Ether Alcohol Sulfates. The Effect of Oxypropylation and Oxybutylation on Surface Active Properties[1]

J. K. WEIL, A. J. STIRTON and M. V. NUÑEZ-PONZOA,
Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

Abstract

The reaction of 1,2-butylene oxide with fatty alcohols of 12 to 18 carbon atoms was investigated and products were compared with those from the propylene oxide reaction. A 60% yield of the first derivative was obtained for the butylene oxide reaction compared with a maximum yield of 50% for the propylene oxide reaction. First and second derivatives were fractionally distilled from the reaction mixtures and characterized as pure ether alcohols and their acetates.

Sulfation of the pure ether alcohols permitted some interesting comparisons of the effect of structural change on surface active properties. Oxybutylation gave slightly greater solubility increases than oxypropylation and both reactions were more effective than oxyethylation. Dioxyalkylated products had lower Krafft points than monooxyalkylated products. A low degree of oxyalkylation had only minor effects on the detergency of alcohol sulfates but polyoxybutylation caused significant reductions in foam height for the 16 and 18 carbon alcohol sulfates. Critical micelle concentration was reduced both by increasing degree of oxyalkylation and molecular weight of epoxide. All of the ether alcohol sulfates were effective lime soap dispersing agents.

Introduction

IT HAS BEEN SHOWN that ether alcohol sulfates derived from propylene oxide are more soluble, give higher yields of monooxyalkylated products, and are only slightly less stable than those derived from ethylene oxide (9). Since 1,2-butylene oxide may become of increasing commercial importance, we have extended our study to include ether alcohol sulfates based on butylene oxide. Additional effort has also been made to isolate pure dioxyalkylated alcohols for characterization and sulfation. The present paper is a study of the effect of these structural changes on the physical properties of ether alcohols and the surface active properties of ether alcohol sulfates.

Experimental

Materials

The normal primary alcohols were the same as those described in the previous publication (9). They were all purified by conventional distillation and crystallization procedures to 97–99% purity according to vapor phase chromatographic analysis. Propylene oxide was the best quality supplied by Eastman Kodak Company. 1,2-Butylene oxide was supplied as experimental samples by Dow Chemical Company. The supplier's estimate of purity is 99%.

Oxyalkylations

Fatty alcohol containing 0.5% KOH was stirred and heated to 160C while passing a slow stream of

nitrogen through the system to flush out oxygen. Nitrogen addition was stopped and epoxide added dropwise with continued stirring and heating under an efficient reflux system. Addition rate was regulated to maintain the temperature between 160 and 180C by controlling the reflux. Temperature control was more difficult wth the less reactive butylene oxide, but changes in reaction temperature did not affect the composition of reaction products.

Distillation

Separation of reaction products was accomplished by vacuum distillation through a one-foot column containing 0.24 in. Cannon stainless steel protruded packing. A capillary N_2 bleed was used during distillation at 0.3 to 0.5 mm. Although either the ether alcohol or its acetate could be distilled, the majority of separations were carried out on the ether alcohol as a matter of convenience.

Acetylation

Gildenberg and Trowbridge's method (5) was used to convert both purified ether alcohols and reaction mixtures to their corresponding acetates. A more complete acetylation of reaction mixtures was obtained when alkaline catalyst was not removed.

Gas-Liquid Chromatography

An F & M Model 720 dual column chromatograph fitted with an eight-foot 20% SE30 silicone gum rubber column, operated isothermally at 280C, was used for all chromatographic analysis. Individual ethers and acetates were injected without modification for purity determinations. Reaction mixtures had to be converted to acetates to obtain an accurate analysis for higher degrees of oxyalkylation.

Sulfation

A 10% molar excess of $ClSO_3H$ was added dropwise to a stirred solution of the individual ether alcohol in cold CCl_4. The reaction mixture was warmed to room temperature with continuous stirring, diluted with an equal volume of cold 95% ethanol and neutralized with 18N NaOH. The pure ether alcholol sulfates were crystallized from the neutralized solution and recrystallized from absolute ethanol after removing insoluble inorganic salts from the boiling solution. Yields of purified product varied from 80% for the monooxypropylated alcohol sulfates to 60% for some of the dioxybutylated alcohol sulfates. Sulfated dioxybutylated dodecanol could not be purified by conventional methods.

