Addition of Bisulfite to α-Olefins: Synthesis of n-Alkane Sulfonates and Characterization of Intermediates

Robert Herke* and **Khalid Rasheed**
Witco Corporation, Organics Div. R&D Labs., Houston, Texas 77045

The free radical-catalyzed bisulfite addition to octene-1, decene-1, dodecene-1 and tetradecene-1 was studied under different conditions. The experimental conditions could be adjusted to yield different ratios of intermediate as well as final compounds. We have separated, purified and positively identified alkane-1-sodium sulfonates of general formula CH_3-$(CH_2)_n$-SO_3Na (n = 7,9,11 and 13), alkane-1-sodium sulfonate-2-sulfinic acids of general formula CH_3-$(CH_2)_n$-$CHSO_2H$-CH_2-SO_3Na (n = 5,7,9 and 11) and alkane-1,2-disodium sulfonates of general formula CH_3-$(CH_2)_n$-$CHSO_3Na$-CH_2-SO_3Na (n = 5,7,9 and 11).

The solubilities and critical micelle concentrations of mono- and disodium alkane sulfonates were determined, and for definite identification ^{13}C nuclear magnetic resonance (NMR) and dispersive X-ray crystallography were employed along with classical wet analytical procedures.

KEY WORDS: **Alkane disulfonate, alkane sulfinate/sulfonate, alkane sulfonate, ^{13}C NMR, identification, solubility, surface tension, surfactant, X-ray crystallography.**

There is a continuing search for surfactants that possess good detergent properties, biodegrade readily and have low toxicity. With this objective in mind a great deal of work has been carried out on the synthesis and properties of alkane sulfonates. One of the synthetic routes involves the addition of sodium bisulfite to α-olefin (1–5). Although early work did not recognize the free radical nature of this reaction (1), investigations by Kharasch *et al.* (2) demonstrated that the process was free-radical catalyzed and suggested an overall mechanistic scheme. Norton *et al.* (3) have screened a series of inorganic free radical initiators for this reaction. Peroxy-esters were found to be the initiators of choice. Bright and colleagues (4) at Unilever examined the kinetics of this reaction by using tert. butyl perbenzoate as initiator. We have in the main followed their procedure.

The absence of the double bond in the alkane chain in these surfactants *vs* those made by air/SO_3 sulfonation (AOS) renders them high bleach stability. However, the absence of alkane hydroxy-sulfonate, found in the AOS, limits their water solubility.

In order to gain better understanding of the complex mixture of products obtained in these reactions, we have undertaken to synthesize, purify, unequivocally identify and evaluate some functional characteristics of the intermediates and final products.

MATERIALS AND PROCEDURES

α-Olefins used in this study were obtained from Chevron Chemical Co., Houston, TX, tert. butyl peroxybenzoate from U.S. Peroxygen, Houston, TX, sulfur dioxide from CMS Laboratory Supply, Houston, TX. Other chemicals used were analytical grade.

Melting points were determined by the capillary tube method in a Mel-Temp II apparatus from Laboratory Devices, USA, Holliston, MA, and are uncorrected.

The solubility determinations were carried out by weighing 30 g of a solution of known concentration in a 100-mL insulated beaker containing a magnetic stirring bar and thermometer. The stirred solution was cooled on a cooling plate (Stir Kool, model SK 12 from Thermoelectrics Unlimited, Wilmington, DE) until crystallization was observed. The sample was now slowly heated (0.5°C/min), and the temperature at which a clear solution was formed was taken to be the solubility at that temperature. Reproducibility of the "clear point" temperature reading was better than ±0.5°C.

The surface tension measurements were carried out by a slightly modified ASTM D-1331 method with a 4-cm platinum ring. The modification consists of using a Cahn RG electrobalance, Cerritos, CA, in conjunction with a Varian model 9176 recorder, Palo Alto, CA, instead of a quartz torsion balance. The platinum ring hangs from a hook connected to one arm of the electrobalance, and after calibrating the recorder with appropriate weights, it is immersed in the solution being measured and pulled out by slowly raising the whole electrobalance with a variable speed electromotor. The force needed for pull is read from the recorder and, after multiplying with a calculated factor, is converted into surface tension expressed as mN/m.

