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Synthesis of Sodium Ethylenesulfonate from Ethanol

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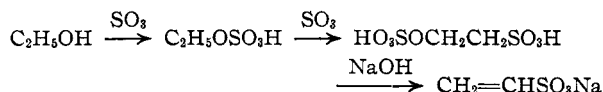
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Ethionic acid has been synthesized by treating ethanol with two moles of sulfur trioxide. The acid has been converted into sodium ethylenesulfonate by treatment with aqueous caustic, the over-all yield being 80% based on ethanol. The stability of sodium ethylenesulfonate under various conditions has been investigated.

Considerable interest in ethylenesulfonic acid, its salts, and derivatives has been shown in recent years.¹⁻⁵ Therefore, we have investigated the possibility of preparing sodium ethylenesulfonate by a simple route from readily available starting materials.

The original synthesis of ethylenesulfonic acid involved the treatment of 1,2-ethanedithionyl chloride with water.⁶ Although the yields in the various steps are good, the procedure is difficult to carry out on a large scale. Anthes and Dudley⁷ prepared ethylenesulfonic acid in 66% yield by heating sodium isethionate with pyrophosphoric acid. Whitmore and Landau⁸ reinvestigated the reported syntheses of sodium ethylenesulfonate from sodium 2-haloethanesulfonate⁸ and from sodium ethionate,⁹ obtaining yields of about 50% in both cases.¹⁰

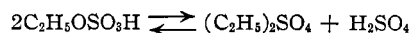
Because of the low cost of the starting materials, attention was centered on the synthesis of sodium ethylenesulfonate from ethionic acid prepared from ethanol and sulfur trioxide. The reactions are shown in the equations



Ethionic acid was prepared by treating one mole of ethanol with one mole of gaseous sulfur trioxide at 0°, raising the temperature, and adding a second mole of sulfur trioxide at 50°; this is a modification of a published procedure.¹¹ Heating the product with aqueous sodium hydroxide converted it into sodium ethylenesulfonate. The yield for the three steps was 80% based on ethanol. For many purposes the solution of sodium ethylenesulfonate can be

used as such. If the crystalline material free from inorganic salts is required, the aqueous solution can be evaporated to dryness and extracted with hot 90% ethanol or glacial acetic acid. This does not yield pure sodium ethylenesulfonate; other sulfonated organic compounds contaminate the product.

Several interesting observations were made in the course of this work. In an attempt to study the synthesis of ethionic acid in a stepwise fashion, attention was first centered on the preparation of ethylsulfuric acid. The addition of one mole of liquid sulfur trioxide to a solution of one mole of ethanol in refluxing sulfur dioxide yielded a product containing 74–86% ethylsulfuric acid, depending on the length of time elapsed between the preparation and the analysis. Diethyl sulfate, sulfuric acid and small amounts of ethionic acid were also present. The existence of the equilibrium



was readily shown by allowing ethylsulfuric acid to stand at room temperature for a week or by heating either ethylsulfuric acid or a mixture of diethyl sulfate and sulfuric acid for 24 hours at 50°. In all three cases a mixture was obtained containing approximately 45% ethylsulfuric acid, 25% diethyl sulfate and 30% sulfuric acid. An equilibrium involving the corresponding methyl compounds has been postulated, but the equilibrium is attained much more slowly.¹² Various other syntheses of ethylsulfuric acid were investigated, such as passing ethylene into concentrated sulfuric acid, with no better results. Apparently pure ethylsulfuric acid has never been prepared.¹³

Surprisingly, the ethylsulfuric acid purity had almost no effect on the yield of ethionic acid. Thus, although analysis showed the presence of only about 50% ethylsulfuric acid in a sample prepared from ethylene and sulfuric acid, reaction with sulfur trioxide followed by alkali gave an 82% yield of sodium ethylenesulfonate. When a mole of ethanol dissolved in liquid sulfur dioxide was treated with two moles of sulfur trioxide¹⁴ and the product was heated with alkali, 77–84% yields of sodium ethylenesulfonate were obtained, although in this case, as mentioned previously, more than 80% ethylsulfuric acid was present after the addition of the first mole of sulfur trioxide.¹⁵ Another unusual

(1) C. S. Marvel, V. C. Menikheim, H. J. Inskip, W. K. Taft and B. G. Labbe, *J. Polymer Sci.*, **10**, 39 (1953).

(2) H. R. Snyder, H. V. Anderson and D. P. Hallada, *THIS JOURNAL*, **73**, 3258 (1951).

