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Alkali Fusion - Gas Chromatography of Alkyl Sulfates

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The alkali fusion of alkyl sulfates was investigated by pyrolyzing a mixture of alkyl sulfates and alkali metal hydroxide between 200—500°C. The pyrolyzates were isolated and identified to be 1-olefins, internal olefins, alcohols, and dialkyl ethers by gas chromatography and IR spectroscopy. The mechanism of this reaction was proposed from these results and an attempt was carried out to estimate the alkyl chain carbon number distribution of the commercially available sodium alkyl sulfates.

The analysis of the lipophylic groups of alkyl sulfates has been carried out by means of acid hydrolysis followed by gas chromatographic identification of the resulting alkyl alcohols.

Knight and Hous[1] reported the decomposition of alkyl sulfates in hot phosphoric acid to result the corresponding olefins, which was comfirmed by several other workers.[2,3] Lew[4] described that the pyrolysis of alkyl sulfates with P_2O_5 gave a mixture of 1-olefin and internal olefin isomers with the same carbon numbers as the alkyl group of the original sulfate, but gave neither alcohols nor dialkyl ethers. The direct pyrolysis of alkyl sulfates without any reagent also yielded the corresponding olefins,[4,5] and alcohols.[5] Moreover, Nishi[6] presented a simple identification method of anionic surfactants by alkali fusion. He reported that the alkyl sulfates were decomposed only to alcohols, but he did not give any detailed discussion. The present paper deals with the mechanism of alkali fusion of alkyl sulfates as compared with that of alkyl sulfonates, which has been reported in the previous paper.[7]

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[1] J. D. Knight and R. Hous, *J. Am. Oil Chem. Soc.*, **36**, 195 (1959).
[2] E. A. Setzkorn and A. B. Carel, *ibid.*, **40**, 57 (1963).
[3] S. Nishi, *Bunseki Kagaku (Japan Analyst)*, **14**, 912 (1965).
[4] H. L. Lew, *J. Am. Oil Chem. Soc.*, **44**, 359 (1967).
[5] T. H. Liddicoet and L. H. Smithson, *ibid.*, **42**, 1097 (1965).
[6] S. Nishi, *Bunseki Kagaku (Japan Analyst)*, **14**, 914 (1965).
[7] T. Nakagawa, K. Miyajima and T. Uno, *J. Gas Chromatog.*, **6**, 292 (1968).

Experimental

Preparation of Sodium *n*-Alkyl Sulfates. One tenth mole of *n*-alkyl alcohol (alkyl carbon numbers: 5, 6, 7, 8, 9, 10, 12, 14 and 16) was placed in a 500 m*l* flask fitted with a mechanical stirrer, a dropping funnel, a thermometer, and a reflux condenser, from the top of which HCl gas was removed. The flask was cooled in an ice bath at 0—5°C and 0.1 mol of chlorosulfonic acid was added dropwise with a thorough agitation. After addition, stirring was continued for two hours at room temperature, then the reaction mixture was allowed to stand overnight, neutralized with sodium hydroxide solution, and evaporated to almost dryness. Alkyl sulfate was extracted from the dried residue with absolute ethyl alcohol for 6 hr by using a Soxhlet extractor to remove the inorganic impurity, *i. e.,* NaCl. After removing ethyl alcohol from the extract, the crude sulfate which still contained a minor amount of unchanged original alcohol was recrystallized twice from absolute ethyl alcohol, rinsed by acetone and dried in the desiccator. The raw materials, *n*-alkyl alcohols, had been purified by distillation and checked cautiously by gas chromatography. The IR spectra of the sulfates, obtained above, did not indicate contamination with the original alcohols.

Preparation of Di-*n*-alkyl Ethers. Di-*n*-alkyl ethers were prepared by Williamson's reaction. One tenth gram atom of sodium metal was dissolved in 0.2 mol of *n*-alkyl alcohol at 100°C with stirring. Then 0.1 mol of *n*-alkyl bromide with the same carbon numbers as the alcohol was added dropwise into the solution. The stirring was continued at 100°C until the pH of the reaction mixture became nearly neutral. After reaction, 100 m*l* of ethyl ether was poured into the reaction mixture and sodium bromide was removed by extracting the ethereal layer with 50 m*l* of water. The ethereal layer was dried over anhydrous sodium sulfate and the ether was removed. The residue was distilled under reduced pressure. Purity of these dialkyl ethers was checked by gas chromatography. The boiling points and the results of elemental analysis are listed in Table 1.

