[Contribution from the Noyes Chemical Laboratory, University of Illinois]

# THE STRUCTURE OF THE BISULFITE COMPOUND OF ACETALDEHYDE

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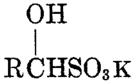
The structure of the compounds resulting from the addition of alkali metal bisulfites to aldehydes and certain ketones has been the subject of much discussion and experimentation. Various investigators have, from time to time, favored either the hydroxysulfonate structure (1, 2, 3) (I), the hydroxysulfite ester formula (4, 5) (II), or a "polymolecule" formula (6, 7) (III). The experiments of Raschig and Prahl (3, 8), Backer and Mulder, (9) and the recent work of Lauer and Langkammerer (10) leave no doubt that the bisulfite compound of formaldehyde is best represented by the hydroxysulfonate structure (I). By inference, other bisulfite compounds should possess the same structure. However, in view of the occasional exceptional behavior of formaldehyde as compared to other aldehydes, it was desirable to investigate the structure of the acetaldehyde bisulfite compound in order to add further evidence on the structure of these compounds.



$$R\overset{\overset{OH}{|}}{C}HSO_3K$$

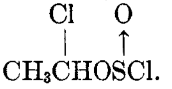
I

$$R\overset{\overset{OH}{|}}{C}HOSO_2K$$

II

$$(RCHO)(SO_2)(HOH)$$

III

In the present work acetaldehyde (IV) was converted to trithioacetaldehyde (11) (V) by means of hydrogen sulfide in the presence of hydrochloric acid. Treatment of a suspension of trithioacetaldehyde in ice-water with chlorine according to the procedure of Müller and Raudenbusch (12), gave a 75% yield of $\alpha$-chloroethanesulfonyl chloride (VI). This compound was a liquid which could be distilled *in vacuo*. It possessed all the properties and reactions of a sulfonyl chloride and none of the reactions of the isomeric structure,  $CH_3\overset{\overset{Cl}{|}}{C}HO\overset{\overset{O}{\uparrow}}{S}Cl$. For example, barium hydroxide at 60–70° caused hydrolysis to the barium salt, VII, which upon treatment with potassium sulfate gave the potassium salt (IX). The latter, with

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phosphorus pentachloride, regenerated the α-chloroethanesulfonyl chloride (VI).

Treatment of an ice-cold ether solution of VI with ammonia produced the

CHART I

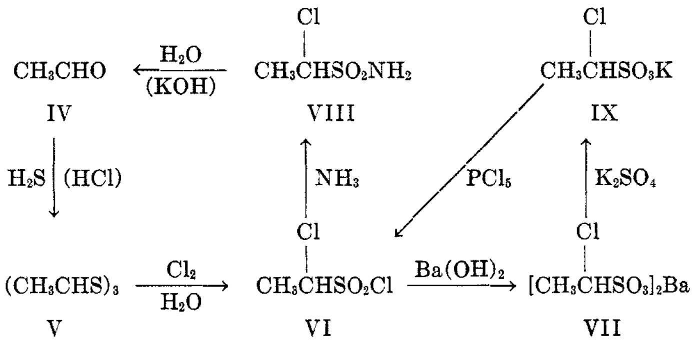
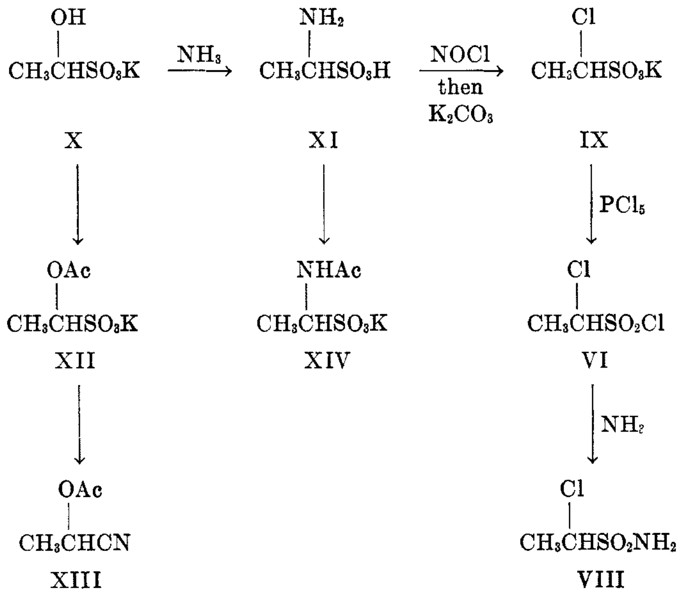