^{13}C nuclear magnetic resonance (NMR) spectrometry for octane- and decane-1-sodium sulfonate, -1,2-disodium sulfonate and -1-sodium sulfonate-2-sulfinic acid was carried out in D_2O. The experimental conditions were Varian VXR 300; field strength 75 MHZ; probe 10 mm broadbanded; decoupling routine Waltz decoupling; interpulse delay time 4 sec; number of transients 2000; lock D_2O; temperature 25°C; concentration 15 wt%; and solvent D_2O.

To calculate the chemical shifts for the individual carbon atoms, the method of Grant and Paul was used (6).

Torsion angles and bond distances were determined on crystals of octane-1-sodium sulfonate-2-sulfinic acid, which confirmed the C_1 position of the sulfonate and the C_2 position of the sulfinate group. The data were collected at 173K on a Nicolet R3 diffractometer (Madison, WI) with a graphite monochromator and MoKα radiation (λ = 0.7107Å). The crystal system is monoclinic, space group $P2_1/c$ (No. 14). The lattice parameters were obtained by the least-squares refinement of 49 reflections with $30.63 < 2\theta < 35.07°$. The data were collected from

---

*To whom correspondence should be addressed at Witco Corporation, Organics Div. R&D Labs., 3200 Brookfield St., Houston, TX 77045.

4.0 to 65° in 2θ by using the omega scan technique, with a 1.5° scan range in omega at 6–12°/min, depending on intensity. Data reduction and decay correction were performed by means of the Nicolet XRD Shelxtl-plus software package.

General procedure. The method described by Bright *et al.* (4) was used. After completion of the reaction, isopropanol and unreacted α-olefin were removed by distillation. The residual mixture, containing alkane-1-sodium sulfonate and alkane-1-sodium sulfonate-2-sulfinic acid, was assayed for sulfinate by adding excess sodium hypochlorite. Unreacted hypochlorite was assayed by adding potassium iodide and titrating the liberated iodine with standard sodium thiosulfate solution. The reaction mixture was treated with the calculated amount of hydrogen peroxide at 80°C. This yields a mixture of alkane-1-sodium sulfonate and alkane-1,2-disodium sulfonate.

Alkane-1-sodium sulfonates. Pure monosulfonates were prepared by fractional crystallization of the reaction mixtures containing mono- and disulfonates, taking advantage of the difference in their water solubilities.

For example, a 40% solution of octane mono- and disulfonates was held at 10°C overnight and the crystalline solid obtained was filtered, washed several times with chilled water and dried in the oven at 105°C. Analysis of this product showed that it contained 1.8% sodium sulfate. Extraction with anhydrous ethanol in a Soxhlet apparatus and removal of solvent *in vacuo* yields the pure octane-1-sodium sulfonate (formula: $C_8H_{17}NaO_3S$, m.p. 210°C). Purity of the sample was confirmed by high performance liquid chromatography (HPLC), and by passing it through a H^+ ion exchange resin (Bio-Rad AG 50W-X8, Bio-Rad Labs., Richmond, CA). Titrating the eluted acid confirmed the purity.

The decane-1-sodium sulfonate (formula: $C_{10}H_{21}NaO_3S$, m.p. 202°C), dodecane-1-sodium sulfonate (formula: $C_{12}H_{25}NaO_3S$, m.p. 191°C) and tetradecane-1-sodium sulfonate (formula: $C_{14}H_{29}NaO_3S$, m.p. 181°C) were purified similarly by fractional crystallization. Using this procedure, we have prepared analytically pure samples.

Alkane-1-sodium sulfonate-2-sulfinic acids. These compounds, although mentioned by Bright *et al.* (4) in their work as a by-product of this reaction, were never isolated and fully characterized.

