compounds the dipole moments of the larger rings appear to approach the values predicted by this equation.

3. From the dipole moment of hexamethyldisiloxane (0.74 *D.*) the silicon–oxygen–silicon bond angle has been calculated; its value appears to be 160 ± 15°.

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[18] Original manuscript received September 18, 1945.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Preparation of Ethylenesulfonic Acid—Salts and Esters

BY WILLET F. WHITMORE AND EDWARD F. LANDAU[1,2]

The preparation of ethylenesulfonic acid has been previously described. Kohler[3,4,5,6] prepared the compound by decomposition of ethanedisulfonyl chloride. Ethylenesulfonic acid has also been prepared by dehydrohalogenation of 2-haloethanesulfonic acid,[4] and by removal of sulfuric acid from ethionic acid.[5]

In the course of this investigation, the preparation of ethylenesulfonic acid by the above methods has been reinvestigated, and improved methods for the isolation of its salts in a pure form have been found.

Kohler described ammonium ethylenesulfonate (m.p. 156°) as a yellow crystalline solid, having a limited solubility in hot 95% ethanol. In contrast to Kohler's description, it was found that by utilizing lower temperatures for the isolation of the ammonium salt, it could be obtained as a colorless crystalline material which was relatively soluble in hot ethanol. However, the melting point reported by Kohler could not be duplicated. It was also observed that exposure to heat (70–80°) caused a yellow discoloration of the salt and decreased its alcohol solubility.

The above-mentioned patents[4,5] described the preparation of sodium ethylenesulfonate, but do not give a method for its isolation. A procedure for the isolation of the purified salt is described below.

No crystalline derivative of ethylenesulfonic acid readily suitable for its characterization has been described in the literature. It was found that the S-benzyl thiouronium salt was easily prepared and had a sharp melting point. Three other aliphatic sulfonic acids were characterized by their S-benzyl thiouronium salts, and are described in Table I.

The esters of ethylenesulfonic acid have received scant attention by previous investigators.

TABLE I

S-BENZYL THIOURONIUM SULFONATES $[C_6H_5CH_2SC(NH_2)_2]$ $[RSO_3]$

Sulfonic acid	M. p., °C.	Sulfur, % Calcd.	Found	
$CH_2{=}CHSO_3H$	145–146	23.27	22.95	23.67
$BrCH_2CH_2SO_3H$	125–126	17.98	18.07	18.27
$ClCH_2CH_2SO_3H$	129–130	20.51	20.72	20.74
$(CH_2{-}SO_3H)_2$	201–202	24.42[a]	24.48	24.72

[a] Calcd. for $[(CH_2SO_3)_2][C_6H_5SC(NH_2)_2]_2$.

The ethyl ester has been prepared by esterification of ethylenesulfonic acid with ketene acetal,[7] and also from ethylene-sulfonyl chloride and ethanol. In the course of this investigation, a series of seven esters of ethylenesulfonic acid from 2-haloethanesulfonyl chloride was prepared by a method the chemistry of which is best illustrated by the following equation.

$$XCH_2CH_2SO_2Cl + ROH \xrightarrow{\text{pyridine}} CH_2{=}CHSO_2OR + HCl + HX$$

where X = Cl, Br; R = an alkyl radical

The pyridine serves both as a dehydrohalogenating agent and a halogen acid acceptor. The most satisfactory results were obtained by using only a slight excess of pyridine and performing the reaction in an inert solvent (methylene chloride). The esters so prepared were colorless liquids having physical properties as described in Table II.

Experimental

Salts of Ethylenesulfonic Acid

(a) Ammonium ethylenesulfonate was prepared by Kohler's procedure[3b] from 1,2-ethanedisulfonyl chloride. The following modifications were employed for its isolation:

The mixture of ammonium sulfonates (ammonium ethylenesulfonate and ammonium 1,2-ethanedisulfonate) was extracted with three 150-ml. portions of hot 95% ethanol. An alcohol insoluble residue of ammonium 1,2-ethanedisulfonate remained. The alcoholic extracts, pale yellow in color, were decolorized by treatment with 5 g. of Darco G-60 and concentrated by distillation under reduced pressure at 50°, to a volume of 200 ml. Upon cooling this solution to 5°, the ammonium ethylenesulfonate separated as a colorless crystalline solid. The yield was 63 g., 55% of the theoretical, based on 200 g. of 1,2-ethanedisulfonyl chloride.

Anal. Calcd. for $C_2H_7SO_3N$: S, 25.60; N, 11.2. Found: S, 25.72, 25.18; N, 10.9.

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[1] An abstract of a dissertation presented in May, 1945, to the Graduate Faculty of the Polytechnic Institute of Brooklyn by Edward F. Landau, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] Kohler, *Am. Chem. J.*, **19**, 728 (1897); **20**, 680 (1898); **21**, 353 (1899).