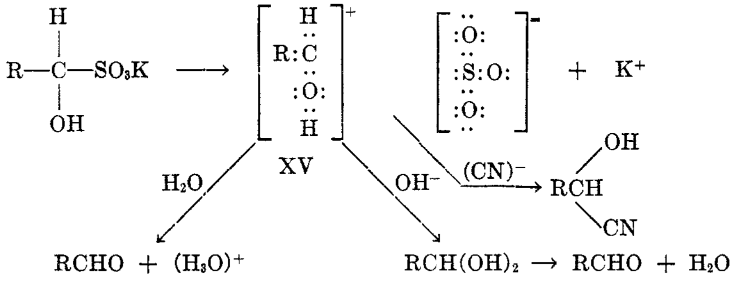
CHART II



α-chloroethanesulfonamide (12) (VIII). The latter was hydrolyzed by dilute alkali back to acetaldehyde, which was characterized by its methone condensation product. This conversion presumably takes place through the intermediate formation of α-hydroxyethanesulfonamide which in turn is hydrolyzed into acetaldehyde, ammonia, and sulfurous acid. The chlorine atom in potassium α-chloroethanesulfonate is not sufficiently reactive to permit the formation of the intermediate α-hydroxyethanesulfonate under the conditions used here, although Bunte (13) has demonstrated the production of acetaldehyde from the chloro salt by hydrolysis at an elevated temperature and pressure. Thus, this set of reactions summarized in Chart I, furnishes a series of six compounds derived from acetaldehyde, all of which contain a carbon-sulfur linkage.

Treatment of either the sodium or potassium bisulfite compound (X) of acetaldehyde with concentrated ammonia and subsequent acidification yielded α-aminoethanesulfonic acid (9) (XI) as previously described by Backer and Mulder. Nitrosyl chloride at 0° converted this aminosulfonic acid into the α-chloroethanesulfonic acid, which was neutralized with potassium carbonate and isolated as the potassium salt (IX), identical with that prepared by the reactions in Chart I. This sample of the salt was also converted to the sulfonamide (VIII) by way of the acid chloride (VI), and identity of the sulfonamides established by a mixed melting point determination. It thus seems clear that the acetaldehyde bisulfite compound (X) possesses the hydroxysulfonate structure, since all of these reactions were carried out under mild experimental conditions, and the possibility of rearrangement seems remote.

The chief point in connection with the chemistry of the bisulfite compounds is their instability, *i.e.*, the reaction which leads to their formation is readily reversible and markedly affected by the presence of acids or alkalies. In these α-hydroxy sulfonates the carbon-sulfur linkage is far more labile than in a simple alkyl sulfonic acid. If the initial step in the dissociation of the bisulfite results in the following ions,



then the carbonium ion (XV) may easily stabilize itself by loss of a proton to the solvent, water, and thus regenerate the aldehyde. It could also combine with a hydroxyl ion forming an aldehyde hydrate which could then lose water. Both of these reactions would be sensitive to the $p$H of the solution. In the presence of sodium cyanide, the cyanide anion would combine with the cation (XV) to produce the cyanohydrin.

Acetylation of the hydroxyl group would prevent the loss of a proton mentioned above, and indeed the acetyl derivative (XII) is far more stable than the original acetaldehyde bisulfite compound (X). The sulfonate group in this acetoxy derivative can be replaced by the cyano group by reaction with the cyanide anion leading to α-acetoxypropionitrile (XIII).

## EXPERIMENTAL

*Potassium α-hydroxyethanesulfonate (X).* A saturated solution containing 240 g. of potassium bisulfite was placed in a three-necked flask equipped with a mechanical stirrer and a reflux condenser and immersed in an ice-bath. The acetaldehyde produced by the depolymerization of 110 g. (0.833 mole) of paraldehyde was condensed directly into the bisulfite solution, stirring and cooling being continued throughout the addition. Precipitation of the addition product was effected by the addition of four volumes of 95% ethanol and cooling in an ice-bath. The precipitated material was collected on a suction filter, washed with several portions of cold 70% ethanol, and dried for forty-eight hours in a vacuum desiccator over sulfuric acid. Yield, 219 g.

One gram of the dried material, when dissolved in a small amount of water and acidified with a drop of hydrochloric acid, reduced only two drops of 0.1 *N* iodine solution indicating the practical absence of free sulfite.

*Potassium α-acetoxyethanesulfonate (XII).* One hundred grams (0.61 mole) of potassium α-hydroxyethanesulfonate, 124 g. (1.22 moles) of acetic anhydride, and 97 g. (1.22 moles) of pyridine were placed in a 500-cc. flask equipped with a stirrer and a reflux condenser. The suspension was stirred and heated with a free flame to gentle boiling. Shortly after refluxing began, the reaction became so vigorous that external cooling was required. In a short time the contents set to a pasty mass and stirring was discontinued. The mixture was cooled, broken up as thoroughly as possible, and transferred to a Büchner funnel by the use of several portions of ether. The washing with ether was continued until the bulk of the acetic anhydride and pyridine was removed. The residue was dissolved in boiling 80% ethanol and treated with two portions of decolorizing carbon. A second recrystallization yielded 46 g. of thick white needles (decomp. at 209–211°, Maquenne block).