The following procedure for octane-1-sodium sulfonate-2-sulfinic acid is typical. A 2-liter, 4-necked round-bottom flask fitted with a stirrer, thermometer, reflux condenser and gas inlet tube was charged with 112 g (1 mole) of octene-1, 63 (0.5 moles) of sodium sulfite, 200 g of isopropanol and 526 g of deionized water. Sulfur dioxide was bubbled into the stirred reaction mixture to saturation. The mixture was heated to reflux, tert. butyl peroxybenzoate (2 g) was added, and a light stream of sulfur dioxide was passed through the mixture during the entire course of reaction (20–25 hr). The progress of the reaction was followed by determining the acidity of the reaction mixture. When the acidity reached 1.10 meq/g, sulfur dioxide addition was replaced by a nitrogen sparge, and the mixture was set for distillation of isopropanol and unreacted octene-1. After removal of alcohol and α-olefin, the mixture was allowed to cool to room temperature. The white crystalline solid was suction-filtered, washed with cold deionized water and dried at 50–60°C under nitrogen. The yield was 190 g (68% of theory) of octane-1-sodium sulfonate-2-sulfinic acid (formula: $C_8H_{17}NaO_5S_2$, decomposed at 160°C).

Titration of a sample dissolved in deionized water with standardized aqueous sodium hydroxide gave an acidity of 3.57 meq/g or an equivalent weight of 280.1 (theor. 280.26). After passing an aqueous solution of a known amount of the sample through an H^+ ion exchange column, the eluate gave an acidity of 7.15 meq/g or an equivalent weight of 139.8 (theor. 140.1). The oxidation equivalence, determined as described in the general procedure above, with sodium hypochlorite gave 7.148 meq/g or an equivalent weight of 139.9 (theor. 140.1).

The structural assignment is based on the ^{13}C NMR spectra and X-ray crystallography work.

By the same procedure we have prepared the decane-1-sodium sulfonate-2-sulfinic acid (formula: $C_{10}H_{21}NaO_5S_2$, decomposed at 160°C), dodecane-1-sodium sulfonate-2-sulfinic acid (formula: $C_{12}H_{25}NaO_5S_2$, decomposed at 160°C) and tetradecane-1-sodium sulfonate-2-sulfinic acid (formula: $C_{14}H_{29}NaO_5S_2$, decomposed at 160°C).

Alkane-1,2-disodium sulfonates. The disulfonates were prepared by first neutralizing the alkane-1-sodium sulfonate-2-sulfinic acids with sodium hydroxide, followed by oxidation with hydrogen peroxide. The following procedure is typical: 140.1 g (0.5 moles) of octane-1-sodium sulfonate-2-sulfinic acid was suspended in 500 g of deionized water, neutralized with 40 g of 50% sodium hydroxide (0.5 moles) and oxidized by slow addition of 45.7 g of 35% hydrogen peroxide (0.5 moles) at 70–80°C. The resulting solution was evaporated to dryness on a rotary evaporator and yielded octane-1,2-disodium sulfonate as a white crystalline solid (formula: $C_8H_{16}Na_2O_6S_2$, decomposed at 260°C). The characterization is based on acid equivalence of 6.281 meq/g, or an equivalent weight of 159.21 after passing it through the H^+ ion exchange resin (theory: 159.12) and on ^{13}C NMR data.

By the same method we have prepared decane-1,2-disodium sulfonate (formula: $C_{10}H_{20}Na_2O_6S_2$, decomposed at 260°C), dodecane-1,2-disodium sulfonate (formula: $C_{12}H_{24}Na_2O_6S_2$, decomposed at 260°C) and tetradecane-1,2-disodium sulfonate (formula: $C_{14}H_{28}Na_2O_6S_2$, decomposed at 260°C).

RESULTS AND DISCUSSION

All the isolated compounds are white crystalline solids. The alkane-sodium sulfonates have sharp melting points: C_8: 210°C; C_{10}: 202°C; C_{12}: 191°C and C_{14}: 181°C. However, the alkane-1-sodium sulfonate-2-sulfinic acids decompose at 160°C and the alkane-1,2-disodium sulfonates decompose at 260°C.

