Staph. aureus the phenylpropyl ether was found to be more efficacious than other ethers of this group.   Halogen seems to enhance the bactericidal action, the *p*-chlorobenzyl ether being a considerably more potent germicide than the benzyl ether.

The antibacterial action of the monoethers of resorcinol has been compared with that of the corresponding nucleus substituted derivatives as reported by previous investigators, and a distinct similarity has been found.

BLOOMFIELD, NEW JERSEY

THE STABILITY OF THE CARBON–SULFUR BOND IN SOME ALIPHATIC SULFONIC ACIDS[1]

BY F. C. WAGNER AND E. EMMET REID

Frequent reference is found in the literature to the preparation and some of the properties of aliphatic sulfonic acids but, with the exception of the study by Spring and Winnsinger[2] of the effect of the sulfonic acid group ($-SO_3H$) on the chlorination of the alkyl residue, no one reaction has been applied to a series of these acids to observe the effect of change of structure on the chemical reactivity.

The stability of the carbon–sulfur bond in a series of mercaptans has recently been investigated.[3]   It seemed of interest to study the sulfonic acids in comparison with the mercaptans.

Discussion of Results

The normal alkyl sulfonic acids from methyl to hexyl and the secondary from isopropyl to *sec.*-hexyl and also benzene and benzyl sulfonic acids have been prepared and their sodium salts heated in excess of sodium hydroxide solution at temperatures from 315 to 375°.

The percentages of the sulfonic acids decomposed in three hours at 345° are plotted in Fig. 1.   Methyl sulfonic acid is remarkably stable while ethyl is decomposed much more rapidly than the other primary acids.   From ethyl on, the decomposition decreases as the carbon chain lengthens, both in the primary and in the secondary series.   The secondary sulfonic acids are decomposed much more rapidly than the corresponding primary acids.   The percentages of the sulfonic acids decomposed are plotted against the temperatures in Fig. 2.   These are the same relations

[2] Spring and Winnsinger, *Ber.*, 16, 327 (1883); 17, 537 (1884).

[3] Billheimer and Reid, THIS JOURNAL, 52, 4338 (1930).

that were found with the mercaptans. However, the sulfonic acids are much more stable than the mercaptans; n-butyl sulfonic acid requires three hours' heating with 1.85 N caustic soda at 365° for 50% decompo-
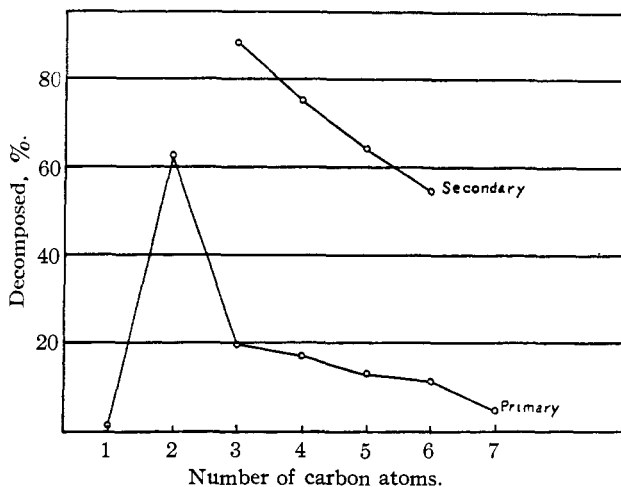

Fig. 1.—Decomposition of aliphatic sulfonic acids with 3.70 N NaOH for 3 hours at 345°.

sition, while the same percentage of decomposition of n-butyl mercaptan could be effected with the same strength of alkali and in the same time at approximately 100° lower temperature. Assuming the usual tempera-
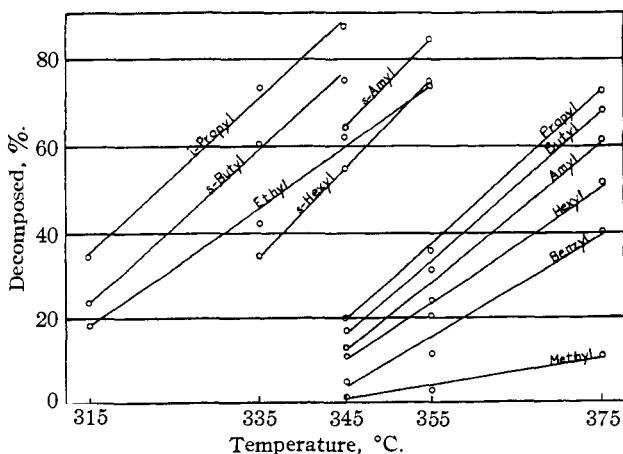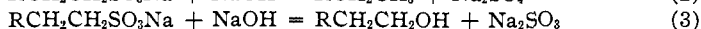

Fig. 2.

ture coefficient, this means that under the same conditions the carbon–sulfur bond in the mercaptans is broken something like a thousand times as rapidly as in the sulfonic acids.

