was removed with a 1:1 mixture by volume of chloroform and ethanol. After the solvent was removed by rotoevaporation, the recovered sulfonate was dried under high vacuum to give 0.8 gram of solids. The distributions of the sulfonate isomers by HPLC analyses before and after silica gel chromatography matched within 1% for each sample.

The determination of sulfonate isomer distributions was accomplished by comparing the ^{13}C NMR spectra of the parent alkylbenzenes with the corresponding sulfonate mixture obtained after sulfonation, and also by the HPLC analysis of these sulfonates (13). The detailed rationale used for determining the sulfonate isomer distributions is given in Appendix 2. Proton-decoupled ^{13}C Fourier-transform magnetic resonance spectra were taken at 28°C, with a varian 200XL spectrometer using the deuterium resonance of solvent deuterochloroform as a lock signal. Proton nuclear magnetic resonance spectra were obtained with the same instrument. Chemical shifts are reported in ppm downfield from TMS (δ scale).

The high pressure liquid chromatograph procedure utilized a reverse phase, Hypersil 5 micron octadecylsilane column (200 × 4.6 mm) typically with a 69% acetonitrile: 31% water mobile phase containing 0.01M tetrabutyl ammonium chloride ion pairing reagents. Our procedure carefully adjusts the percent acetonitrile for each surfactant. This is important to achieve separation of most sulfonate isomers. A Hewlett Packard 1084B instrument with a UV detector was used at 225 nm.

*To whom correspondence should be addressed.

RESULTS AND DISCUSSION

Sulfonation of Dialkylbenzenes. As examples of dialkylbenzenes, monoisomeric methylphenyl, ethylphenyl and isopropylphenyl undecanes were sulfonated with sulfur trioxide in 1,2-dichloroethane solvent. For the para substituted dialkylbenzene derivatives there are only two possible sulfonate isomers that can be formed. The isomer containing the sulfonate ortho to the long alkyl chain is designated as the 2-sulfonate, while the isomer with the sulfonate ortho to the short alkyl group is designated as the 3-sulfonate (Scheme 1).

The sulfonate isomer distributions obtained in a series of para substituted undecyl ethylbenzene derivatives with variable points of attachment of the aryl along the undecyl chain are shown in Table 1. The amount of the 3-sulfonate isomer increases from 52 to 90% as the position of the aryl group on the long alkyl chain changes from the terminal C1 to midchain C6 position. As the aryl group becomes attached closer to the midpoint of the chain, the effective steric hindrance increases for the positions ortho to the long chain, resulting in the enrichment of the 3-sulfonate isomers. Table 1 also indicates that the greatest change in sulfonate isomer distribution occurs as the aryl attachment changes from C1 to C2 (52% vs 82% 3-sulfonate) followed by a more gradual increase as the ring attachment approaches midchain. The sulfonate isomer distribution produced was also found to be relatively insensitive to the reaction temperature over a 100°C range. A comparison is shown in Table 1 for the sulfonation of 4-(4-ethylphenyl) undecane at −20 and 83°C.

The effect of the steric interaction due to the size of the short alkyl group on the benzene ring is shown in Table 2. Sulfonations of 4-(4-methylphenyl) undecane and 4-[4-(2-propyl)phenyl] undecane were performed at −20°C and the results compared to the previously discussed 4-(4-ethylphenyl) undecane. As the short alkyl group is changed from methyl, to ethyl, to isopropyl the formation of the 3-sulfonate isomer becomes less favorable and decreases from 92 to 66%. Although the results are qualitatively expected based on the relative sizes of the short alkyl groups, the isopropyl derivative gives much less of the 3-sulfonate isomer than would be expected just based on the increased carbon number. This result must also be due to increased steric hindrance by the midchain attachment of the propyl group.

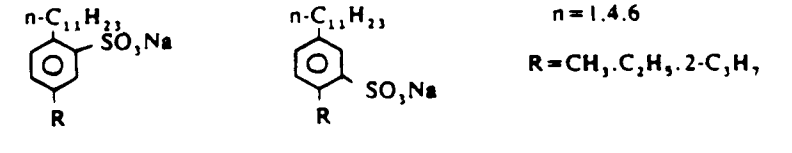
The sulfonate isomer distribution of meta and ortho substituted dialkyl benzenes are potentially more complex than the para substituted analogues since they each possess four chemically nonequivalent possible sulfonation sites. Experimentally, however, only two sulfonate isomers of each were actually observed from the sulfonation of 4-(3-ethylphenyl) undecane (meta substituted analogue) and 4-(2-ethylphenyl) undecane (ortho substituted analogue). For the sulfonation of the meta dialkylbenzene analogue, 4-(3-ethylphenyl) undecane, the 4- and 6-sulfonate isomers were formed in 90 and 10% selectivities, respectively, as the only two sulfonates. The sulfonation occurs solely at the positions ortho to the ethyl and undecyl groups in a ratio similar to that observed for the para undecylethylbenzene analogue. In this case, however, each of these positions are also para to an alkyl group, and therefore electronically favored sites (Scheme 2).

For steric reasons, sulfonation did not occur between the two alkyl groups at position 2. Furthermore, position 5 is electronically unfavorable because it is meta to both alkyl groups.