The solubilities in water (Fig. 1) show sharp differences between the mono- and disulfonates. The monosulfonates have a steep temperature dependence, and the overall solubility decreases with increase in the carbon chainlength at a given temperature. The disulfonates have a much lower temperature dependence and higher overall solubility. They also show differences in solubility with changes in carbon chainlength. The limited solubility at lower temperature is putting a certain constraint on the applications of these surfactants, thus categorizing the C_{12} and C_{14} as "hot water surfactants." Mixtures of mono- and disulfonates with the same alkane chainlength show increased solubility.

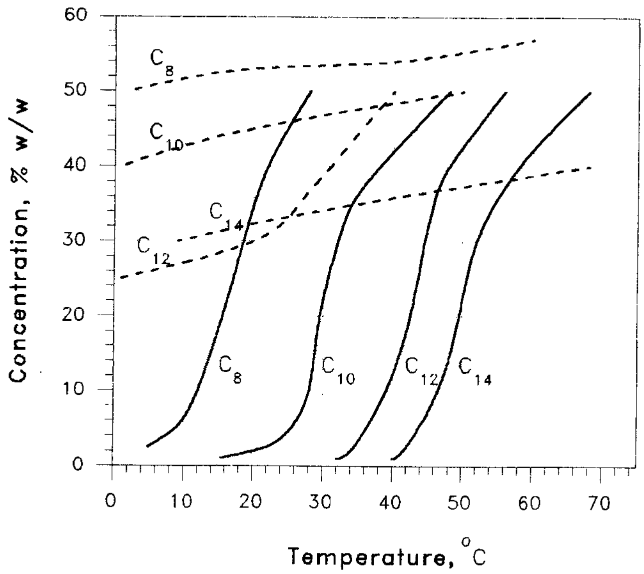


FIG. 1. Solubility of the sodium alkane sulfonates in water. The full lines represent the alkane-1-sodium sulfonates and the dashed lines represent the alkane-1,2-disodium sulfonates.

TABLE 1

Critical Micelle Concentrations (CMC) and Static Surface Tensions at the CMC for the Alkane Sodium Sulfonates Investigated

	CMC (gMol/L)	Surface tension (mN/m)
C_8-Monosulfonate	107.0×10^{-3}	30.5
C_8-Disulfonate	331.2×10^{-3}	30.0
C_{10}-Monosulfonate	17.4×10^{-3}	30.0
C_{10}-Disulfonate	252.9×10^{-3}	30.0
C_{12}-Monosulfonate	7.4×10^{-3}	31.0
C_{12}-Disulfonate	26.9×10^{-3}	28.0
C_{14}-Monosulfonate	1.7×10^{-3}	34.0
C_{14}-Disulfonate	6.3×10^{-3}	30.0

We did not determine the water solubilities for alkane-1-sodium sulfonate-2-sulfinic acids in detail, but we estimate these to be similar to the analogous alkane-1,2-disodium sulfonates.

The static surface tension measurements for octane-1-sodium sulfonate and octane-1,2-disodium sulfonate, presented in Figure 2, are typical for the series. The critical micelle concentration (CMC) and the corresponding measured surface tensions for the series are presented in Table 1. The shape of the curve above the CMC shows strong micellar associations. The values are typical for alkane sulfonates and show them to be good surfactants. In each case the monosulfonates are better surfactants with lower CMCs. In the course of this work we have observed that for mixtures of mono- and disulfonates the CMC values are additive, but the surface tension at CMC was found to be lower than that for either of the individual components.

