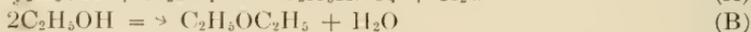
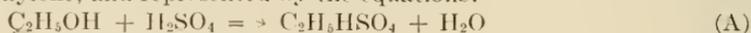


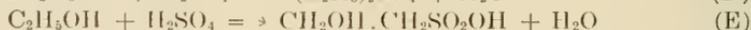
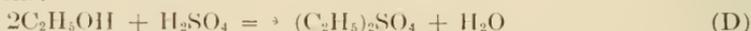
THE ETHYL-SULPHURIC ACID REACTION.

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Since the time of Williamson's classical work on etherification published in 1850, the reactions between ethyl alcohol and sulphuric acid have been familiar to chemists although not thoroughly understood. There are three important reactions, leading respectively to ethyl-sulphuric acid, ethyl ether, and ethylene, and represented by the equations:



In the last two reactions the sulphuric acid acts as a dehydrating agent. Other reactions of less importance are known, leading to ethyl sulphate, isethionic acid, and ethionic acid, respectively, in accordance with the equations:



No attempt is made to show the intermediate steps in the formation of the products mentioned.

The reactions depend on temperature and on the proportions of substances present. That leading to ethyl-sulphuric acid occurs at ordinary as well as higher temperatures, the others only inappreciably at ordinary temperatures.

In the writer's laboratory the first three reactions have been the subject of investigation. The formation of ether was examined as to its completeness and limitations by Miss Lena M. Sutton and the results were presented in outline to this Academy (Proceedings 1910), and published in full in the *Journal of the American Chemical Society* (1913, 35, 794). The same reaction is being made the subject of further study at present as to the nature and quantities of the by-products. The formation of ethylene is also at present under investigation as to its temperature limitations, speed, and side-reactions. The ethyl-sulphuric acid reaction was last year made the subject of examination by Mr. J. M. Albertson, Assistant in Chemistry, as a thesis for the Master of Science degree, and the results are here presented in outline.

Plan of the Work.

It will be seen from equation (A) that in the formation of ethyl-sulphuric acid one of the two acid hydrogens of the sulphuric acid is replaced by the ethyl group and neutralized, so that just half of the original acidity disappears

when the reaction is complete. The degree of completeness of the reaction at any time can therefore be measured by titration of the reaction mixture with standard alkali, if there are no complications due to other reactions. This was the method followed, and methyl orange was used as the indicator. Regarding complications due to other reactions, it might be feared that dilution of the mixture before titration might reverse the reaction appreciably before the neutral point was reached, and the significance of the titration results be thus impaired. Also, disappearance of acidity might be due in appreciable measure to the reactions shown in equations (D), (E) and (F).

To determine the first point, titrations were made at various time intervals after dilution, and it was found unexpectedly that no increase in acidity occurred even in twenty-four hours. This was surprising, considering the rapidity of the reaction in the other direction (as will be shown), and the fact that the conditions of equilibrium reached were found to be approximately equivalent to half completeness in the original direction. There is apparently some marked auto-catalytic effect involved.

The essential correctness of the assumption that the completeness of the ethyl-sulphuric acid reaction was really measured by the titration was confirmed by actually isolating the product in the form of its potassium salt, as follows: To the mixture was added calcium carbonate as long as effervescence resulted, converting both the ethyl-sulphuric acid and the unchanged sulphuric acid into their calcium salts; the calcium sulphate was then filtered out and washed, and to the filtrate containing calcium ethyl-sulphate potassium carbonate solution was added until the precipitation of calcium carbonate was just complete; the filtrate from this was evaporated to dryness, and the potassium ethyl-sulphate weighed. The yield corresponded in one case to a 57 per cent completeness of reaction as compared with 59 per cent by the titration method for the same conditions; in another case the yield indicated a completeness of 60.9 per cent, and the titration one of 60.0 per cent.

To determine the speed and completeness of the original reaction, as shown by equation (A), the procedure was as follows: Equal molecular quantities of absolute alcohol and pure sulphuric acid were mixed, with precautions as to cooling to prevent a rise in temperature above that for which data were sought; it was found practicable to obtain satisfactory results at temperatures ranging from 20 to 140° C. The mixture was kept in a bath of water or sulphuric acid maintained at a constant temperature; duplicate samples were withdrawn at intervals, diluted with water, and titrated with standard sodium hydroxide.

Results.

The results obtained may be briefly stated as follows: The completeness of the reaction ranged from 58 per cent at 20° to a maximum of 60.4 per cent at 50°, and to 42.6 per cent at 140°, as calculated from the titrations, being almost constant, at 58 to 60.4 per cent, from 30° to 90°.

The time necessary for the establishment of equilibrium varied from 2.5 hours at 20° to less than 10 minutes at 70°; observations could not be completed in less than 5 minutes. This speed of reaction proves unnecessary and even undesirable the much longer time and higher temperature generally recommended for the preparation of ethyl-sulphuric acid and its salts.

Above 70° there was found to be after the first 10 minutes a very slow but steady increase of acidity with lapse of time, probably due to the formation of ether, the odor of which was observed, according to the equation



It is evident that there would be a doubling of the acidity of the ethyl-sulphuric acid, or a return to the acidity of the original sulphuric acid, if the formation of ether were complete. To determine how rapidly this proceeded, the usual mixture of alcohol and sulphuric acid was kept at 140°; the titrations ranged from 15.2 cc alkali at the end of 5 minutes to 23.0 cc at the end of an hour. The original acidity would have corresponded to 19.7 cc if there had been no change in volume, but loss of ether would increase the concentration of other substances, so the increase in acidity was due in part to this loss of ether. The odor of ether was observed at as low a temperature as 70°, though the ether reaction is generally thought to begin at much higher temperatures—about 130°.

When the original mixture of alcohol and sulphuric acid was allowed to stand at room temperature for a considerable time, after the rapid decrease in acidity due to the formation of ethyl-sulphuric acid, practically reaching equilibrium in 2.5 hours, there was a very slow further decrease in acidity, the titration figure changing from 13.9 to 13.8 cc in 2 days, 13.6 cc in 7 days, 13.4 cc in 2 weeks, and 13.3 cc in 3 weeks. This was probably due to the formation of ethyl sulphate according to equation (D), or possibly that of isethionic acid or ethionic acid by reactions (E) and (F). This point might well receive further attention.