Measurement of Surface Active Properties

Evaluations for detergent and other surface active properties were carried out as described in earlier publications (1,8). Calcium stability was measured by the method of Wilkes and Wickert (10), lime soap dispersing power by the method of Borghetty and Bergman (2), wetting time by the Draves test (3), and foam height by the Ross-Miles test (6).
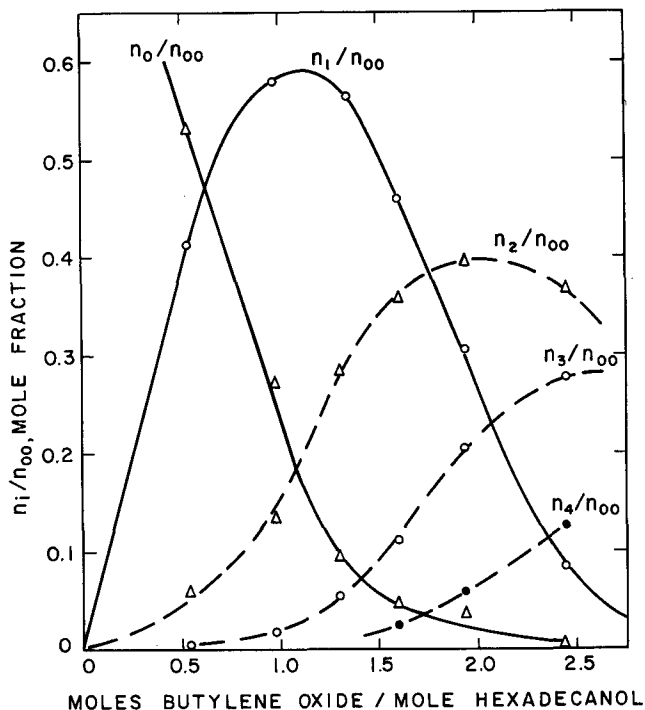
FIG. 1. Composition of products with different additions of 1,2-butylene oxide to hexadecanol: n_0/n_{oo} = hexadecanol; n_1/n_{oo} = first derivative; etc.

TABLE II

Effect of Oxyalkylation on Freezing Point, °C

Alkylene oxide	Hexadecanol		Octadecanol	
None	49		58	
	First derivative	Second derivative	First derivative	Second derivative
O⟨CH₂CH₂ ($\overset{O}{\overbrace{CH_2CH_2}}$)	43	37	52	45
$\overset{O}{\overbrace{CH_3CHCH_2}}$	39	19	41	30
$\overset{O}{\overbrace{C_2H_5CHCH_2}}$	26	10	36	19

monooxyalkylated product at the expense of the parent alcohol with corresponding reduction of more highly oxyalkylated products.

Figure 1 shows how the yield of each addition product varies with different amounts of total butylene oxide added. Compositions were determined by GLC analysis of the acetates. This shows that a maximum yield of first derivative close to 60% is obtained as slightly more than one mole of butylene oxide is added and that a 40% yield of second derivative is obtained as slightly more than two moles of butylene oxide are added.

Individual monooxybutylated and dioxybutylated alcohols were separated by careful fractional distillation. Their freezing points, refractive indices, and purity are listed in Talbe I along with the same properties for the acetates.

Table II compares the freezing point of oxybutylated hexadecanol and octadecanol with corresponding oxypropylated (9) and oxyethylated (11) products. The freezing point depression compared to the parent alcohol is in the order: oxyethylation < oxypropylation < oxybutylation. Dioxyalkylation caused greater reduction than monooxyalkylation. Since melting point is related to Krafft point, it might be expected that the lower melting ether alcohols would produce the more soluble ether alcohol sulfates.