Other Reagents. Reagent grade LiOH, NaOH, KOH, RbOH, CsOH, were used. *cis-n*-2-Octene (K & K Laboratories Inc.), and *trans-n*-3-octene, *trans-n*-4-octene (Aldrich Chemical Co., Inc.), and other olefins (Tokyo Kasei Kogyo Co., Ltd.) were used without further purification. All the olefins were pure enough to use for the standard of gas chromatography.

Pyrolysis Apparatus. A Shimadzu Pyrolyzer Model PYR-1A was used. The apparatus was equipped with 170 mm length and 6 mm i. d. quartz pipe which was heated externally by nichrome wire. Its temperature was measured by thermocouple and heating was controlled by a voltage regulator. The pyrolyzer and the gas chromatography were connected in series. The alkali fusion was carried out in a platinum boat in the quartz pipe in an atomosphere of nitrogen.

Gas Chromatographic Conditions.

Apparatus:	Shimadzu Gas Chromatograph Model GC-1C
Packing:	20 wt% Apiezon L, 20 wt% squalane, 10 wt% DEGS and 20 wt% PEG 20 M coated on 60/80 mesh Chromosorb W pretreated with HCl and DMCS-methanol.
Column:	Stainless steel U tube, 3 mm i. d.
Carrier gas:	Nitrogen
Detector:	FID

The column temperature, column length, and nitrogen flow rate were appropriately adjusted in each case.

Isolation of the Pyrolyzates. Two grams of a sodium *n*-alkyl sulfate prepared was ground quickly and mixed uniformly with 10 g of alkali metal hydroxide in a mortar and put in a stainless steel reactor, which

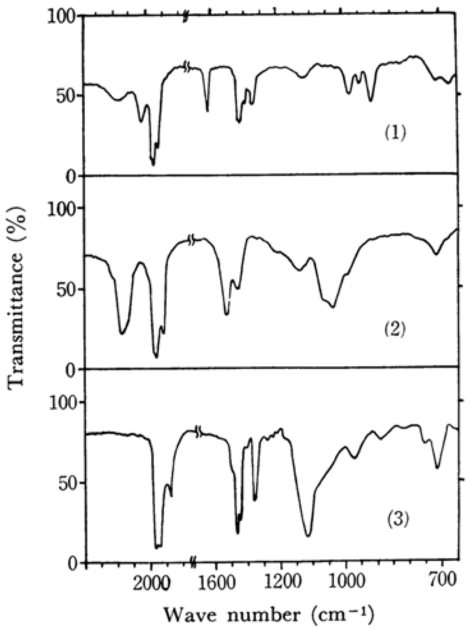


Fig. 1. Infrared spectra of alkali fusion products of sodium *n*-octyl sulfate.

(1) A mixture of *n*-1-octene and internal octene isomers
(2) *n*-Octyl alcohol
(3) Di-*n*-octyl ether

TABLE 1. BOILING POINTS AND RESULTS OF ELEMENTAL ANALYSIS OF DI-*n*-ALKYL ETHERS

Compound	Boiling point	Elemental analysis			
		Calcd		Found	
		C	H	C	H
$(n\text{-}C_6H_{13})_2O$	73—75°C/2 mmHg	77.35	14.01	77.59	14.20
$(n\text{-}C_8H_{17})_2O$	113—114°C/1 mmHg	79.26	14.14	79.55	14.00
$(n\text{-}C_{10}H_{21})_2O$	156—158°C/1.7 mmHg	80.46	14.18	80.75	14.46
$(n\text{-}C_{12}H_{25})_2O$	194—195°C/1 mmHg	81.28	14.21	81.55	14.49