For the sulfonation of the ortho dialkylbenzene analogue, 4-(2-ethylphenyl) undecane, the HPLC of the reaction mixture showed only two sulfonate isomers and the ^{13}C NMR showed no evidence for sulfonation ortho to either alkyl group (Scheme 3). Sulfonation occurs solely at the two electronically favored positions which are para to the alkyl groups to give the 4-and 5-sulfonate isomers. Even though the positions sulfonated above are once removed from the alkyl groups, some steric influence, due to the size of the closest alkyl groups, results in 60 and 40% selectivities.

Sulfonation of trialkylbenzenes. As examples of trialkylbenzenes, the sulfonations of monoisomeric alkyl ortho, meta and para xylenes were investigated. The sulfonate isomer distributions for the sulfonation at −20°C of a series of undecyl ortho-xylene isomers with 1,3,4 ring substitution are shown in Table 3. Of the three possible sulfonate isomers per molecule, only two, the 2- and 3-sulfonates, were observed. Apparently, the ring position ortho to two alkyl groups is the most sterically unfavorable for sulfonation. The ^{13}C NMR data indicate that sulfonation of 1,3,4-substituted ortho-xylenes occurs predominantly ortho to the more sterically demanding long chain alkyl group. This is in contrast to the dialkylbenzenes, where sulfonation occurred predominantly near the least sterically hindering alkyl group, as expected.

Thus, for 1-(3,4-dimethylphenyl) undecane, sulfonation occurs almost exclusively at position 2, while even for the most sterically demanding midchain attached [2-(3,4-dimethylphenyl) undecane] the 2-sulfonate is still formed in a surprising 89% selectivity. It is proposed that these results are due to the fact that the 2 position on the ring, even though sterically unfavorable (Scheme 4), is the only sulfonation site which is para to an alkyl group and is, therefore, electronically favored for sul-



2-sulfonate 3-sulfonate

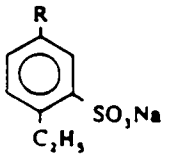
Scheme 1

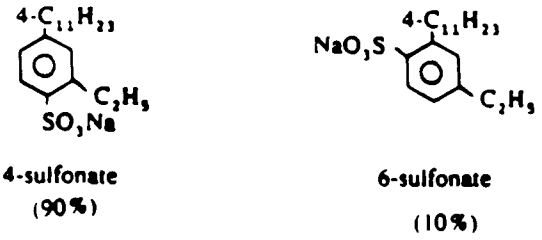
TABLE 1

Isomer Distributions of Para-Alkylethylbenzene Sulfonates

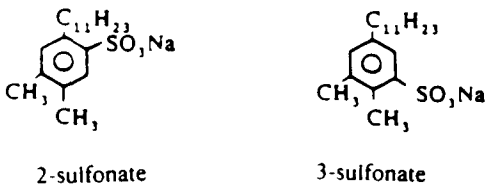
R	Reaction Temp (°C)	3-Sulfonate[a] (%)
1-$C_{11}H_{23}$	−20	52
2-$C_{12}H_{25}$	−20	82
4-$C_{11}H_{23}$	−20	87
4-$C_{11}H_{23}$	83	90
6-$C_{11}H_{23}$	−20	88

[a]General structure of 3-sulfonate =





Scheme 2



Scheme 4

fonation. Table 3 further shows the insensitivity of these results to temperature since the sulfonation of the 6-undecyl derivative at 83°C gives almost identical isomer distributions as the sulfonation performed at −20°C. A comparison of the sulfonate isomer distributions obtained from the sulfonation of the previously discussed 4-(4-methylphenyl) undecane and 4-(3,4-dimethylphenyl) undecane, 92% the 3-sulfonate vs 90% the 2-sulfonate, shows the magnitude of the para directing effect of an alkyl substituent (Scheme 5).

The structures of the corresponding alkylbenzenes before sulfonation are very similar except that the ortho-xylene derivative contains an additional methyl group which directs the sulfonation to the position ortho to the 4-undecyl group.

The para directing influence of an alkyl group on sulfonation selectivity was also observed for undecyl meta and para-xylene derivatives. The sulfonation of 4-(2,4-dimethylphenyl) undecane and 4-(2,5-dimethylphenyl) undecane, gave 99% selectivites to the respective sulfonate isomers shown in Scheme 6 with the sulfonate para to an alkyl group.

