

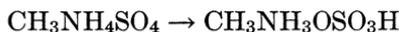
In the preparation of ethanethiol¹²⁶ the use of calcium ethyl sulfate reduces the formation of sulfide to a minimum, probably because calcium hydroxide is a somewhat weaker base than sodium hydroxide, which would reduce the amount of ethanethiol present as a salt in the solution. *n*-Butyl sulfide has been obtained in good yields¹²⁷ by refluxing a solution containing sodium sulfide and sodium *n*-butyl sulfate for several hours. If the solution is distilled slowly a considerable amount of 1-butanethiol is produced indicating the stepwise nature of the reaction. Isoamyl sulfide has been prepared¹²⁸ from calcium isoamyl sulfate and an alkali sulfide.

Esters of carboxylic acids are obtainable by heating the free acids with alkyl hydrogen sulfates provided that there is some reagent to remove free sulfuric acid.¹²⁹ Ammonium sulfate or a secondary or tertiary phosphate is suitable for this.

The pyrolysis behavior of alkyl hydrogen sulfates and their salts may be generalized by the statement that all the compounds except the methyl ester yield chiefly olefins and the behavior of the methyl compound depends upon the particular salt employed. By heating to 130–140° methyl hydrogen sulfate is converted into methyl sulfate and sulfuric acid.¹³⁰ The reaction is reversible, the reaction mixture at 150–160° containing approximately three moles of methyl hydrogen sulfate to one of sulfuric acid and of methyl sulfate.¹³¹ This reaction is reversed at ordinary temperatures by dissolving methyl sulfate in 100% sulfuric acid.¹³²



Methyl ammonium sulfate rearranges¹³³ upon heating to methylammonium hydrogen sulfate. The reaction begins at 100° and pro-

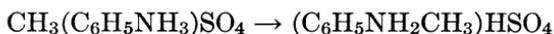


ceeds rapidly at 220° and above. As indicated by the change in acidity of the mixture it was found to be practically complete in 15 minutes at 275°. Above 220° a side reaction occurs to a slight extent, ethylene being evolved.



An 85.6% yield of methylamine was first reported as obtainable under the best conditions, but later workers¹³⁴ found the products of the reaction to be a mixture of the salts of the three methylamines, the maximum yield of methylamine obtainable being only 27% of the

theoretical amount. Methyl phenylammonium sulfate was found⁴¹ to rearrange more readily than the simple ammonium salt.



Heating the pyridine salt of a higher-molecular-weight alkyl hydrogen sulfate above 130° gives an emulsifying agent¹³⁵ which may be $(\text{RNC}_5\text{H}_5)\text{HSO}_4$. Potassium methyl sulfate decomposes at 220° to 280° with formation of methyl ether.¹³⁶ This reaction is accelerated by the presence of methyl sulfate. Sodium methyl sulfate gives a 7%



yield of methyl sulfate in addition to the methyl ether reaction.



Calcium, barium, strontium, and lithium methyl sulfates give only a trace of methyl ether, methyl sulfate being the main product. These salts decompose below 200° and for the strontium salt decomposition was evident even at room temperature.

The decomposition of ethyl hydrogen sulfate in a vacuum¹³⁷ gives a small yield of ethyl sulfate, but at ordinary pressures the reaction is the common one leading to the formation of ethylene.¹³⁸ The reverse reaction will be mentioned later (see p. 25). Distillation of a mixture containing barium ethyl sulfate gives ethyl sulfate as one of the chief products.¹³⁹ The potassium salts of ethyl, isobutyl, and isoamyl hydrogen sulfates give both the olefin and the corresponding alcohol¹⁴⁰ when heated above 250°. In addition, the ethyl compound yields a small amount of ethyl ether. Ethyl, *n*-propyl, and isobutyl ammonium sulfates do not rearrange^{133,141} to amine salts, the olefins being evolved instead. *n*-Octyl barium sulfate⁶ gives octylene at 100°. Heating an alkyl hydrogen sulfate to about 300° with a salt capable of reacting with the resulting sulfuric acid to give an inert compound facilitates formation of the olefin.¹⁴²

INDIVIDUAL ALKYL HYDROGEN SULFATES AND THEIR DERIVATIVES

Methyl Hydrogen Sulfate. Equimolecular quantities of methanol and sulfuric acid at a temperature of 100° or below give only methyl hydrogen sulfate,¹⁴³ whereas the use of an excess of alcohol and distillation of the reaction mixture converts the first product into methyl ether. The rates of formation of methyl hydrogen sulfate at 40° and 50° and that for methyl ether formation at 100° have been determined¹⁴⁴ by measuring the acid concentrations of the reaction mix-

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