There are obviously three possible reactions

$$RCH_2CH_2SO_3Na + NaOH = RCH{=}CH_2 + NaHSO_3 \qquad (1)$$
$$RCH_2CH_2SO_3Na + NaOH = RCH_2CH_3 + Na_2SO_4 \qquad (2)$$
$$RCH_2CH_2SO_3Na + NaOH = RCH_2CH_2OH + Na_2SO_3 \qquad (3)$$

The experimental work shows that sodium sulfite, with only traces of sulfate, is formed. Berthelot reported reaction (1) as the primary reaction on fusing the potassium salts with potash. In view of this, in several of the runs the residual gas left in the bomb after the slight pressure had been released was swept out by nitrogen and bubbled through dilute bromine water. No appreciable decolorization occurred at any time. Thus, qualitatively at least, reaction (1) is eliminated and reaction (3) remains as the most probable. In one experiment an unsuccessful attempt was made to isolate the alcohol as the half-ester of phthalic acid but none could be separated. It is possible that a small amount of the alcohol could escape detection but it is much more probable that the alcohol had reacted with the alkali at the high temperature of the experiments to form the corresponding acid.

$$RCH_2OH + NaOH = RCOONa + 2H_2$$
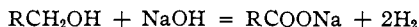
The solutions resulting from the decomposition of n-butyl and n-amyl sulfonic acids were, in several cases, acidified and gave distinct odors of butyric and valeric acids. Hence it may be concluded that the decomposition is according to reaction (3).

That the chief reaction is a simple one was further adduced by calculation of the velocity constants at the various temperatures by use of the usual expression for second order reactions. The validity of this expression was checked by varying the times of several runs both in the case of n-butyl and of n-amyl sulfonic acid. The good agreement of the values for K_{355} for one hour (11.76×10^{-4}) and K_{335} for three hours (11.75×10^{-4}) for n-butyl and for K_{335} for one and one-half hours (33.5×10^{-4}) and K_{335} for three hours (32.0×10^{-4}) for n-amyl justify the use of this expression.

In addition the fractional life found was used to check back against the times measured and again good agreement was found.

By use of the velocity constants and the integrated form of the Arrhenius equation, values of Q, Table I, were calculated. As can be seen, these values vary slightly in degree but not in order of magnitude.

Experimental

Some of the sulfonic acids were prepared by Hemilian's[4] modification of Strecker's synthesis[5] while the others were made by oxidation of the mercaptans to the corresponding sulfonic acids by concentrated nitric

[4] Hemilian, *Ann.*, **168**, 146 (1873).

[5] Strecker, *ibid.*, **148**, 92 (1868).

TABLE I

VALUES FOR K CALCULATED FROM THE FORMULA

$$K = \frac{1}{t(a - b)} \ln \frac{b(a - x)}{a(b - x)} \qquad t = 180 \text{ min.}$$

All values of K multiplied by 10^4

Sulfonate	K_{315}	K_{233}	K_{344}	K_{355}	K_{375}	K_{355}/K_{344}	Q
Methyl			0.440	0.988	3.558	2.24	54,700
Ethyl	6.43	19.3	32.4	46.1		1.42	36,000
Propyl			7.21	14.12	45.13	1.96	48,600
Butyl			5.55	11.75	40.8	2.12	52,800
Amyl			4.34	8.66	32.0	2.00	53,000
Hexyl			3.77	7.13	23.53	1.89	48,600
Benzyl			1.54	3.70	16.24	2.40	62,500
Isopropyl	13.65	45.76	68.6				38,700
Sec.-butyl	8.55	30.89	47.31	88.30		1.87	42,800
Sec.-amyl			34.70	68.02		1.96	51,800
Sec.-hexyl		13.53	25.96	47.38		1.82	47,500
Benzene			23.73	37.89	72.04	1.60	29,300