Ether alcohol sulfates were each purified by at least two crystallizations from ethanol. With the exception of the sulfated dioxybutylated dodecanol which could not be purified by this method, analyses for sodium and sulfur were within a few tenths of theoretical values. The sulfated monooxypropylated alcohols were solids melting at some value in the range 130 to 140C, the dioxypropylated derivatives melted at 80 to 95C and the monooxybutylated derivatives at 70 to 90C. Two of the dioxybutylated derivatives were viscous liquids at room temperature and dioxybutylated octadecyl sulfate melted at 35C.

Surface active properties of ether alcohol sulfates are compared in Table III. Solubility is most con-

The critical micelle concentration was measured by the pinacyanole chloride dye titration method, and the Krafft point was measured as the temperature at which 1% dispersion became a clear solution on gradual heating. Detergency was measured as the increase in reflectance, ΔR, after washing 10 swatches of standard soiled cotton (4) in 1 liter of detergent solution in the Terg-O-Tometer for 20 min at 60C and 110 cpm. The results are recorded in Tables III and IV.

Results and Discussion

The composition of products obtained from the oxybutylation of dodecanol, tetradecanol, hexadecanol and octadecanol was determined by vapor phase chromatographic analysis of the acetylated reaction mixtures, confirmed in most cases by distillation analysis. Although the composition of products from the butylene oxide reaction does not exactly fit the statistical pattern predicted by Weibull and Nycander's equation (7), the value for the distribution constant, c, is close to 0.3. The distribution constant is a ratio of reaction rate of ether alcohol to that of the parent alcohol and may be compared with 0.5 for the propylene oxide reaction, and 3 for the ethylene oxide reaction. Thus, the butylene oxide reaction would be expected to produce the highest yields of

TABLE I

Properties of Individual Ether Alcohols and Their Acetates

	Ether alcohol				Acetate		
	F. P., °C	n_D^{40}	n_D^{60}	Purity[a] %	F. P., °C	n_D^{40}	Purity[a] %
$C_{12}H_{25}OCH_2CH(C_2H_5)OH$	1	1.4359	1.4279	99	−15	1.4398	99
$C_{12}H_{25}[OCH_2CH(C_2H_5)]_2OH$	−28	1.4378	1.4301	99	−37	1.4329	90
$C_{14}H_{29}OCH_2CH(C_2H_5)OH$	14	1.4389	1.4311	99	−2	1.4328	93
$C_{14}H_{29}[OCH_2CH(C_2H_5)]_2OH$	−8	1.4400	1.4325	98	−15	1.4351	95
$C_{16}H_{33}OCH_2CH(C_2H_5)OH$	26	1.4411	1.4337	99	12	1.4353	99
$C_{16}H_{33}[OCH_2CH(C_2H_5)]_2OH$	10	1.4418	1.4344	96	4	1.4372	90
$C_{18}H_{37}OCH_2CH(C_2H_5)OH$	36	1.4432	1.4357	99	23	1.4378	95
$C_{18}H_{37}[OCH_2CH(C_2H_5)]_2OH$	19	1.4438	1.4363	92	15	1.4391	98

[a] Purity by GLC analysis.