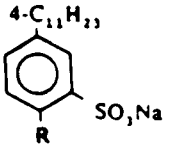
In contrast to the ortho-xylene derivatives where the site para to the 3-methyl group was more sterically hindered, and therefore less favorable for sulfonation,

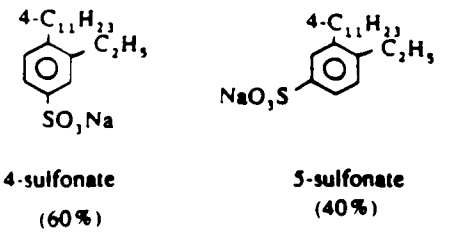
TABLE 2

Isomer Distributions for Para-Undecylalkylbenzene Sulfonates

R	3-Sulfonate[a] (%)
CH_3	92
C_2H_5	87
2-C_3H_7	66

[a]General structure of 2-sulfonate =





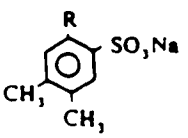
Scheme 3

TABLE 3

Isomer Distributions for Undecyl Ortho-Xylene Sulfonates

R	Temp (°C)	2-Sulfonate[a] (%)
1-$C_{11}H_{23}$	−20	99
2-$C_{12}H_{25}$	−20	92
4-$C_{11}H_{23}$	−20	89
6-$C_{11}H_{23}$	−20	89
6-$C_{11}H_{23}$	83	87

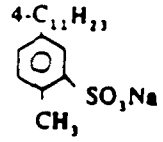
[a]General structure of 2-sulfonate =



the 5-position para to the 2-methyl group in the meta-xylene derivative is also sterically the most favored sulfonation site. On the other hand, the site which is para to the long alkyl chain in the para-xylene derivative is sterically similar to the alternative position ortho to the 2-methyl group.

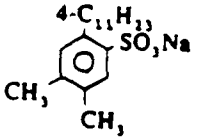
In the sulfonation of another meta-trialkylbenzene derivative, 4-(3,5-dimethylphenyl) undecane, where each of the three sites available for sulfonation are not only para to an alkyl group but are also ortho to two alkyl groups, the sulfonation occurs to give 98% selectivity to the sulfonate isomer shown in Scheme 7. Thus, in this case, where electronic influences are similar, steric effects determine the sulfonate isomer distribution.

Sulfonations of 2-(3,4-dimethylphenyl) dodecane with various sulfonating agents and solvents. Since of all



3-sulfonate

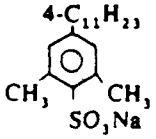
(92%)



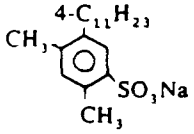
2-sulfonate

(90%)

Scheme 5



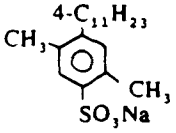
Scheme 7



meta-xylene sulfonate

5-sulfonate isomer

(99%)



para-xylene sulfonate

4-sulfonate isomer

(99%)

Scheme 6

the alkylated benzenes which were investigated, the 1,3,4 ring substituted ortho-xylene derivatives are unique in that the electronically most favored sulfonation position is also sterically less favorable. The sulfonation of 2-(3,4-dimethylphenyl) dodecane was investigated further to determine if the para directing influence of the alkyl groups was as predominant using different sulfonating agents and conditions.

Table 4 summarizes these results. The reaction of the neat hydrocarbon with sulfur trioxide vapor diluted with argon gave a similar 2-sulfonate isomer distribution as reactions conducted in the solvents 1,2-dichloroethane or liquid sulfur dioxide (90–93%). Sulfur trioxide adducts with weakly complexing donors, SO_3-dioxane and SO_3-phosphate gave results similar to uncomplexed SO_3. Sulfur trioxide adducts with strongly complexing donors, such as SO_3-pyridine or SO_3-dimethylformamide were inactive as sulfonating agents up to 100°C. The results from the sulfur trioxide complexes suggest that sulfur trioxide dissociates from the donor before sulfonation can occur (14). If sulfonation were occurring while the SO_3 and adduct were still in the associated,

$$SO_3 - \text{Donor} \rightleftharpoons SO_3 + \text{Donor}$$

form, less sulfonation might be expected to occur ortho to the long chain because of the greater steric bulk of the complexed sulfonating agent. The results in Table 4 do not show a decrease in selectivity for the sterically hindered para position of 2-(3,4-dimethylphenyl) dodecane for the sulfonations using SO_3 adducts.

$$\text{Arene} + SO_3 \rightarrow \text{Arene } SO_3H$$

Sulfonations were also conducted using different sulfonating agents. The reaction of 2-(3,4-dimethylphenyl) dodecane in excess sulfuric acid for 1 hr at 100°C gave 85% selectivity to the 2-sulfonate, which represents significantly less para selectivity than when sulfur trioxide was used. Longer reaction times, however, decreased the amount of the 2-sulfonate with a corresponding increase in the 3-sulfonate, thus indicating that an isomerization is occurring after the initial sulfonation. After 6 hr, only 54% of the 2-sulfonate isomer remains. This isomer distribution does not change significantly on further heating. The dependence of the formation of the 2-sulfonate isomer with time under these conditions is shown in Figure 1. The isomerization may be occurring via a mechanism of protonation, desulfonation, and resulfonation shown in Scheme 8 to give more of the thermodynamically favored isomer (15).

When this molecule was sulfonated with 1.1 equivalents of sulfur trioxide in sulfuric acid as the solvent at 22°C, 74% of the 2-sulfonate was formed. Under the same conditions, but at 100°C, a similar 78% sulfonate isomer distribution was obtained, indicating that sulfuric acid has a greater effect on the sulfonate selectivity than does temperature.