The assignment of the measured ^{13}C NMR chemical shifts to specific carbon atoms in the alkane chain for the octane- and decane-sulfonates as well as for sulfonate/sulfinates is presented in Table 2. For comparison we included data from the literature for octane, which has only four peaks (equivalent carbon atoms). Calculating the shifts by the method of Grant and Paul (6) gives relatively good agreement with the measured values. When we eliminate the known peaks and compare the incremental substituent effects for other substituents known from the literature, the conclusion is self-evident. Our results

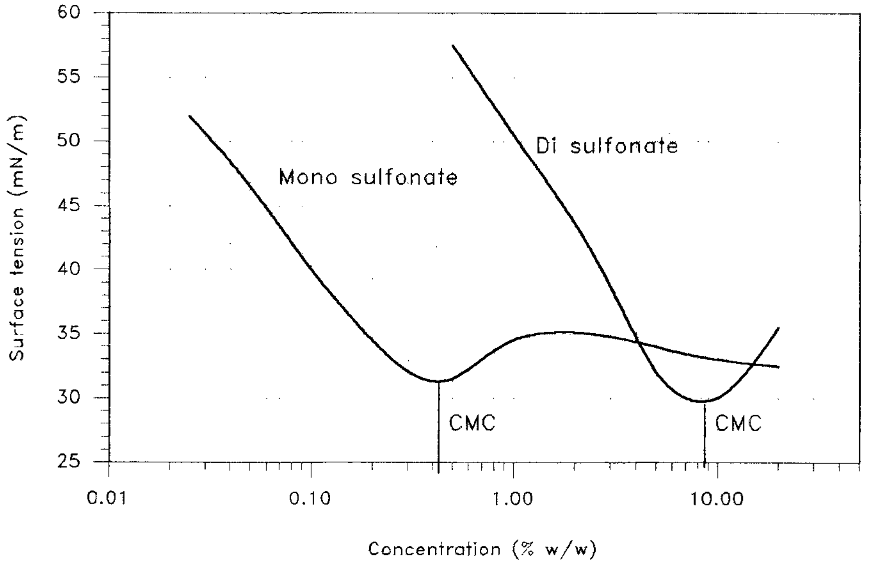


FIG. 2. Static surface tension of the decane-1-sodium sulfonate and decane-1,2-disodium sulfonate. These are typical curves for the series.

TABLE 2

Measured and Calculated ^{13}C NMR Chemical Shifts for Octane- and Decane-sodium Sulfonates and Sulfonate/sulfinates[a]

		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
n-Octane	M[b]	13.6	22.7	32.1	29.4						
	C[b]	13.9	23.0	32.4	29.8						
n-Octane monosulfonate	M	52.2	25.2	29.3	29.8	29.9	32.5	23.3	14.6		
	C	52.2	25.2	29.3	29.8	29.8	32.4	23.0	13.9		
n-Octane disulfonate	M	52.2	57.7	29.3	26.8	30.6	31.6	22.7	14.3		
	C	52.2	57.7	29.3	26.8	29.8	32.4	23.0	13.9		
n-Octane sulfonate-sulfinate	M	47.8	62.5	27.5	26.7	29.4	31.8	22.8	14.3		
	C	47.8	62.5	27.5	26.5	29.8	32.4	23.0	13.9		
n-Decane monosulfonate	M	52.1	25.2	29.4	29.9	30.2	30.3	30.0	32.5	23.2	14.3
	C	52.2	25.5	29.3	29.9	30.2	30.2	29.8	32.4	23.3	13.9
n-Decane disulfonate	M	52.4	57.9	31.0	27.0	29.4	29.5	29.9	32.1	22.9	14.3
	C	52.2	58.0	29.3	26.9	30.2	30.2	29.8	32.4	23.3	13.9
n-Decane sulfonate-sulfinate	M	47.8	62.7	27.0	27.9	29.7	29.8	30.1	32.3	23.1	14.4
	C	47.8	62.8	24.9	26.8	30.2	30.2	29.8	32.4	23.0	13.9

[a] Note: numbering of carbon atoms starts on the end carbon atom with the attached sulfonate.

[b] M = measured value; C = calculated value.