was heated at 400°C for one hour. After reaction, the products were cooled and extracted with ethyl ether, and the extract was filtered, dried, and condensed carefully. Distillation of the residue gave *n*-alkyl alcohol, di-*n*-alkyl ether and a mixture of 1-olefin and internal olefin isomers with the same number of carbon atoms as the alkyl group of the original sulfates. Pentenes and hexenes were, however, so volatile that they could not be isolated. The products were identified employing authentic samples by gas chromatography and IR spectroscopy. The IR spectra of *n*-octyl alcohol, di-*n*-octyl ether, and a mixture of *n*-1-octene and internal octenes, which were the alkali fusion products of sodium *n*-octyl sulfate, and the corresponding gas chromatograms are shown in Figs. 1 and 2, respectively. Discussion on the identification of the alkali fusion products is given below.

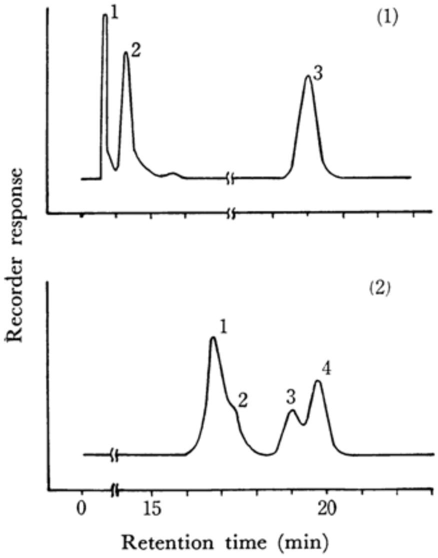


Fig. 2. Gas chromatogram of alkali fusion products of sodium *n*-octyl sulfate.

(1) 1. Overlapping peak of *n*-octene isomers
  2. *n*-Octyl alcohol
  3. Di-*n*-octyl ether
(2) 1. *n*-1-Octene
  2. *n*-4-Octene
  3. *n*-3-Octene
  4. *n*-2-Octene

Results and Discussion

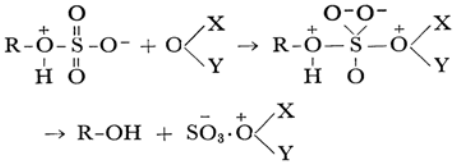
Identification of Alkali Fusion Products. The identification of the alkali fusion products of alkyl sulfates to be *n*-1-olefins, a mixture of internal olefins, higher alcohols, and dialkyl ethers are based on a comparison of their retention times and IR spectra with those of authentic samples.

The absorption bands of IR spectrum (Fig. 1 (1)) at 990 cm^{-1} and at 910 cm^{-1} indicate the formation of monosubstituted ethylene group and the bands at 965 cm^{-1} and 680 cm^{-1} suggest the existence of *trans*- and *cis*-disubstituted ethylene group, respectively.

On the other hand, the formation of 2,2-disubstituted and trisubstituted ethylene group is ruled out because of the absence of the absorption bands near 890 cm^{-1} and between 800 cm^{-1} and 840 cm^{-1}, respectively. According to these observations, it is concluded that the olefinic compounds obtained from the alkali fusion reaction of sodium *n*-octyl sulfate are *n*-1-octene and a mixture of *trans* and *cis* internal octene isomers, and that the branching of the alkyl group does not take place during the reaction. The IR spectra of alkali fusion products of sodium *n*-octyl sulfate shown in Figs. 1(2) and 1(3) agreed with those of authentic *n*-octyl alcohol and di-*n*-octyl ether, respectively.

Figure 2 shows the gas chromatograms of alkali fusion products of sodium *n*-octyl sulfate. The peak 1 in Fig. 2(1) is the overlapping peak of *n*-1-octene and internal octene isomers that can not be separated under the conditions (20 wt% Apiezon L, 75 cm, 220°C, 40m*l*). Peak 2 and peak 3 are assigned to *n*-octyl alcohol and di-*n*-octyl ether by comparing the retention times with those of authentic samples. Further separation of the olefinic products was carried out under the conditions (20 wt% squalane, 3 m, 100°C, 30 m*l*). In Fig. 2(2), the peak assignments to *n*-1-octene, *n*-2-octene, *n*-3-octene, and *n*-4-octene are based on a comparison of their retention times with those of standard *n*-1-octene, *cis*-*n*-2-octene, *trans*-*n*-3-octene, and *trans*-*n*-4-octene, respectively. The peak 1 is identified to be *n*-1-octene. Because a mixture of *trans*- and *cis*-*n*-2-octene gave only a single peak whose retention time agreed with that of standard *cis*-*n*-2-octene, it is assumed to be impossible to separate the mixture of *trans*- and *cis*-octene isomers from each other under the above conditions. Thus the peaks 2, peak 3, and peak 4 may be identified to be a mixture of *trans*- and *cis*-*n*-4-octenes, *n*-3-octenes, and *n*-2-octenes, respectively.