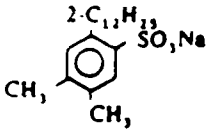
Chlorosulfonic acid was also used as a sulfonating agent at −20°C and gave sulfonate isomer distributions similar to sulfur trioxide, although because of its

TABLE 4

Sulfonation of 2-(3,4-Dimethylphenyl)Dodecane

Reagent/Solvent	% 2-Sulfonate[a]	Temp (°C)
SO_3 vapor[b]	90	50
$SO_3/C_2H_4Cl_2$[c]	92	−20
SO_3/SO_2[d]	93	−20
SO_3-dioxane/$C_2H_4Cl_2$[d]	94	22
$(SO_3)_2$-dioxane/$C_2H_4Cl_2$[d]	94	83
$(SO_3)_3$-$(EtO)_3P{=}O/C_2H_4Cl_2$[d]	93	22
SO_3-pyridine/$C_2H_4Cl_2$[d]	no reaction	100
SO_3-DMF/$C_2H_4Cl_2$[d]	no reaction	100
H_2SO_4[d]	85	100
SO_3/H_2SO_4[d]	78	22
SO_3/H_2SO_4[d]	74	100
$ClSO_3H/C_2H_4Cl_2$[c]	95	83

[a]2-Sulfonate =



[b]SO_3 (1.1 equiv.) is bubbled through the neat hydrocarbon at the reaction temperature using argon as a carrier gas.

[c]SO_3 (1.1 equiv.) in $C_2H_4Cl_2$ is added to the hydrocarbon in $C_2H_4Cl_2$ at the reaction temperature.

[d]The hydrocarbon is added neat to sulfonating agent at the reaction temperature.

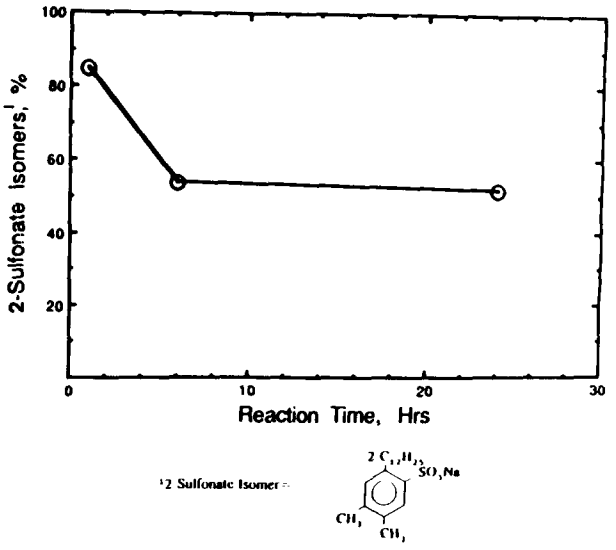


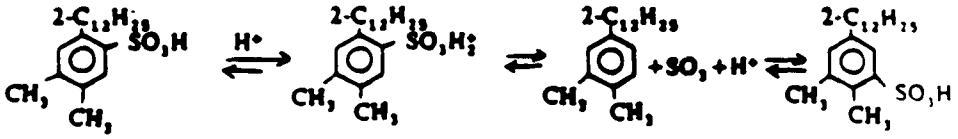
FIG. 1. The Sulfonation of 2-(3,4-Dimethylphenyl) dodecane With H_2SO_4 at 100°C vs Time.

structure it proceeds through a more complex mechanism (16).

From this investigation of the sulfonation of di- and trialkylbenzenes with sulfur trioxide, the following trends were observed. In a molecule in which all sites available for sulfonation are ortho to alkyl groups, sulfonation is favored at the least hindered sites. However, when sites both ortho and para to alkyl groups are available for sulfonation, sulfonation is favored para in preference over ortho even when the para site is sterically less favorable. On the other hand, sulfonation does not occur at sites ortho to two alkyl groups if less hindered ortho or para sites are available. If all of the sites on the benzene molecule are ortho to two alkyl groups then sulfonation will occur with the most favored site determined by steric effects. Sulfonation does not occur at a site which is only meta to alkyl groups if other positions are available for sulfonation.

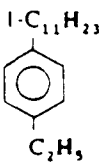
The effect of temperature between −20 and 83°C and the presence of weak Lewis bases have only minor effects on sulfonate isomer distributions. For the sulfonation of 1,3,4 ring substituted xylenes, the presence of strong Bronsted acids causes some isomerization of the electronically favored most hindered product to the thermodynamically favored least hindred product.

The knowledge of these facts allows a qualitative prediction of the sulfonate isomer distribution if the structure of the alkylbenzenes are known. This could be especially useful in the sulfonation of commercial blends of di- and trialkylbenzes. In some cases, such as with alkylated para- or meta-xylenes, the sulfonation is predetermined due to the structure of the hydrocarbon to give almost exclusively one sulfonate isomer.

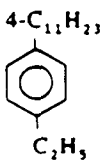


Scheme 8

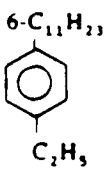
APPENDIX 1.