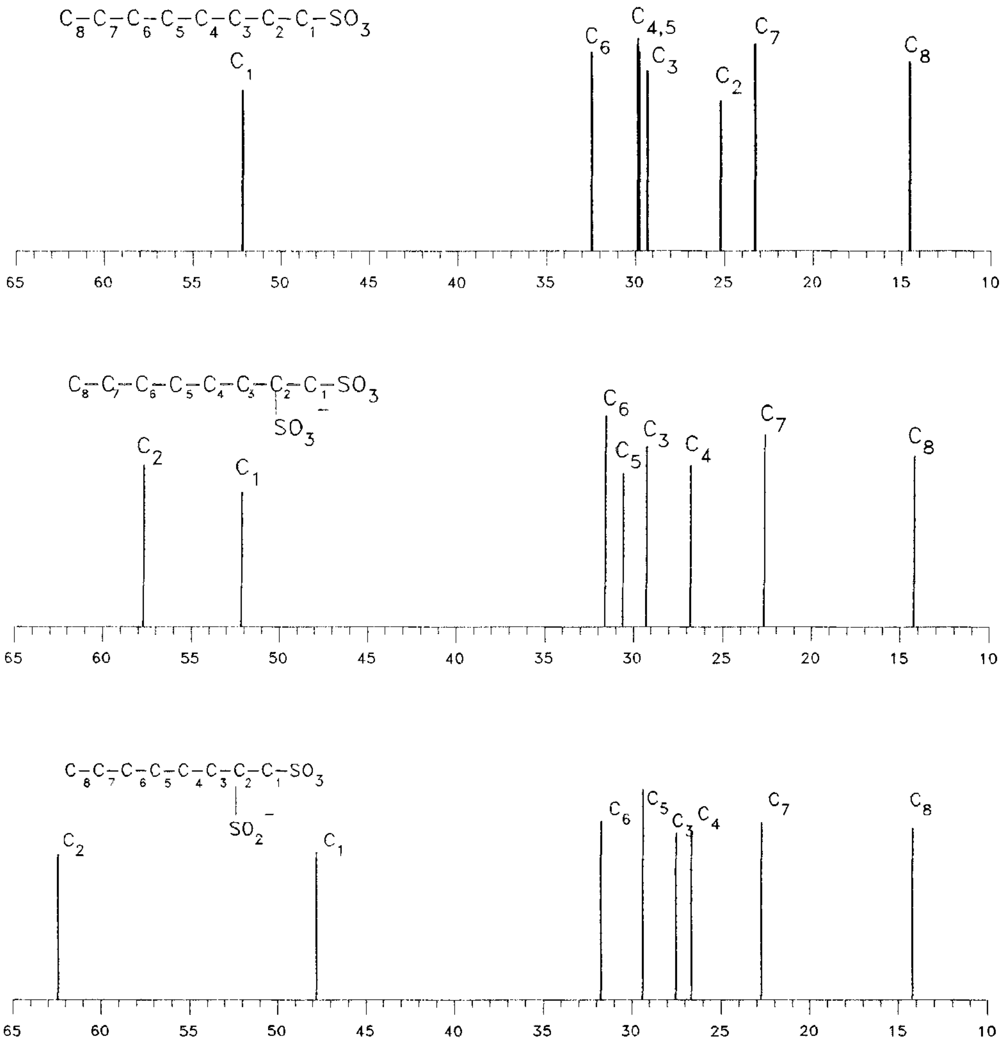


FIG. 3. Simplified graphic presentation of the ^{13}C NMR spectra of octane-1-sulfonate, octane-1,2-disulfonate and octane-1-sulfonate-2-sulfinate.