Reaction Mechanism. The mechanism of acid hydrolysis of an alkyl sulfate is represented as follows:[8)]



$$R-\underset{H}{\overset{+}{O}}-\underset{O}{\overset{O}{S}}-O^- + O\langle^{X}_{Y} \rightarrow R-\underset{H}{\overset{+}{O}}-\underset{O}{\overset{O^-O^-}{S}}-\overset{+}{O}\langle^{X}_{Y}$$

$$\rightarrow R-OH + \overset{-}{SO_3}\cdot\overset{+}{O}\langle^{X}_{Y}$$

On the other hand, although alkyl sulfates are stable in the alkaline medium,[9)] they are hydrolyzed to the corresponding alcohols in the fused alkali metal hydroxide. The mechanism of this reaction may be considered to be

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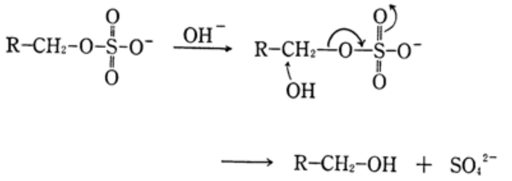
8) V. A. Motsavage and H. B. Kostenbauder, *J. Colloid Sci.*, **18**, 603 (1960).

9) R. Aoki and E. Iwayama, *J. Pharm. Soc. Japan*, **80**, 1749 (1960).



$$R{-}CH_2{-}O{-}\overset{O}{\underset{O}{S}}{-}O^- \xrightarrow{OH^-} R{-}\underset{OH}{CH_2}{-}O{-}\overset{O}{\underset{O}{S}}{-}O^- \longrightarrow R{-}CH_2{-}OH + SO_4^{2-}$$

In order to elucidate the mechanism of formation of dialkyl ether, *n*-alkyl alcohol was heated with an excess amount of KOH at 400°C in a sealed glass tube. In the reaction products obtained, an appreciable amount of di-*n*-alkyl ether and a mixture of *n*-1-olefin and internal olefin isomers were detected by gas chromatography and IR spectroscopy. From these facts the mechanism of formation of di-*n*-alkyl ether and olefins may be considered to be the dehydration of one molecule of water from two molecules of *n*-alkyl alcohol, and one molecule of water from one molecule of *n*-alkyl alcohol, respectively. The formation route of internal olefins from 1-olefin was discussed in the previous paper.⁷⁾

Effect of Alkali Metal Hydroxide and Reaction Temperature. The variation of the reaction temperature between 200°C and 500°C did not affect the kinds of the reaction products obtained. The pyrolysis without any reagent also gave the same products, but the temperature at which the reaction occured was higher than that of the pyrolysis with alkali metal hydroxide. The relation between the reaction temperature and the relative retention value against *n*-octane (the internal standard) of *n*-octenes produced by alkali fusion of sodium *n*-octyl sulfate with KOH is shown in Fig. 3. Such relation suggests that the addition of KOH accelerates the reaction. These effects, however, are not so remarkable as in the case of alkyl sulfonates.