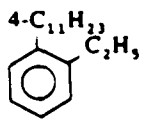
1-(4-ethylphenyl) undecane
1-C11PEB



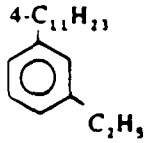
4-(4-ethylphenyl) undecane
4-C11PEB



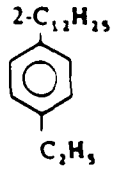
6-(4-ethylphenyl) undecane
6-C11PEB



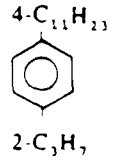
4-(2-ethylphenyl) undecane
4-C11OEB



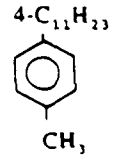
4-(3-ethylphenyl) undecane
4-C11MEB



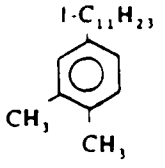
2-(4-ethylphenyl) dodecane
2-C12PEB



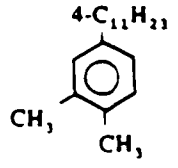
4-(4-(2-propyl)phenyl) undecane
4-C11PIPB



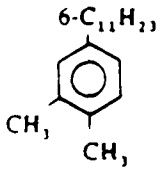
4-(4-methylphenyl) undecane
4-C11PMB



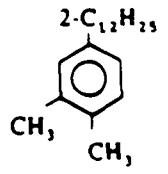
1-(3,4-dimethylphenyl) undecane
1-C11OX



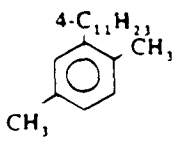
4-(3,4-dimethylphenyl) undecane
4-C11OX



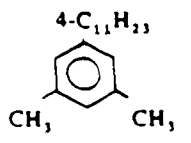
6-(3,4-dimethylphenyl) undecane
6-C11OX



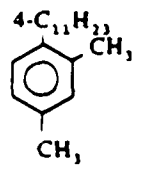
2-(3,4-dimethylphenyl) dodecane
2-C12OX



4-(2,5-dimethylphenyl) undecane
4-C11PX



4-(3,5-dimethylphenyl) undecane
4-C11MX-1,3,5



4-(2,4-dimethylphenyl) undecane
4-C11MX-1,2,4

APPENDIX 2.

Determination of sulfonate isomer distributions. Figure 2 shows the proton decoupled ^{13}C NMR spectra which were used to determine the sulfonate isomer distribution for a mixture of sodium 4-(4-ethylphenyl) undecane sulfonates. In these spectra the lines at 77.6, 76.9 and 76.3 ppm are due to the carbon atom of deuterated chloroform ($CDCl_3$) split into three lines by dueterium coupling. The peaks to the left of $CDCl_3$ are resonances due to the carbons of the aromatic ring while the peaks to the right are due to the aliphatic carbon atoms of the alkyl groups. Sulfonation of the parent hydrocarbon causes significant chemical shift changes in the aromatic region of the ^{13}C NMR spectrum, however, these changes were not systematic enough so as to be correlatable to the position of sulfonation. Previously, other investigators have reported that ^{1}H and ^{13}C NMR chemical shifts of the aromatic region are useful for determining the position of sulfonation in monoalkylbenzenes (17). For the sulfonation of the di- and trialkylbenzenes discussed in the present report, the changes that occurred in the aliphatic region of the ^{13}C NMR spectrum were used as the basis for determining the sulfonate isomer distributions.

For this example, and every other sulfonate spectrum that was examined, the additional resonances present in the aliphatic carbon region of the sulfonate spectrum were used to deduce the sulfonate isomer distributions. The new resonances with the largest chemical shift differences were assigned to the aliphatic carbon atoms which were alpha to the aromatic ring (benzylic) and ortho to the sulfonate group. Chemical shift differences as large as 6 ppm were observed for the benzylic carbon of the long alkyl chain, 3 ppm for the benzylic carbon in ethyl groups and approximately 1 ppm for the benzylic methyl groups. The resonances

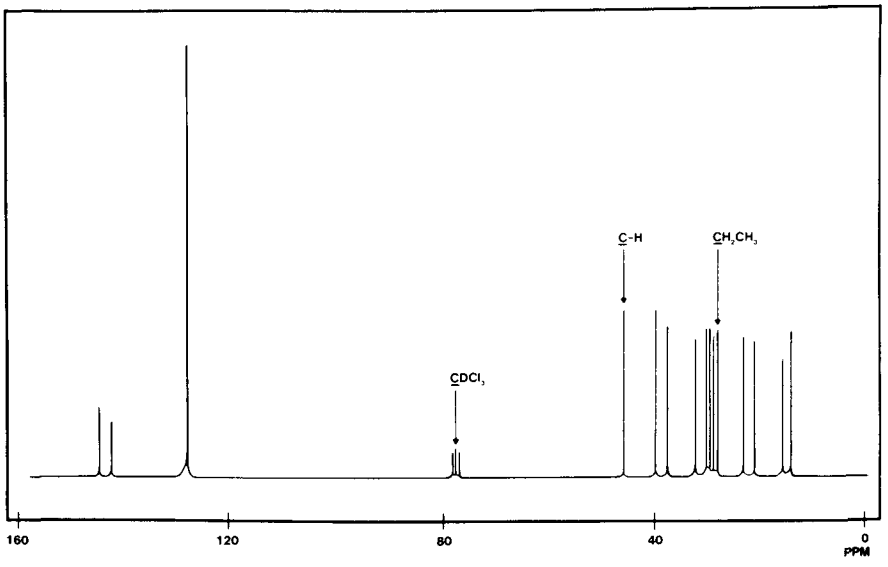


FIG. 2a. ^{13}C NMR Spectrum of 4-(4-Ethylphenyl) Undecane.

