Sulphur By-Products of the Preparation of Ether.

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The formation of ethyl ether from alcohol and sulphuric acid was first explained by Williamson in 1852. According to his theory the first reaction is the formation of ethyl sulphuric acid and water, according to the equation,

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

The ethyl sulphuric acid then reacts with more alcohol to form ether and sulphuric acid,

$$C_2H_5HSO_4 + C_2H_5OH = C_2H_5OC_2H_5 + H_2SO_4.$$

If these changes were the only ones taking place a limited quantity of sulphuric acid might convert an unlimited quantity of alcohol into ether and water.

Experience has shown, however, that there is a limit to the quantity of alcohol that can be converted into ether by a given weight of sulphuric acid, and two explanations have been offered for the limitation.

Many writers accept the theory that the water produced in the first reaction so dilutes the sulphuric acid that the change can not continue. It has been shown, however, by Evans and Sutton, that the water does not accumulate enough to prevent the reaction but distills over with the ether, normal results having been obtained when starting with very dilute sulphuric acid, the acid becoming concentrated enough for its normal effect by the time the proper temperature (140°) is reached.

Others, including the present writers, accept the explanation that the sulphuric acid employed is gradually converted into other sulphur compounds, either carried out of the generator with the ether and water, or, if remaining, incapable of inducing the formation of ether. The purpose of the work here reported was to determine the quantities of these sulphur by-products formed during the heating.

Numerous by-products have been reported by previous workers, including the following: Sulphur dioxide, sulphurous acid, ethyl sulphurous acid; sulphuric anhydride, ethyl sulphuric acid, ethyl sulphate;

ethyl sulphonic acid, isethionic acid, ethionic acid, butyl sulphonic acid and the ethyl esters of these acids.

Experimental.

Outline.

The experimental work consisted of the preparation of ether in the usual way from ordinary alcohol and strong sulphuric acid, maintaining as nearly as practicable a constant temperature of 140°, as long as ether resulted from introducing fresh alcohol. The distillate and residue were then examined quantitatively for by-products containing sulphur, which were determined as of three classes: sulphurous acid and sulphites, sulphuric acid and sulphates, and sulphonic acids and sulphonates; no distinction was made between the different possible substances within any class, as between the acid and its esters, except in the case of sulphuric acid and its esters.

Sulphuric Acid Used.

Twenty-five cubic centimeters of commercial concentrated acid were used, so-called 66° Baumé or 1.84 sp. gravity. Unfortunately an accurate determination of its concentration was not made, but assuming that the material used was in accordance with its specification it contained about 95 per cent H_2SO_4, and the weight of pure acid used was 43.7 grams. This figure agrees fairly well with the total sulphur found in the products, which was equivalent to 45.25 grams of sulphuric acid. The work is being repeated with accurate observations.

In the percentages given below reference is made to the total sulphur found by direct analysis of the products, and not this 43.7 grams of sulphuric acid.

Ether Preparation.

The apparatus included a 250 cc. distilling flask provided with a thermometer dipping into the liquid, and a dropping funnel delivering alcohol just above the surface and bent away from the thermometer; the flask was attached to a condenser, connected with a 2½ liter receiving bottle, followed by two wash-bottles containing bromine water, the entrance tube of each reaching to the bottom, to catch any possible sulphur dioxide escaping from the receiving bottle. Each bottle was provided with a safety tube reaching nearly to the bottom, which in

the case of the wash-bottles served also for the introduction of bromine as needed.

In the flask were placed 25 cc. concentrated sulphuric acid and 25 cc. ordinary strong alcohol, so-called 95 per cent; the mixture was heated to 140° and the temperature maintained as nearly constant as possible, alcohol being run in continuously from the funnel. The distillation lasted a total of 33½ hours exclusive of interruptions. Air was then aspirated through the whole apparatus to sweep out remaining vapors; a small quantity of black residue was left in the flask.

Examination of the Distillate.

The distillate measured 4,100 cc. from 4,700 cc. of alcohol used; it was acid to litmus and its gravity was 0.830 at 18°.

The apparent loss is due largely to the formation of ethylene, evidence of which was shown by a layer of ethylene bromide in the wash bottles.

One liter of the distillate was saponified with an excess of sodium hydroxide, to convert all esters into the corresponding sodium salts, and distilled down to 50 cc., the distillate being again distilled down to about 5 cc. and the residues were mixed. It was alkaline.

Sulphur as Sulphur Dioxide and Sulphites.