TABLE III
Surface Active Properties of Ether Alcohol Sulfates

R[OCH2CH]iOSO3Na / R'			Krafft point 1% solution	cmc,[a] millimoles, per liter	Calcium stability, ppm CaCO3	Lime soap dispersing power, %	Detergency, 60C ΔR [c] 0.05% + 0.2% B,[d] 300 ppm	Foam height 60C, mm 0.05% + 0.2% B,[d] 300 ppm
R	R'	i						
C12H25		0	16°	.....	650	30	18	185
	CH3	1	clear at 0	2.69	>1800	14	22	210
		2	clear at 0	1.54	>1800	6	21	205
	C2H5	1	clear at 0	1.8	>1800	10	22	225
		2	clear at 0	0.8	>1800	10	21	208
C14H39	......	0	30	.....	465	19	29	230
	CH3	1	14	0.58	>1800	8	26	220
		2	clear at 0	0.36	>1800	9	23	200
	C2H5	1	13	0.43	>1800	9	25	200
		2	clear at 0	0.20	>1800	19	22	175
C16H33	.....	0	45	[b]	...[b]	..[b]	28	240
	H	1	36	0.22	1060	3	....	......
		2	24	0.14	1600	3	.	.
	CH3	1	27	0.16	780	8	27	185
		2	19	0.076	>1800	7	26	175
	C2H5	1	23	0.12	940	9	26	155
		2	21	0.061	1100	8	24	50
C18H37	......	0	56	.....[b]	.....[b]	....[b]	28	190
	H	1	46	0.11	.....[b]	9	29	100
		2	40	0.07	>1800	16	.	......
	CH3	1	43	.....[b]	...[b]	8	28	100
		2	31	0.041	1285	7	25	90
	C2H5	1	38	.....	560	10	25	75
		2	24	0.051	775	11	26	35

[a] Critical micelle concentration by the pinacyanole chloride method.
[b] Not soluble enough for test conditions.
[c] Increase in reflectance after washing standard soiled cotton (4) in the Terg-O-Tometer.
[d] Builder: 55% Na5P3O10; 24% Na2SO4; 10% Na4P2O7; 10% Na metasilicate, 1% CMC.

veniently compared by Krafft point or the temperature at which a 1% dispersion becomes clear on gradual heating. In each case oxyalkylation decreased the Krafft point, dioxyalkylation causing a greater decrease than monooxyalkylation. Effectiveness of oxyalkyl groups is in the order, oxybutyl > oxypropyl > oxyethyl.
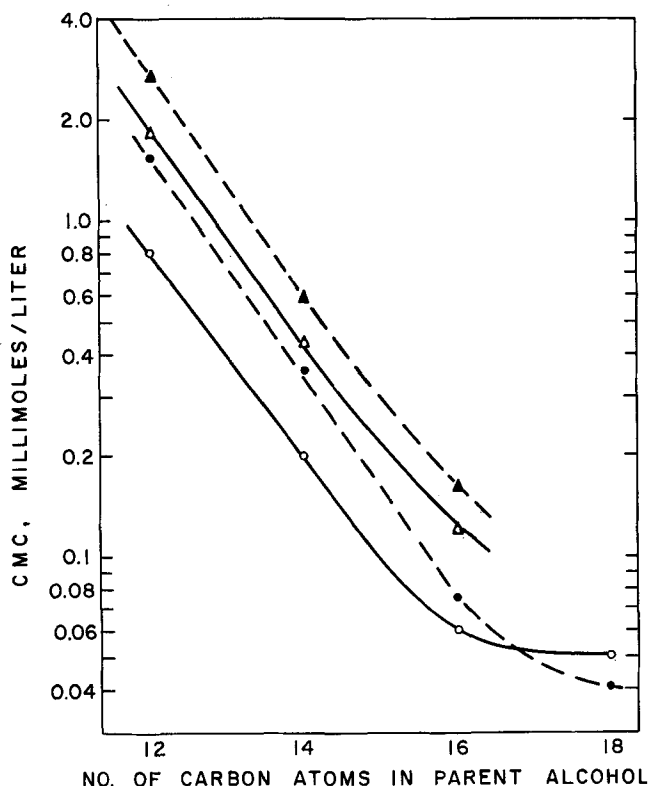

FIG. 2. Critical micelle concentration of ether alcohol sulfates by the pinacyanole chloride method:

— ▲ — — — — ▲ — ROCH2CH(CH3)OSO3Na;
— △ ——————— △ — ROCH2CH(C2H5)OSO3Na;
— ● — — — — ● — R[OCH2CH(CH3)]2OSO3Na;
— ○ ——————— ○ — R[OCH2CH(C2H5)]2OSO3Na.