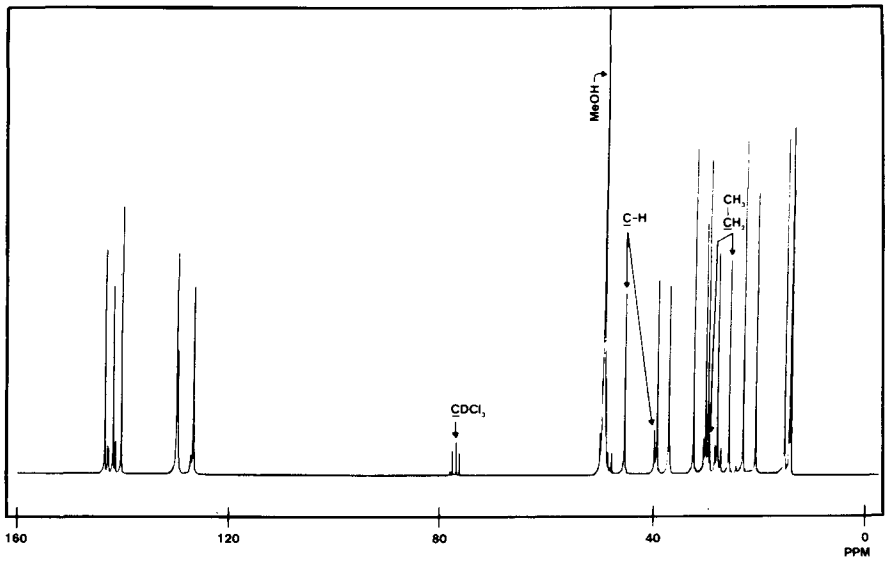


FIG. 2b. ^{13}C NMR Spectrum of Sodium 4-(4 Ethylphenyl) Undecane Sulfonate.

TABLE 5

^{13}C NMR Chemical Shifts[2] For Di- and Trialkylbenzenes and Their Corresponding Sulfonates