(3) C. G. Overberger, D. E. Baldwin and H. P. Gregor, *ibid.*, **72**, 4864 (1950).

(4) A. Lambert and J. D. Rose, *J. Chem. Soc.*, 46 (1949).

(5) W. F. Whitmore and E. F. Landau, *THIS JOURNAL*, **68**, 1797 (1946).

(6) E. P. Kohler, *Am. Chem. J.*, **19**, 728 (1897); **20**, 680 (1898).

(7) J. A. Anthes and J. R. Dudley, U. S. Patent 2,597,696 (1952); *C. A.*, **47**, 2196 (1953).

(8) O. Nicodemus and W. Schmidt, German Patent 678,730 (1939); *C. A.*, **33**, 9326 (1939).

(9) W. Neugebauer and H. Mengel, German Patent 677,843 (1939); *C. A.*, **33**, 9325 (1939).

(10) Whitmore and Landau⁸ determined the purity of their products by elementary analysis and by conversion to the S-benzylthiuronium salt, which was purified by recrystallization. We have found that the most reliable analysis for sodium ethylenesulfonate is quantitative hydrogenation of the double bond in the presence of a palladium-charcoal catalyst, and this was used in all our work.

(11) U. S. Dept. of Commerce, O.T.S., PB Report 70344, frame 16385-7.

(12) J. Guyot and L.-J. Simon, *Compt. rend.*, **169**, 655 (1919).

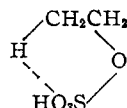
(13) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 23–27.

(14) K. Daimler and K. Platz, U. S. Patent 1,913,794 (1933); *C. A.*, **27**, 4248 (1933).

(15) Evidence indicated that the formation of ethylsulfuric acid is rapid in refluxing sulfur dioxide, but that the formation of ethionic acid is slow at this temperature. About ten hours were required for completion of the reaction.

feature of the synthesis of ethionic acid is the constant presence of about 20% sulfuric acid in the product. This is probably formed by dehydration of ethionic acid to carbyl sulfate by sulfur trioxide, since several samples of ethionic acid on standing precipitated what appeared to be crystals of carbyl sulfate.

The sulfonation of ethylsulfuric acid is a rather unusual reaction. The mechanism would be readily understandable if ethylene were an intermediate, since the reaction would then involve an electrophilic attack by sulfur trioxide on the double bond.¹⁶ However, the formation of ethylene at -10° ¹⁵ is highly unlikely and no ethylene could be detected at 50° . An alternative mechanism would involve an electrophilic displacement of hydrogen by sulfur trioxide. Although such displacements are rare, sulfur trioxide is a very strong electrophilic reagent and the removal of a proton would be facilitated by the formation of a quasi six-membered ring.



There are numerous statements in the literature regarding the instability of sodium ethylenesulfonate.¹⁷ Two reactions are possible, polymerization and hydration of the double bond. To investigate the suppression of polymer formation, sodium ethylenesulfonate was prepared by neutralizing pure ethylenesulfonic acid with aqueous sodium hydroxide in the presence of various possible polymerization inhibitors; the results are shown in Table I. The superior results obtained with sodium nitrite in comparison with the organic inhibitors were undoubtedly due to the greater solubility of sodium nitrite in water. That cupric acetate in small quantities can enhance the polymerization of vinyl monomers is well known, and it would appear that sodium sulfite was taking part in some sort of oxidation-reduction polymerization.

TABLE I

EFFECT OF POLYMERIZATION INHIBITORS ON THE STABILITY OF SODIUM ETHYLENESULFONATE

Inhibitor ^a	Sodium ethylenesulfonate recovery, %	
	Immediately	After 3 months
None	74	36
<i>p</i> - <i>t</i> -Butylcatechol	90	43
<i>p</i> -Nitrobenzoic acid	87	58
Hydroquinone monobenzyl ether	91	..
Sodium nitrite	96, 99 ^b	..
Cupric acetate	38	..
Sodium sulfite	43	..

^a Approximately 0.1% based on the weight of sodium ethylenesulfonate. ^b On a larger scale.

Table II shows the effect of temperature and pH on solutions of sodium ethylenesulfonate containing hydroquinone monobenzyl ether or sodium nitrite as stabilizers. Although both compounds acted as stabilizers under all conditions investi-

gated, it is obvious that sodium ethylenesulfonate is unstable at 100° at pH 10, presumably because of a base-catalyzed hydration of the double bond to form sodium isethionate.⁶ Why sodium nitrite was a better stabilizer than hydroquinone monobenzyl ether under these conditions is not known. Very surprisingly, sodium nitrite appeared to be a poor stabilizer in heated solutions at pH 7.