acid. Hemilian's process consisted in refluxing together the alkyl halide with an aqueous solution of ammonium sulfite, the reaction taking place according to the equation

$$C_2H_5I + (NH_4)_2SO_3 = C_2H_5SO_3NH_4 + NH_4I$$
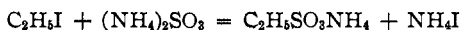
This method was chosen because of the ease of manipulation and on account of the quantities desired. It had been employed by many workers but Hemilian was the only one who reported any yields. He claimed a 90% yield for the above case but this yield was never realized in this work. Also, due to the lower cost and greater ease of handling, the bromides were used in most cases above ethyl. This method, however, failed in the case of sec.-amyl, n-hexyl, sec.-hexyl and benzene sulfonic acids. In order to prepare the first three of these, the bromide was converted to the mercaptan, which was then oxidized by nitric acid to the corresponding sulfonic acid. The benzene sulfonic acid, free of the di-sulfonic acid, was prepared

TABLE II

BOILING POINTS OF INTERMEDIATES USED IN PREPARATION OF SULFONIC ACIDS

Alcohols	B. p. (760 mm.), °C.	Halides	B. p. (760 mm.), °C.
		Methyl iodide	42.4–42.8
		Ethyl iodide	72.0–72.4
Propyl	97.0–98.0	Propyl bromide	70.9–71.2
Isopropyl	....	Isopropyl bromide	59.4–59.8
Butyl	117.2–117.6	Butyl bromide	101.2–101.5
Sec.-butyl	99.0–100.0	Sec.-butyl bromide	91.0–91.5
Amyl	137.8	Amyl bromide	129.6–129.8
Sec.-amyl	119.3–119.6	Sec.-amyl bromide	118.6–118.9
Hexyl	100.5–101.0 (90 mm.)	Hexyl bromide	87.8–88.2 (90 mm.)
Sec.-hexyl	137.8–139.3	Sec.-hexyl bromide	143.6–144.1
		Benzyl chloride	179.2–179.6

by hydrolysis of the acid chloride which had been cut on a precision still. Table II gives the constants of the intermediates used in these preparations.

The Preparation.—Hemilian's procedure was used for the preparation of the majority of the sulfonic acids, the exceptions being *n*-hexyl, *sec.*-amyl, *sec.*-hexyl, and benzene sulfonic acids. The first three of these were made by converting the bromide to the mercaptan and oxidizing the latter by concentrated nitric acid to the sulfonic acid. The acid solution was then evaporated to a negative test for nitrates, when it was neutralized by barium carbonate and evaporated to crystallization. In the case of benzene sulfonic acid, the acid chloride was hydrolyzed to the free acid, which in turn was converted to the barium salt by barium carbonate. The salts prepared by the Hemilian process were likewise converted to the barium salt for purification. The ammonium salts secured by this process were never isolated. The solutions, in some cases, were converted to the barium salt by boiling with an excess of barium hydroxide until free of ammonia, when the excess barium was precipitated by a stream of carbon dioxide; in other cases, litharge was used to remove the ammonia, the lead precipitated by hydrogen sulfide and the free acid thus obtained neutralized by barium carbonate. The barium salts were then purified by recrystallization from water and extraction by hot alcohol. The purity was calculated on the barium content found on precipitation as barium sulfate and was in all cases better than 99.5% as shown in Table III, which also gives the approximate yields of the barium salts obtained, calculated from the halides used.

TABLE III

BARIUM ALKYL SULFONATES

| Ba salt of | Yield, % | Barium analysis, % | | Av. |
		Calcd.	Found	
Methyl sulfonic	56.5	41.94	42.06, 42.03, 42.02	42.04
Ethyl sulfonic	62.0	38.63	38.58, 38.60	38.59
Propyl sulfonic	50.0	35.81	35.83, 35.81	35.82
Isopropyl sulfonic	52.0	35.81	35.63, 35.63	35.63
Butyl sulfonic	60.0	33.37	33.34, 33.34	33.34
Sec.-butyl sulfonic	50.0	33.37	33.24, 33.30	33.27
Amyl sulfonic	70.0	31.24	31.17, 31.27	31.22
Sec.-amyl sulfonic	50.0	31.24	31.22, 31.17	31.20
Hexyl sulfonic	62.0	29.37	29.37, 29.36	29.37
Sec.-hexyl sulfonic	52.0	29.37	29.37, 29.37	29.37
Benzene sulfonic	. .	30.42	30.34, 30.38	30.36
Benzyl sulfonic	50.0	28.64	28.56, 28.54	28.55

The Decomposition.—Preliminary test runs showed the barium salts were not all sufficiently soluble to obtain solutions of the desired concentrations so conversion to the sodium salts was found necessary. This was accomplished by addition of sodium carbonate to solutions of the

barium salts.   The solutions of the sodium salts so obtained were analyzed by evaporation of a sample to dryness, ashing to sodium sulfate and correcting this value for the slight excess of sodium carbonate present by titration of a second sample with standard acid.   Approximately molal solutions of all the acids were prepared in this way.