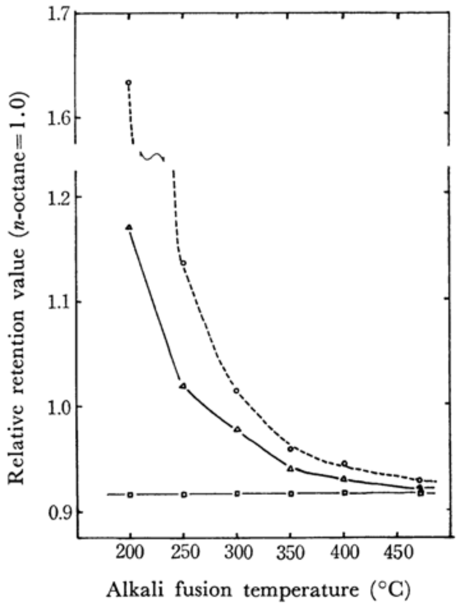


Fig. 3. Relation between alkali fusion temperature and relative retention value of *n*-1-octene from sodium *n*-octyl sulfate.

○···○ with KOH
□—□ standard *n*-1-octene
△—△ without KOH

Practical Application

The present method was applied to determine the alkyl chain carbon number distribution of the commercially available sodium alkyl sulfates (SDS). Three to five milligrams of a mixture of the same amount of SDS and KOH was put in a platinum boat in the pyrolyzer which had been heated at 400°C and the volatile reaction products were swept into a column by the continuous nitrogen stream which flowed in series from the pyrolyzer to gas chromatograph. The chromatogram of the sample B in Table 2 obtained by this method is shown in Fig. 4 (1). The chromatographic conditions were 20 wt% PEG 20M, 1.5 m, 120—240°C, temperature programming rate 10°C/min, 40 m*l*.

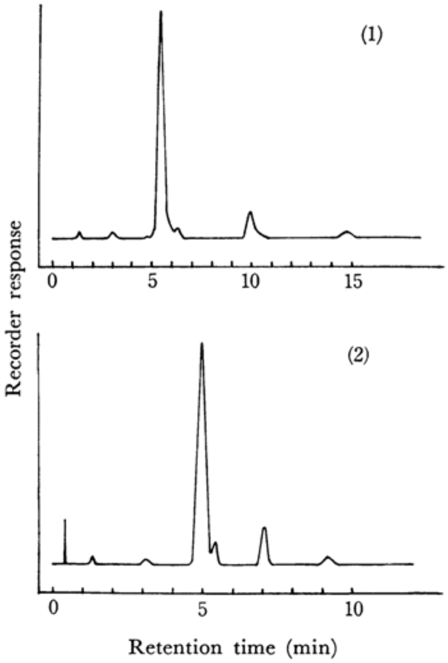


Fig. 4. Gas chromatogram of SDS.

(1) Olefinic products of alkali fusion of SDS
(2) Acetates from the same SDS

Under these conditions, the peaks of the alcohols did not interfere the separation of the olefinic products by which the alkyl carbon number distribution of the SDS was determined. On the other hand, the alcohols obtained by the acid

TABLE 2. ALKYL CARBON NUMBER DISTRIBUTION OF SDS

		Based on acetate* from SDS		Alkali fusion of SDS	
		A	B	A	B
Alkyl chain carbon number distribution, wt%	C_8	2.78	1.78	2.79	1.14
	C_{10}	2.54	1.82	2.28	1.85
	C_{12}	59.25	82.59	58.49	83.59
	C_{14}	23.83	11.48	25.79	10.56
	C_{16}	8.52	2.32	7.57	2.82
	C_{18}	3.08	trace	3.08	trace
Average molecular weight		299.76	291.00	299.85	291.37
Average alkyl chain carbon number		12.84	12.21	12.85	12.24

* Acetate from acetylation of alcohol obtained by acid hydrolysis of SDS was analyzed in Shimadzu Gas Chromatograph Model GC-1C with 75 cm × 3 mm, 10 wt% DEGS on Chromosorb W (AW, HMDS); column temp., 150—210°C, temp. programming rate, 10°C/min, nitrogen, 40 m*l*/min.

hydrolysis of the same SDS were acetylated by acetic anhydride in pyridine and the alkyl carbon number distribution was measured by the peaks of the acetates (Fig. 4 (2)) in order to confirm the reliability of this method. The distribution values are listed in Table 2 together with the average molecular weight and the average alkyl carbon number calculated from them. The agreement between these two methods is satisfactory. The qualitative and quantitative analysis of the lipophylic groups of *n*-alkyl sulfates can be successfully carried out by this method rapidly and briefly.