TABLE II

STABILIZATION OF SODIUM ETHYLENESULFONATE SOLUTIONS WITH HYDROQUINONE MONOBENZYL ETHER AND WITH SODIUM NITRITE

Temp., °C.	pH	Sodium ethylenesulfonate recovery, % ^a		
		With hydroquinone monobenzyl ether ^b	With sodium nitrite ^b	No stabilizer
100	10	33	76	9
100	3	97	100	40
50	10	102	97	7
50	3	100	99	31

^a After heating for 24 hours. ^b 0.1% based on sodium ethylenesulfonate.

Crystalline sodium ethylenesulfonate is surprisingly unstable and thus far efforts to stabilize the solid material have been only partially successful. Thus, *p*-*t*-butylcatechol and *p*-nitrobenzoic acid, as shown in Table I, did not prevent solid sodium ethylenesulfonate from polymerizing on standing at room temperature, presumably because of poor dispersion in the aqueous solutions used to prepare the sodium salt. Similarly, when an alcoholic solution of ethylenesulfonic acid was neutralized with alcoholic sodium hydroxide in the presence of hydroquinone monobenzyl ether, pure sodium ethylenesulfonate crystallized. The purity of this product dropped to 50% after 2.5 months at room temperature, probably indicating that an insufficient amount of stabilizer had been carried down with the precipitate. Unfortunately, the stabilizing effect of sodium nitrite on solid sodium ethylenesulfonate over a period of time was not determined.

Experimental¹⁸

Analytical Procedures.—Sodium ethylenesulfonate was determined by quantitative hydrogenation in water solution in the presence of a palladium-charcoal catalyst. Other possible components of the reaction mixtures were shown not to interfere.

The sulfonation mixtures were analyzed as follows. A sample was added to cold water and diethyl sulfate was extracted with petroleum ether; the extracted diethyl sulfate was hydrolyzed to potassium ethyl sulfate by heating with methanolic potassium hydroxide and the excess base was titrated. The standard Zeisel method for ethoxyl content by titration of a neutralized sample with barium chloride using tetrahydroxyquinoline as a colorimetric end-point indicator. Ethionic acid was determined by conversion to sodium ethylenesulfonate with 100% excess base at 60° for one hour, the ethylenesulfonate being determined by quantitative hydrogenation.¹⁹ Although the analyses were not very precise, they served to show the trends in the reactions.

Preparation of Sodium Ethylenesulfonate.—Eighty grams (1 mole) of sulfur trioxide (Sulfan B, General Chemical Co.)

(18) Analyses were performed by the Analytical Division of Hercules Experiment Station.

(19) We are greatly indebted to Dr. A. E. Reynolds and Mr. R. H. Phillips of these laboratories for the development of this procedure.

(16) F. G. Bordwell, C. M. Suter and A. J. Webber, *THIS JOURNAL*, **67**, 827 (1945).

(17) See, for example, C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 646.

was distilled into a flask containing 45 g. (0.98 mole) of ethanol (water content 0.24%) over a period of 80 minutes. The vapors were passed over the surface of the alcohol, which was stirred and kept at 0–5°; the reaction was exothermic but not violent. The temperature of the flask was then raised to 50° and a second mole of sulfur trioxide was distilled in at the same rate. No condensable material was found in a Dry Ice-trap connected to the flask, and only a small amount of air, free of unsaturates, was obtained in a gas collector. Ethionic acid was obtained as a viscous, pale amber oil, which deposited white crystals on standing.

The ethionic acid was added drop by drop to a solution of 128 g. (3.2 moles) of sodium hydroxide in 384 ml. of water kept at 65° and the resulting solution was heated at 65–70° for two hours. The solution was cooled, neutralized to pH 8 with sulfuric acid, chilled and filtered. The precipitate of Glauber salt was washed with three 50-ml. portions of ice-water. Analysis showed that the combined pale yellow filtrates (557 g.) contained 17.9% sodium ethylenesulfonate, a yield of 80%.

Preparation of Ethylsulfuric Acid in Sulfur Dioxide.—To a refluxing solution of 33.5 g. (0.73 mole) of anhydrous ethanol in 100 ml. of liquid sulfur dioxide was added 58.4 g. (0.73 mole) of liquid sulfur trioxide at a rate of approximately 0.5 ml. per minute. The sulfur dioxide was allowed to distil overnight, the last traces being removed *in vacuo*, and ethylsulfuric acid was obtained as a pale amber oil.