[4] German Patent 678,730.

[5] German Patent 677,843.

[6] U. S. Patent 2,348,705.

[7] McElvain, Jelinek and Rorig, THIS JOURNAL, **67**, 1578 (1945).

TABLE II

ESTERS OF ETHYLENESULFONIC ACID, $CH_2{=}CHSO_2OR$

R	B. p., °C.	Mm.	$n^{20}D$	d^{20}_4	Sap. value Calcd.	Sap. value Found	MD^d (obs.)	% yield
Methyl[a]	90–91	15	1.4316	1.248	459	454	25.34	25
n-Propyl	108–110	18	1.4368	1.156	373	376	34.03	50
i-Propyl[b]	67–70	4	1.4321	1.132	373	368	34.37	33
n-Butyl	115–117	15	1.4416	1.122	341	343	38.67	61
n-Amyl[c]	130–131	17	1.4412	1.087	314	333	43.05	40
i-Amyl	122–124	15	1.4415	1.082	314	311	43.51	63
n-Hexyl	145–146	15	1.4430	1.050	291	289	48.51	30

[a] A 10% excess of methanol was employed. [b] Product decomposed by distillation at pressures greater than 5 mm. [c] *n*-Amyl ester was not refractionated. [d] The molar refraction of the $—SO_2O—$ group was evaluated by difference average value, 9.7 ± 0.2.

The product obtained by the above procedure was a colorless crystalline material having a decomposition temperature of 145–165°, depending upon the rate of heating. It was soluble in 95% ethanol to the extent of 0.2–0.25 g./ml. at 25°. Upon heating a sample of this material at 70° for four hours, it turned yellow and was practically insoluble in 95% ethanol. No definite melting or decomposition temperature could be obtained on the heat-treated material.

(b) Sodium ethylenesulfonate was prepared from sodium 2-bromoethanesulfonate[8] and from sodium 2-chloroethane sulfone[9] by the procedure as described.[4] The kinetics of this conversion have recently been reported.[10] The product was isolated as follows.

The neutralized aqueous solution containing sodium ethylenesulfonate and sodium halide was concentrated to dryness under reduced pressure at 50°. The separation of the sulfonate and the sodium halide was accomplished by extraction of the former with hot glacial acetic acid. The sulfonate was precipitated from the acetic acid solution by addition of an equal volume of ether. Crystallization of this material from hot 85% aqueous ethanol resulted in a 50% yield of sodium ethylenesulfonate, free from sodium halide. A second crystallization from 95% ethanol was sometimes necessary.

Anal. Calcd. for $C_2H_3SO_3Na$: S, 24.64. Found: 24.70, 24.78.

Sodium ethylenesulfonate was also prepared from sodium and barium ethionate.[5] The product was separated from inorganic sulfates by alcohol extraction. Yields of 50–55% were obtained.

The identity of the ethylenesulfonates obtained by the above procedures was confirmed by preparation of the S-benzyl thiouronium ethylenesulfonate, m. p., 145–146°.

S-Benzyl Thiouronium Sulfonates

A solution of 2.3 g. of S-benzyl thiouronium chloride[11] in 7 ml. of hot water was added to a solution of 0.01 mole of the sodium or ammonium salt of the sulfonic acid in 5 ml. of hot water. The product which precipitated was recrystallized from 8 ml. of hot water and, in general, two recrystallizations sufficed to obtain a pure product with a sharp melting point.

Esters of Ethylenesulfonic Acid

A solution of 0.1 mole of the alcohol and 0.11 mole of either 2-chloroethanesulfonyl chloride or 2-bromoethanesulfonyl chloride, in 75 ml. of methylene dichloride, was cooled to 0°. Dry pyridine (0.22 mole) was added slowly with efficient stirring. The temperature was kept below 10° during the addition, which required from two to three hours. The reaction mixture was then allowed to come slowly to room temperature. Dilute hydrochloric acid (100 ml.) was added and the lower layer, a solution of the ester in methylene chloride, after washing with water, was drawn off, dried over sodium sulfate, and the ester recovered and vacuum distilled. Contact with these esters caused a severe dermatitis similar to a mustard burn.

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Summary

1. Ammonium and sodium ethylenesulfonate have been prepared and improved methods for their isolation described.

2. Seven aliphatic esters of ethylenesulfonic acid have been prepared from 2-haloethanesulfonyl chloride by condensation with the appropriate alcohol in the presence of pyridine.

3. Four S-benzyl thiouronium alkyl sulfonates have been prepared and described.

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(8) Marvel and Sparberg, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y.

(9) U. S. Patent 1,888,794; copper catalyst was found unnecessary.

(10) Landau, Whitmore and Doty, THIS JOURNAL, **68**, 816 (1946).

(11) Donleavy, *ibid.*, **58**, 1004 (1936).