The alkaline residue was diluted and an aliquot part was acidified with hydrochloric acid and distilled into bromine water to convert the sulphur dioxide evolved into sulphuric acid, which was determined as barium sulphate; the sulphur found amounted to 1.03 per cent of that employed as sulphuric acid. The contents of the two wash-bottles containing bromine water were freed from bromine and precipitated with barium chloride and 0.96 per cent of the original sulphur found. During the preparation of ether, therefore, 1.99 per cent. of the sulphur of the acid used was lost from the generating flask in the form of sulphur dioxide and sulphites.

Sulphur as Sulphuric Acid and Sulphates.

An aliquot part of the alkaline residue from the saponification was analyzed for sulphates by precipitation as barium sulphate. The sulphur found amounted to 89.42 per cent of the total found.

In order to distinguish between sulphuric acid, ethyl sulphuric acid and ethyl sulphate in the ether distillate, the residue on evaporation of an aliquot part was dissolved in water and precipitated with barium chloride; the barium sulphate corresponded to 46.54 per cent of the total sulphur as sulphuric acid. The total acidity of another aliquot part of the residue of the ether distillate was determined by titration with standard alkali; the free sulphuric acid already found as described was subtracted, and the remaining acidity considered as due to ethyl sulphuric acid, the sulphur in this form amounting to 8.49 per cent of the total sulphur. The total sulphur in the ether distillate (89.42) less the sulphur as sulphuric acid (46.54) and that as ethyl sulphuric acid (8.49) would represent the sulphur as ethyl sulphate, namely, 34.39 per cent of the total sulphur.

As several months elapsed between the preparation of the ether and this examination of the product it is probable that there had been considerable change from ethyl sulphate into ethyl sulphuric acid and sulphuric acid, on account of the hydrolytic action of the water present. At the temperature of 140°, however, sulphuric acid (boiling point of the dihydrate is given as 170-199°) might distill as readily as ethyl sulphate (boiling point 208°); nothing seems to be known as to the possibility of ethyl sulphuric acid distilling as such.

Sulphur as Sulphonic Acids and Sulphonates.

The filtrate from the barium sulphate precipitate obtained in the determination of sulphur as sulphuric acid and sulphates was evaporated to dryness and the residue subjected to a Carius determination for sulphur; 4.62 per cent of the total sulphur was found.

Examination of the Residue.

Sulphur as Sulphur Dioxide.

The residue, weighing 3 grams, stood several months in the closed distilling flask. Air was aspirated through the flask and then through bromine water, and 0.15 per cent of the total sulphur was found in the bromine water.

Sulphur as Sulphuric Acid.

The residue was extracted with water and an aliquot part of the filtrate was treated with barium chloride; 1.69 per cent of the total sulphur was found.

Sulphur as Sulphates.

An aliquot part of the filtrate from the black residue was saponified with sodium hydroxide and total sulphuric acid determined as barium sulphate. Deducting the sulphuric acid found without saponification treatment, 0.99 per cent of the original sulphur was found as sulphates, presumably ethyl sulphuric acid and ethyl sulphate.

Sulphur as Sulphonic Acids and Sulphonates.

The filtrate from the barium sulphate obtained in the determination of sulphur as sulphates was evaporated to dryness with potassium nitrate and barium hydroxide, and the residue after ignition, was treated with dilute nitric acid, filtered and weighed as barium sulphate, showing 1.02 per cent of the original sulphur.

Sulphur in the Insoluble Carbonaceous Residue.

The extracted black residue was fused with potassium nitrate and barium hydroxide and the resulting barium sulphate was weighed. It corresponded to 0.12 per cent of the original sulphur.

Conclusions.

From the following results it appears that the formation of ether ceases because of the disappearance of the sulphuric acid from the generating flask.

Sulphur was found in the following forms and proportions, referred to their total as 100 per cent.

Sulphur dioxide escaping from the receiver during distillation		0.96 per cent.
Sulphur dioxide and sulphites in ether distillate		1.03
Sulphuric acid and sulphates in ether distillate		89.42
Sulphuric acid in ether distillate	46.54	
Ethyl sulphuric acid in distillate	8.49	
Ethyl sulphate in ether distillate	34.39	

Sulphonic acids and sulphonates in distillate	4.62
Sulphur dioxide in residue	0.15
Sulphuric acid in residue	1.69
Ethyl sulphuric acid and ethyl sulphate in residue	0.99
Sulphonic acids and sulphonates in residue	1.02
Sulphur in insoluble carbonaceous residue	0.12
Total	100.00