In carrying out the reaction, 5 cc. of solution mixed with 5 cc. of approximately 4 N sodium hydroxide was heated in a steel bomb for three hours to temperatures ranging from 315 to 375°.   The products of the reaction were then washed from the bomb into excess acidified standard iodine solution and the excess back titrated by standard thiosulfate solution.   This gave the values called percentage splitting on the sulfite basis. The possibility of sulfate splitting was checked by precipitation of the sulfate from the oxidized solution.   This value always ran slightly higher than that on the sulfite basis but not sufficiently so to be of any consequence. Table IV gives a summary of the values found in the decompositions.

TABLE IV

ALKALINE DECOMPOSITION OF ALIPHATIC SULFONIC ACIDS

The bomb solution was made up of 5.0 cc. of the sodium sulfonate solutions of the specified concentrations and 5.0 cc. of 3.70 N sodium hydroxide solution.   The period of heating was three hours.   Where several runs were made at the same temperature, the average is given in the last column.

Sulfonate	Concn., moles/liter	Temp., °C.	% Splitting, sulfite basis	Av.
Methyl	1.031	345	1.5	
		355	2.8	
		375	11.0	
Ethyl	1.016	315	18.8	
		335	45.1	
		345	62.7	
		355	73.7, 74.0	73.8
Propyl	0.9800	345	20.2	
		355	36.0	
		375	71.1, 73.4, 73.3	72.6
Butyl	0.9401	345	17.3	
		355	32.1, 31.6	31.8
		375	71.2, 69.7, 70.4, 64.5, 65.1	68.2
Amyl	1.008	345	13.3	
		355	24.0, 24.7	24.3
		375	61.8, 61.6	61.7
Hexyl	1.061	345	11.7	
		355	20.7	
		375	51.7, 51.2	51.5
Benzyl	1.014	345	5.0	
		355	11.5	
		375	40.2, 40.0	40.1
Isopropyl	0.9975	315	35.0	
		335	73.6	
		345	88.6	

TABLE IV   (Concluded)

Sulfonate	Concn., moles/liter	Temp., °C.	% Splitting, sulfite basis	Av.
Sec.-butyl	0.9226	315	24.1	
		335	60.8	
		345	75.2	
		355	91.3, 91.8	91.5
Sec.-amyl	1.145	345	64.2, 64.2	64.2
		355	84.8	
Sec.-hexyl	1.015	335	35.0	
		345	54.2, 55.6	54.9
		355	75.0	
Benzene	0.9876	345	5.0	
		355	11.5	
		375	40.0, 40.2	40.1

Summary

1.   A series of aliphatic sulfonic acids has been prepared.

2.   The decomposition of the sodium salts of these acids in alkaline solution at high temperatures and pressures has been determined.

3.   The order of the reaction has been determined and the course of the reaction indicated.

4.   The velocity constants and heats of activation have been calculated.

BALTIMORE, MARYLAND

THE OCCURRENCE OF TRUE HYDRAZONE STRUCTURES IN THE SUGAR SERIES[1]

BY M. L. WOLFROM AND CLARENCE C. CHRISTMAN[2]

In the condensation reactions of sugars with amino compounds, it is of interest to determine whether the products possess a cyclic or an open-chain structure.   These two types of structures are illustrated by the formulas
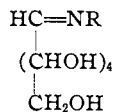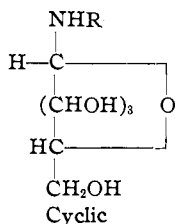
Cyclic   Open chain

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[1] That part of this work concerned with the structure of d-galactose p-nitrophenylhydrazone was presented before the Division of Organic Chemistry at the 81st meeting of the American Chemical Society, Indianapolis, Indiana, March 31, 1931.

[2] Graduate Council Research assistant, The Ohio State University.