TABLE 3

Incremental Substituent Effects on ^{13}C NMR Chemical Shifts for Sulfonate- and Sulfinate-group

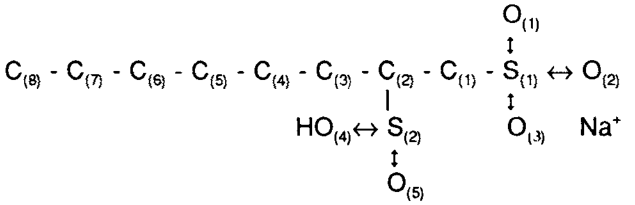
	Sulfonate		Sulfinate
Carbon atom	Terminal	Internal	Internal
α	38.3	32.5	37.3
β	2.2	0	−4.4
γ	−3.1	−3.0	−3.1

TABLE 4

Bond Distances in Å from Dispersive X-ray Crystallography for Octane-1-sodium Sulfonate-2-sulfinic Acid Crystals

C_1-C_2[a]	1.522	C_1-S_1	1.778
C_2-C_3	1.516	C_2-S_2	1.830
C_3-C_4	1.538		
C_4-C_5	1.534	S_1-O_1	1.459
C_5-C_6	1.532	S_1-O_2	1.470
C_6-C_7	1.533	S_1-O_3	1.458
C_7-C_8	1.542		
		S_2-O_4	1.597
Na-O_1	2.454	S_2-O_5	1.488
Na-$O_1{}'$	2.348		
Na-O_3	2.373	O_4-H	0.860
Na-$O_3{}'$	2.324		
Na-O_5	2.439	Na-Na′	3.137
Na-$O_5{}'$	2.312		

[a]Numbering of atoms corresponds to formula below:



$$C_{(8)}-C_{(7)}-C_{(6)}-C_{(5)}-C_{(4)}-C_{(3)}-\underset{\underset{\underset{O_{(5)}}{\updownarrow}}{HO_{(4)}\leftrightarrow S_{(2)}}}{\underset{|}{C_{(2)}}}-C_{(1)}-\overset{\overset{O_{(1)}}{\updownarrow}}{\underset{\underset{O_{(3)}}{\updownarrow}}{S_{(1)}}}\leftrightarrow O_{(2)}\quad Na^{+}$$

indicate that the sulfinate functionality in the internal position has a somewhat larger effect on the α and β carbon atoms than the sulfonate group.

Our calculated incremental substituent effects on ^{13}C NMR shifts of sulfonate and sulfinate group on the α, β and γ carbon atoms in alkyl chains from the measured values are presented in Table 3.

Figure 3 shows graphically the measured peaks for octane-sulfonates for easier comparison. The chemical shifts are in ppm from trimethylsilane (TMS). These tentative conclusions will need verification from other model compounds.

Further confirmation of the sulfonate sulfinic acid structure assignment is obtained from dispersive X-ray crystallography data for octane-1-sodium sulfonate-2-sulfinic acid (Table 4). The C–C bond distances obtained for C_1–C_2 and C_2–C_3 *vs* the bond distances for the remaining carbon atoms are the result of substitution of sulfonate (C_1) and a sulfinic acid functionality (C_2). In addition, the bond distances between C_1–S_1 and C_2–S_2 clearly show the different nature of the two sulphur atoms.

ACKNOWLEDGMENTS

We thank Chevron's Kingwood Technology Center for running ^{13}C NMR spectra, and S.H. Simonsen and Dr. K.A. Abboud from the University of Texas, Austin, for X-ray crystallography. We also thank the Organic Division of Witco Corporation for permission to publish this work.

REFERENCES

1. Kolkar, I., and A. Lapworth, *J. Chem. Soc. 127*:307 (1925).
2. Kharasch, M.S., E.M. May and F.R. Mayo, *J. Org. Chem. 3*:175 (1938).
3. Norton, C.J., N.F. Seppi and M.J. Reuter, *Ibid. 33*:4158 (1968).
4. Bright, S.C., C.E. Stubbs and L. Thompson, *J. Appl. Chem. Biotechnol. 25*:901 (1975).
5. Norton, C.J., and D.E. Drayer, *Hydrocarbon Process.*:140 (1970).
6. Silverstein, R.M., G.C. Bassler and T.C. Morril, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, New York, NY, 1981.

[Received April 25, 1991; accepted June 30, 1991]