An analytical sample was prepared by two further recrystallizations and rendered anhydrous by boiling with toluene.

*Anal.* Calc'd for $C_4H_7KO_5S$: S, 15.39; K, 18.97.
Found: S, 15.35; K, 18.65.

*α-Aminoethanesulfonic acid (XI).* Eighty-eight grams (2 moles) of freshly distilled acetaldehyde was added slowly to a cooled solution of 210 g. (2 moles) of sodium bisulfite in 300 cc. of water, the solution being stirred and the temperature kept at 20° or below during the addition. After the addition of 300 cc. of concentrated ammonia, the solution was stirred and heated at 70° for thirty minutes. The cooled solution was acidified by the addition of 150 cc. of concentrated hydrochloric acid and placed in the ice-box overnight. The amino acid was collected on a suction filter and washed with a small portion of ice-water. A yield of 120 g. of white crystals decomposing at 260° was obtained (14).

*Potassium α-acetamidoethanesulfonate (XIV).* Twenty grams of α-aminoethanesulfonic acid and 11 g. of potassium carbonate were dissolved in 100 cc. of water. Thirty grams of acetic anhydride was added and the solution heated at 70° for thirty minutes. The thick, clear syrup resulting from concentration of the solution on the steam-bath set to a brittle glass upon cooling but could not be induced to crystallize. This was redissolved in water, placed in a continuous extractor and extracted with ether for several hours. Reevaporation of the aqueous solution yielded a gum which crystallized when rubbed with a spatula. Two recrystallizations from 80% ethanol yielded 18 g. of transparent prisms which decomposed at 180°.

*Anal.* Calc'd for $C_4H_8O_4KNS$: K, 19.05. Found: K, 19.13.

*Potassium α-chloroethanesulfonate (IX).* (a) *From α-aminoethanesulfonic acid.* Twenty-five grams of α-aminoethanesulfonic acid was suspended in 100 cc. of concentrated hydrochloric acid. While the suspension was stirred and cooled in an ice-bath a rapid stream of nitrosyl chloride was passed into it. After approximately one hour the gas stream was interrupted and the solution allowed to come to room temperature. When the brown color of the nitrosyl chloride was discharged, the solution was again cooled and the passage of the gas resumed. This process was continued until all of the suspended material had dissolved. The solution was concentrated in a vacuum desiccator over sodium hydroxide until only a trace of chloride remained. Further concentration on the steam-bath produced a viscous brown oil which was diluted with water, neutralized with potassium carbonate, and evaporated to dryness. The residue was dissolved in methanol, treated with charcoal, and allowed to crystallize. A second recrystallization from methanol produced 16 g. of glistening white plates, m.p. 325° (decomp., Maquenne block).

(b) *From α-chloroethanesulfonyl chloride.* The general procedure of Müller and Raudenbusch (12) was followed. Eighteen grams of α-chloroethanesulfonyl chloride (preparation described below) was added to a saturated solution containing 35 g. of barium chloride octahydrate. The chloride dissolved fairly rapidly and the solution became noticeably warm. After the initial reaction had subsided the solution was heated to 60–70° for one hour and filtered while hot. The barium was precipitated by the addition of sulfuric acid, which was in turn removed by shaking the solution with lead carbonate. Removal of the lead by saturating the solution with hydrogen sulfide left a fairly pure solution of the acid which was reconverted to the barium salt by the addition of barium carbonate. This was decolorized with charcoal, filtered, and evaporated to dryness. The residue was recrystallized from aqueous ethanol to obtain 10.6 g. of the crystalline barium salt.

*Anal.* Calc'd for $C_4H_8BaCl_2O_6S_2+H_2O$: Ba, 31.06. Found: Ba, 30.89.

The barium salt was added to a solution containing the theoretical amount of potassium sulfate, filtered, and evaporated to a small volume. Upon cooling, 8.18 g. of the potassium salt crystallized, m.p. 327° (decomp., Maquenne block).

*Anal.* Calc'd for $C_2H_4ClKO_3S$: K, 21.41. Found: K, 21.40.

*Attempted hydrolysis of potassium α-chloroethanesulfonate.* One-half gram of potassium α-chloroethanesulfonate was treated as described below under the hydrolysis of α-chloroethanesulfonamide. Although heating was continued for one hour, no precipitate appeared in the methone solution. A sample of the alkaline salt mixture yielded no precipitate when acidified with nitric acid and treated with silver nitrate solution.