The critical micelle concentration was reduced by oxyalkylation. The cmc also decreased, but not in a simple mathematical relation, with increased size of the oxyalkyl group. Figure 2 shows how the cmc varies with the number of carbon atoms in the parent alcohol, for the first and second derivatives of propylene oxide and butylene oxide. The lines are parallel and appear to follow the expected logarithmic relationship but become erratic at longer chain lengths.

All of the ether alcohol sulfates have good calcium stability and are effective lime soap dispersing agents.

Detergency and foam height measurements are also shown in Table III. In some cases oxyalkylation caused a slight decrease in detergency. Oxybutylation reduced the foaming properties of the longer chain alcohol sulfates and dioxybutylated products had low and unstable foams.

Sulfated oxybutylated alcohol sulfates with an average of about one oxybutyl group are compared with pure monoether alcohol sulfates in Table IV. As had been found in the case of oxypropylation (9), mixtures had the same properties as the pure compounds within the limits of measurement.

The data of comparative oxyalkylation indicates the importance of bulk in relation to surface active properties. The effect of bulk is to increase solubility and improve lime soap dispersing power, and

TABLE IV
Properties of Sulfated Ether Alcohol Reaction Mixtures

R[OCH2CH(C2H5)]nOSO3Na		Calcium stability, ppm CaCO3	Lime soap dispersing power, %	Detergency, 60C, ΔR 0.05% + 0.2% B	Foam height, 60C, mm 0.05% + 0.2% B
R	n				
C12H25	0.99	>1800	10	23	210
	1	>1800	9	22	225
C14H29	1.19	>1800	13	26	188
	1	>1800	9	25	200
C16H33	1.30	1190	12	24	145
	1	940	9	26	155
C18H37	0.98	740	13	27	105
	1	560	10	26	75

also, because of increase in chain length, to decrease cmc. It is interesting to observe that these changes do not have a marked effect on detergent properties.

Stability to acid hydrolysis was measured on a 0.05 normal solution of the ether alcohol sulfate in 0.05 normal hydrochloric acid at 80C. First order reaction constants were found to be 0.010 min^{-1} for $C_{16}H_{33}OCH_2CH(C_2H_5)OSO_3Na$ and 0.018 min^{-1} for $C_{16}H_{33}[OCH_2CH(C_2H_5)]_2OSO_3Na$ compared with 0.007 min^{-1} for the monooxypropylated product and 0.013 min^{-1} for the dioxypropylated product. The first 25% of the hydrolysis of both dioxyalkylated materials proceeded at a slower rate (0.010 min^{-1}) before increasing to the rates shown above. All of the ether alcohol sulfates were stable to alkali, showing less than 2% hydrolysis after 3 hr in boiling 2N alkali.

Biodegradability measurements by the river water die away test indicate that all of these materials are very soft, being destroyed according to the methylene blue test in about two days.

REFERENCES

1. Bistline, R. G., Jr., A. J. Stirton, J. K. Weil and E. W. Maurer, JAOCS *34*, 516–518 (1957).
2. Borghetty, H. C., and C. A. Bergman, Ibid. *27*, 88–90 (1950).
3. Draves, C. Z., Am. Dyestuff Reptr. *28*, 425–428 (1939).
4. Draves, C. Z., and O. L. Sherburne, Ibid. *39*, 771–772 (1950).
5. Gildenberg, L., and J. R. Trowbridge, JAOCS *42*, 69–71 (1965).
6. Ross, J., and G. D. Miles, Oil and Soap *18*, 99–102 (1941).
7. Weibull, B., and B. Nycander, Acta Chem. Scand. *8*, 847–858 (1954).
8. Weil, J. K., A. J. Stirton, R. G. Bistline, Jr., and E. W. Maurer, JAOCS *36*, 241–244 (1959).
9. Weil, J. K., A. J. Stirton and Elizabeth A. Barr, Ibid. *43*, 157–160 (1966).
10. Wilkes, B. G., and J. N. Wickert, Ind. Eng. Chem. *29*, 1234–1239 (1937).
11. Wrigley, A. N., A. J. Stirton and E. Howard, Jr., J. Org. Chem. *25*, 439–444 (1960).