Anal.: $C_2H_5OSO_2H$, 86; $(C_2H_5)_2SO_4$, 7; H_2SO_4 , 6.

Repetition of the experiment on an eight-mole scale gave the following results.

Anal.: $C_2H_5OSO_2H$, 74; $(C_2H_5)_2SO_4$, 13; H_2SO_4 , 13; ethionic acid, 5.

Stability of Ethylsulfuric Acid.—Two 5-g. samples of ethylsulfuric acid were placed in glass-stoppered bottles; one was allowed to stand one week at room temperature, and the other was heated 24 hours at 50°.

Anal.	Room temp.	50°
$C_2H_5OSO_2H$	47	44
$(C_2H_5)_2SO_4$	18	25
H_2SO_4	25	28

Equilibrium between Ethylsulfuric Acid and Diethyl Sulfate.—A mixture of 25 g. (0.162 mole) of diethyl sulfate and 15.9 g. (0.162 mole) of concentrated sulfuric acid was heated at 50° for 24 hours, cooled and analyzed.

Anal.: $C_2H_5OSO_2H$, 42; $(C_2H_5)_2SO_4$, 21; H_2SO_4 , 27.

Ethylsulfuric Acid from Ethylene and Sulfuric Acid.—Two moles of 100.5% sulfuric acid was placed in a gas washing bottle which was heated to 70°. Ethylene (Matheson) was passed in at a rate of 300 ml. per minute until two moles had been absorbed, nine hours being required. Using 98% sulfuric acid, 11 hours were required for one mole of acid to absorb one mole of ethylene. In both experiments a dark-brown oil was obtained.

Anal.	100% acid	98% acid
$C_2H_5OSO_2H$	47	55
$(C_2H_5)_2SO_4$	27	24
H_2SO_4	18	21
Ethionic acid	4	0

Ethionic Acid from Ethylsulfuric Acid Prepared from Ethylene and Sulfuric Acid.—To 1.5 moles of ethylsulfuric acid, prepared as described above from 100.5% sulfuric acid and ethylene, was added 1.5 moles of liquid sulfur trioxide at such a rate that the temperature remained at 50°. The resulting dark-brown oil was converted into sodium ethylenesulfonate as described previously. The yield based on ethylene was 82%.

Ethionic Acid from Ethanol and Sulfur Trioxide in Sulfur Dioxide.—One mole of anhydrous ethanol dissolved in 60 ml. of liquid sulfur dioxide was placed in a flask and two moles of sulfur trioxide dissolved in 160 ml. of sulfur dioxide was added drop by drop to the refluxing solution; the resulting mixture was refluxed for ten hours. The sulfur dioxide was distilled, the last traces being removed *in vacuo* and the resulting ethionic acid, obtained as a pale amber oil containing white crystals, was converted into sodium ethylenesulfonate. The yield was 77% based on ethanol.

Several repetitions of the above experiment gave yields of 81–84%, no increase in yield being found when a 10% excess of sulfur trioxide was used.

Stabilizers for Sodium Ethylenesulfonate.—Five-gram samples of ethylenesulfonic acid were dissolved in 25 ml. of water and titrated in the cold to a pH of about 8 with 2 M sodium hydroxide. The resulting solutions, after the addition of 0.005 g. of stabilizer, were evaporated to dryness *in vacuo* from a bath at 50°. The results are shown in Table I, the analyses being calculated on a dry basis.

Hydroquinone Monobenzyl Ether and Sodium Nitrite as Stabilizers for Sodium Ethylenesulfonate.—A 20% solution of sodium ethylenesulfonate in water was prepared from ethylenesulfonic acid and sodium hydroxide. One portion of this solution was stabilized with 0.1% hydroquinone monobenzyl ether based on sodium ethylenesulfonate, a second portion was stabilized with 0.1% sodium nitrite, while a third was not stabilized. The stabilized and unstabilized solutions were treated as shown in Table II.

Hydroquinone Monobenzyl Ether as a Stabilizer for Crystalline Sodium Ethylenesulfonate.—A solution of 5 g. of ethylenesulfonic acid and 0.005 g. of hydroquinone monobenzyl ether in 100 ml. of alcohol was neutralized to pH 8 with a concentrated alcoholic sodium hydroxide solution. The mixture was chilled and filtered, the white crystals of sodium ethylenesulfonate being dried to constant weight *in vacuo* at room temperature. An 89% yield of pure sodium ethylenesulfonate was obtained. After 2.5 months at room temperature the purity had dropped to 50%.

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