	Long chain		Short chain			
Compound[b]	R $\underline{C}$HR	$\underline{C}H_2R$	$\underline{C}H_2CH_3$	$\underline{C}H_3$	Other aliphatic carbons	Aromatic carbons
1-C11PEB		35.6	28.4		14.1,15.6,22.7,29.4,29.6,29.7, 31.6,32.0	127.7,128.3,140.1,140.3
1-C11PEBS		35.3,32.4	28.1,25.3		14.1,15.3,22.6,29.1,29.3,29.6, 30.2,30.9,31.4,31.9	126.9,127.3,129.2,129.6,130.0, 130.4,138.1,139.3,139.7,140.9, 141.0,141.1
4-C11PEB	45.5		28.5		14.1,14.2,15.5,20.8,22.7,27.8, 28.5,29.9,32.0,37.1,39.4	127.5,127.6,143.4,143.6
4-C11PEBS	45.2,39.2		28.0,25.4		14.1,14.4,14.8,15.2,20.4,20.6, 22.4,27.6,29.0,29.2,29.8,31.9, 36.5,36.7,38.7	127.0,127.2,129.3,129.8,139.3, 140.5,140.7,141.5,142.5,143.8
6-C11PEB	45.7		28.5		14.1,15.5,22.6,27.4,32.1,37.0	127.5,127.6,141.3,143.6
6-C11PEBS	45.5,36.7		28.5,25.4		14.0,14.8,15.2,17.9,22.4,26.8, 27.2,31.8,32.0,32.4,36.5	127.0,127.2,129.2,129.7,139.6, 140.7,142.6,143.8
4-C11OEB	39.5		25.9		14.1,14.5,15.8,20.9,22.7,27.8, 29.3,30.1,32.0,37.2,39.3	125.4,125.8,126.0,128.4,142.1, 144.3
4-C11OEBS	39.2		25.9		14.0,14.1,14.3,15.4,15.5,20.7, 22.6,27.8,29.3,29.7,30.0,31.9, 36.9,38.4,38.9	123.7,124.1,125.7,126.5,128.3, 139.5,140.5,142.1,144.4,144.8, 147.3
4-C11MEB	45.8		29.0		14.1,14.2,15.7,20.8,22.7,27.7, 29.3,29.8,31.9,37.0,39.3	124.9,125.1,127.3,128.0,143.9, 146.4
4-C11MEBS	45.5,38.7		28.9,25.8		14.1,14.2,14.5,20.6,22.7,27.6, 29.2,29.8,32.0,36.7	124.2,128.0,128.6,138.2,142.2, 149.1
2-C12PEB	39.5		28.4		14.1,15.5,22.3,22.7,27.8,29.4, 29.6,29.7,31.9,38.5	126.9,127.7,141.4,145.2
2-C12PEBS	39.4,34.5		28.0,25.3		14.1,14.8,15.2,21.9,22.7,25.3, 27.5,27.7,29.3,29.5,29.6,29.7, 29.8,30.2,31.9,38.0,38.2	126.3,126.8,126.9,129.2,129.4, 130.2,139.8,140.2,140.4,140.9, 143.9,145.1
4-C11PIPB	45.3		33.6		14.1,14.2,20.7,22.6,27.7,29.2, 29.7,31.9,36.9,39.2	126.1,127.4,143.7,145.9
4-C11PIPBS	45.3,39.6		33.4,32.0		14.0,14.4,20.3,20.6,22.5,22.6, 23.7,23.9,27.1,27.7,28.9,29.0 29.2,29.8,30.3,31.9,36.6,38.8, 39.2	126.0,126.4,126.8,127.1,128.0, 129.7,140.2,141.5,142.6,143.4, 144.8,145.2
4-C11PMB	45.4			21.0	14.1,14.2,20.7,21.0,22.7,27.7, 29.3,29.8,31.9,37.0,39.3	127.5,128.8,135.0,143.3
4-C11PMBS	45.2			19.8	14.1,20.5,22.6,27.6,29.2,29.8, 31.9,36.5,38.7	126.9,129.6,131.3,133.6,140.8 143.9
1-C11OX		35.6		19.7,19.3	14.1,22.7,29.4,29.5,29.6,29.7, 31.8,32.0	125.7,129.5,129.8,133.5,136.2, 140.2
1-C11OXS	32.0			19.4,18.5	14.1,22.7,27.7,29.5,29.7,29.8, 29.9,30.6	128.8,131.0,133.0,137.9,138.1, 138.2
4-C11OX	45.4			19.9,19.3	14.1,14.2,20.8,22.7,27.7,29.3, 29.8,31.9,37.0,39.3	125.0,129.0,129.4,133.6,136.0, 143.9
4-C11OXS	45.4,39.6			19.7,18.7, 16.0	14.1,14.5,20.4,22.9,27.1,28.0, 28.2,28.8,30.2,32.0,36.8,39.2	125.5,128.3,129.7,131.5,133.0, 137.5,138.8,141.0,142.6,143.0
6-C11OX	45.6			19.9,19.3	14.1,22.6,27.4,32.0,37.0	124.9,129.0,129.4,133.6,136.0, 143.9
6-C11OXS	45.4,39.7			19.6,18.7, 15.9	14.0,20.5,22.3,22.4,22.5, 22.7,26.8,27.2,32.0,32.4, 36.4,36.5,36.6	124.9,128.3,128.7,131.5,132.0, 133.1,137.6,138.8,138.9,141.0, 142.5,143.5
2-C12OX	39.5			19.9,19.3	14.1,22.4,22.7,27.8,29.4, 29.6,29.7,29.8,31.9,38.5	124.3,128.4,129.5,133.7,136.2, 145.6
2-C12OXS	39.4,34.3			20.4,18.7, 19.6,15.8	14.1,22.0,22.6,27.6,29.5, 29.6,29.7,29.9,30.0,31.9, 34.3,38.0	124.0,128.0,128.4,130.6,132.0, 133.0,133.1,138.7,139.0,143.8, 144.0

(Continued)

TABLE 5 (Continued)

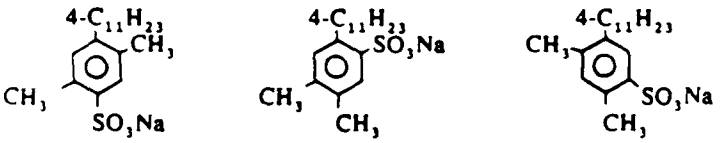
Compound[b]	Long chain R CHR	Long chain CH_2R	Short chain CH_2CH_3	Short chain CH_3	Other aliphatic carbons	Aromatic carbons
4-C11PX	39.8			21.2,19.5	14.1,14.4,20.7,22.7,27.6, 29.3,29.9,31.9,36.9,39.2	125.9,126.4,129.8,132.9,135.2, 144.6
4-C11PXS	39.5			20.0,18.9	14.1,14.3,20.6,22.4,27.4, 29.3,32.0,36.7,38.8	128.6,129.3,133.0,133.6,137.8, 147.3
4-C11MX-1,3,5	45.8			21.4	14.1,14.2,20.9,22.7,27.8, 29.4,29.9,32.0,37.1,39.4	125.5,127.4,137.4,144.3
4-C11MXS-1,3,5	45.3			23.7	14.0,14.1,20.6,22.6,27.6, 29.2,29.7,31.9,36.7,39.0	129.4,137.1,138.1,147.7
4-C11MX-1,2,4	39.5			20.9,19.9	14.0,14.1,20.7,22.7,27.6, 29.3,30.0,31.9,36.9,39.3	125.6,126.8,130.8,134.3,135.8, 141.7
4-C11MXS-1,2,4	39.6			20.9,19.9, 19.5,19.6	14.0,14.1,20.5,22.6,27.6, 29.3,29.8,31.8,36.9,38.9	124.8,132.8,133.2,138.9,139.1, 141.9

[1]Measured in ppm downfield from TMS (δ). Deuterated chloroform was used as a lock signal with a triplet located at 77.6, 77.0, 76.4 ppm.