*α-Chloroethanesulfonyl chloride (VI).* (a). *From potassium chloroethanesulfonate.* To 9.65 g. (0.05 mole) of the potassium α-chloroethanesulfonate obtained from α-aminoethanesulfonic acid was added 10.5 g. (0.05 mole) of phosphorus pentachloride. In a short time the reaction began to take place spontaneously with the liberation of considerable heat and the mixture partially liquefied. The reaction flask was provided with a reflux condenser and heated at 80° for nine hours. The mixture was distilled under reduced pressure. The fraction boiling 80–81° at 22 mm. weighed 4.8 g. and was converted to the amide by the procedure described below.

(b). *From trithioacetaldehyde* (*12*). Trithioacetaldehyde was prepared by a slight modification of the method of Suyver (11). Eighty-five grams of freshly distilled acetaldehyde was added to 300 cc. of 6 *M* hydrochloric acid. The mixture was shaken in contact with hydrogen sulfide for eight hours. The precipitated solid was removed by filtration and recrystallized from 80% ethanol to yield 75 g. of material melting 77–80°. No attempt was made to separate the α- and β-isomers, since either is reported to serve equally well for the preparation of the sulfonyl chloride (12).

Thirty grams of trithioacetaldehyde was suspended in 600 cc. of water and stirred at ice-bath temperature while a rapid stream of chlorine was passed into the suspension. The addition of chlorine was continued until 122 g. had been absorbed. The chlorosulfonyl chloride was extracted with ether, washed with sodium thiosulfate solution followed by water and dried over magnesium sulfate. After the removal of the ether the chloride was distilled under reduced pressure. The yield was 39 g., b.p. 48–53° at 3 mm.

*α-Chloroethanesulfonamide* (*VIII*) (*12*). Thirty-five grams of α-chloroethanesulfonyl chloride was dissolved in 100 cc. of dry ether. The solution was cooled to 0° and maintained at that temperature while a rapid stream of ammonia was passed into it for a period of thirty minutes. The precipitated ammonium chloride was removed by filtration and washed with two 10-cc. portions of ether. The combined filtrate and washings were evaporated under reduced pressure, and the residual oil allowed to stand overnight in a vacuum desiccator over sulfuric acid. Crystallization was induced by rubbing with a spatula. Two recrystallizations from benzene yielded 21 g. of soft white crystals m.p. 65–66°.

*Anal.* Calc'd for $C_2H_6ClNO_2S$: S, 22.30. Found: S, 21.89.

Samples of α-chloroethanesulfonyl chloride prepared by each of the methods described above yielded amides melting at the same temperature and showing no depression of melting point when mixed.

*Hydrolysis of α-chloroethanesulfonamide.* One-half gram of α-chloroethanesulfonamide was placed in a flask containing 20 cc. of 5% potassium hydroxide solution. A moderately rapid stream of nitrogen gas was bubbled through the solution while it was heated to boiling. The emergent gases were passed into a cooled solution composed of 20 cc. of water, 1 g. of sodium acetate, 0.5 cc. of glacial acetic acid, and 5 cc. of 5% alcoholic dimethyldihydroresorcinol. Shortly after the boiling point was reached, the contents of the reaction flask began to darken and a precipitate appeared in the methone solution. The heating was continued until the boiling solution began to foam badly. The precipitate from the methone solution was separated by filtration and recrystallized from water-ethanol. It melted at 137–139° and showed no depression of melting point when mixed with an authentic sample of acetaldehyde dimethone.

*Acetoxypropionitrile* (*XIII*). The method used was similar to that used by Lauer and Langkammerer (10) in the preparation of acetoxyacetonitrile. Twenty and six-tenths grams (0.1 mole) of potassium acetoxyethanesulfonate and 4.9 g. (0.1 mole) of sodium cyanide were dissolved in 50 cc. of water and allowed to stand at room temperature for one hour. The colorless liquid which separated on top of the aqueous solution was extracted with ether and the extract dried over sodium sulfate. After removal of the ether, distillation of the oil yielded 5.85 g. of a colorless liquid, b.p. 75–77° at 25 mm. $n_D^{20}$ 1.4027.

## SUMMARY

A study has been made of some derivatives of α-chloroethanesulfonyl chloride. Although its potassium salt was resistant to alkaline hydrolysis,

its amide was readily converted into acetaldehyde by heating with dilute alkali.

The presence of a carbon-to-sulfur linkage in potassium acetaldehyde bisulfite has been demonstrated by its conversion through α-aminoethanesulfonic acid, potassium α-chloroethanesulfonate, and α-chloroethanesulfonyl chloride to α-chloroethanesulfonamide.

URBANA, ILL.

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