[b]See Appendix 1 for the structures of the alkylbenzenes corresponding to the shorthand notation. The letter S denotes the corresponding sulfonate derivatives.

3-sulfonate isomer (87%) 2-sulfonate isomer (13%)

Scheme 9



Scheme 10

of the benzylic carbons in alkyl groups which are meta to the sulfonate have significantly smaller chemical shift differences of 0.3 ppm or less.

In the hydrocarbon spectrum in Figure 2a the resonances at 45.5 and 28.5 ppm are attributed to the benzylic carbons of the undecyl and ethyl groups, respectively. In the sulfonate spectrum in Figure 2b, the resonances at 39.2 and 25.4 ppm, which were not present in the hydrocarbon spectrum, are assigned to the isomers with sulfonate groups ortho to the undecyl and ethyl groups, respectively. Therefore, in this example, the pair of resonances at 45.2 and 25.4 ppm are attributed to the major 3-sulfonate isomers and the pair of resonance at 39.2 and 28.0 ppm represent the minor 2-sulfonate isomers. Integration of these lines gives the relative amount of the sulfonate isomers, as can be seen in Scheme 9.

In every case the reasoning used to determine the sulfonate isomer distribution was based on the assumption that compared to the corresponding unsulfonated alkylbenzene, the relatively large shifts of the benzylic carbon in the alkyl groups are due to their ortho orientation to the large sulfonate group. Table 5 summarizes the ^{13}C NMR data for the alkylbenzene sulfonates and their hydrocarbon precursors discussed in this paper.

As additional confirmation that the correlation between the ^{13}C NMR chemical shifts and the ortho orientation of the sulfonate and alkyl groups is valid, ^1H NMR spectra were used to confirm structures whenever single sulfonate isomers were formed. For the three xylene sulfonates shown in Scheme 10, the aromatic protons did not show measurable coupling constants, consistent with their para orientation. Any other sulfonate isomer would have given larger coupling constants of 3–6 Hz consistent with meta or ortho orientations of the protons.

The sulfonate isomer of the above ortho-xylene derivative, but with the sulfonate ortho to the 4-methyl group (thus giving the protons on the ring a meta orientation), gave a coupling constant of 3 Hz for the meta protons in the ^1H NMR.

Since the accuracy of the NMR method for determining the sulfonate isomer distribution is only accu-

rate to within approximately ± 5%, the HPLC method was used to quantify the results. The HPLC and NMR methods were in close agreement in every case. In addition, the HPLC method was more accurate in determining minor amounts of sulfonate isomers.

REFERENCES

1. Puerto, M.C. and W.W. Gale, *Soc. Pet. Eng. J. 17*:193 (1977).
2. Comberiati, J.R., A.M. Zammerilii, B.D. Taylor and N.S. Dala, *Dept. of Energy Report,* DOE/METC/TPR-83-3 (November, 1982).
3. Bolsman, T.A.B.M., Presented at the Second European Symposium on Enhanced Oil Recovery in Paris, France, November 8-10, 1982.
4. Barakat, Y., L.N. Fortney, R.S. Schechter. W.H. Wade and S.H. Yiv, *J. Colloid Int. Sci. 92*:561 (1983).
5. Puerto, M.C. and R.L. Reed, *Soc. Pet. Eng. J.* 23:669 (1983).
6. Bolsman, T.A.B.M. and G.J.R. Daane, *SPE Reservoir Engineering 1*:53 (1986).
7. Salter, S.J., Paper SPE 12036, Presented at the 58th Annual Technical Conference in San Francisco, CA, October 5-8, 1983.
8. Bolsman, T.A.B.M. and G.J.R. Daane, Presented at the Third European Meeting on Improved Oil Recovery in Rome, Italy, April 16-18, 1985.
9. Puerto, M.C. and R.L. Reed, Paper SPE 14290, Presented at the SPE 60th Annual Technical Conference in Las Vegas, NV, September 22-25, 1985.
10. Cole, E.L., *Dept. of Energy Report,* DOE/BC/10830-9 (December, 1988).
11. Salter, S.J., Paper SPE 14106, Presented at the SPE 1986 International Meeting of Petroleum Engineers in Beijing, China, March 1-20, 1986.
12. Grey, R.A. and L.J. Karas, in *"Catalysis of Organic Reactions"*, edited by P.N. Rylander, H. Greenfield and R.L. Augustine, Marcel Dekker, NY, 1988, Vol. 22, pp. 307-322.
13. Verkruyse, L.A., R.V. Lewis, K.O. Meyers and S.J. Salter, Paper SPE 11781, Presented at the International Symposium on Oil Field and Geothermal Chemistry in Denver, CO, June 1-3, 1983.
14. Gilbert E.E., *Sulfonation and Related Reactions,* Robert E. Krieger Publishing Company, New York, 1977, pp. 7-18.
15. Gilbert, E.E., *Ibid.* pp. 427-434.
16. Gilbert, E.E., *Ibid.* pp. 84.
17. El-Emary, M. and L.O. Morgan, *J. Am. Oil Chem. Soc. 55*:593 (1978).

[Received June 9, 1989; accepted October 13, 1989]
[JS/D5733]