posing substances. More cases are being studied with a view to throw more light on the subject.

Investigations on similar lines are being continued.

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THE ETHYL-SULFURIC ACID REACTION.

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Since the time of Williamson's classical work on etherification published in 1850 some of the reactions between ethyl alcohol and sulfuric acid have been well known. There are three more important reactions, leading, respectively, to ethyl-sulfuric acid, ethyl ether, and ethylene, as represented by the equations:

$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5HSO_4 + H_2O \qquad (A)$$

$$2C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O \qquad (B)$$

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O \qquad (C)$$

Three other reactions of less importance are known, leading, respectively, to ethyl sulfate, isethionic acid, and ethionic acid, in accordance with the equations:

$$2C_2H_5OH + H_2SO_4 \longrightarrow (C_2H_5)_2SO_4 + H_2O \qquad (D)$$

$$C_2H_5OH + H_2SO_4 \longrightarrow CH_2OH.CH_2SO_2OH + H_2O \qquad (E)$$

$$C_2H_5OH + 2H_2SO_4 \longrightarrow CH_2HSO_4.CH_2SO_2OH + 2H_2O \qquad (F)$$

No attempt is here made to show the intermediate steps in the formation of the products mentioned; it is believed, however, that ethyl-sulfuric acid reacts with alcohol to form ether, as shown in the equation:

$$C_2H_5HSO_4 + C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2SO_4 \qquad (G)$$

The speed of these reactions varies with the temperature, that leading to ethyl-sulfuric acid (A), reaching equilibrium within two or three hours at 20° and within ten minutes at 70° or above, as will be shown later; the other reactions are very slow at ordinary temperatures; about 140° is most favorable for the ether reaction (B), and about 160° for the ethylene reaction (C).

The completeness of the ethyl-sulfuric acid reaction (A) was shown by Claesson[1] to be 57 to 59% with equimolecular quantities; the temperature is not stated in the abstracts accessible to the writer.

With a view to getting more detailed information as to the speed and degree of completeness of the ethyl-sulfuric acid reaction at different temperatures the work here reported was undertaken.

In this laboratory the formation of ether was examined as to its com-

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[1] *J. prakt. Chem.*, [2] **19**, 227 (1879).

pleteness and limitations, and the results were published in THIS JOURNAL by Evans and Sutton.[1] The same reaction is being further studied as to the nature and quantities of the by-products. The formation of ethylene (C) is also under investigation as to its temperature limitations, speed, and side-reactions.

Plan of the Work.

It will be seen from Equation A that in the formation of ethyl-sulfuric acid one of the two acid hydrogens is replaced by the ethyl group, and, therefore, 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 determined by titration of the reaction mixture with standard alkali if there are no complications due to other reactions. This was the method employed, and methyl orange was used as the indicator.

It might be thought that dilution of the mixture with water would reverse the original reaction appreciably before the neutral point was reached in the titration, and thus the significance of the results be impaired. It was found, however, that titrations made at intervals after the dilution showed no increase in acidity during twenty-four hours at room temperature.

It might also be thought that part of the disappearance of acidity might be due in appreciable measure to the reactions shown in Equations D, E and F. That this complication was not serious was shown by isolating the ethyl-sulfuric acid as its potassium salt and comparing the yield with the degree of completeness of the ethyl-sulfuric acid reaction as shown by titration; close agreements were obtained.

Experimental.

Speed and Completeness of the Esterification Reaction.—To determine the speed and completeness of the ethyl-sulfuric acid reaction the procedure was as follows: Equimolecular quantities of 99.9% alcohol (sp. gr. 0.7943 at 15.5°) and pure sulfuric acid containing 95% H_2SO_4 were mixed, with cooling to prevent a rise in temperature above that for which results were sought; it was found practicable by the use of ice to obtain satisfactory data for temperatures ranging from 20 to 140°. The mixture was then kept in a bath of water or sulfuric acid at a constant temperature, and duplicate samples were withdrawn at intervals, diluted with water, and titrated with standard sodium hydroxide solution.

In each experiment one-fourth-gram-molecular quantities were used by mixing 14.4 cc. of the alcohol and 13.3 cc. of the sulfuric acid in a small flask in an ice bath, the acid being added with constant stirring; the resulting temperature was 20°, and the volume 27.0 cc., showing a slight contraction. The flask was then placed in a bath at the tempera-

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[1] THIS JOURNAL, 35, 794 (1913).

ture for which observations were to be made, and duplicate 1 cc. samples were withdrawn with a pipet for titration, with care as to uniformity of manipulation. The standard sodium hydroxide solution was of such strength that 1 cc. of the pure sulfuric acid required 40 cc. for titration. If, then, the reaction leading to ethyl-sulfuric acid did not occur 1 cc. of the mixture would require 40 × 13.3 ÷ 27, or 19.7 cc. of the standard alkali; if, however, the reaction were complete half the acidity would disappear and the titration would require 19.7 ÷ 2, or 9.85 cc. of the alkali; the degree of completeness of the reaction can, therefore, be obtained by interpolation between these values.

TABLE I.

Time, min.	Temperature.												
	20.	30.	40.	50.	60.	70.	80.	90.	100.	110.	120.	130.	140.
10.......	16.5	14.7	14.2	14.0	14.5	13.8	13.9	14.0	14.2	14.4	14.4	14.6	15.6
20.......	16.2	14.1	14.0	13.7	13.8	13.8	13.9	14.0	14.6	15.0	15.3	15.5	16.4
30.......	16.0	14.0	13.9	13.8	13.8	13.9	13.9	14.2	15.0	15.7	15.6	16.0	17.0
40.......	15.6	14.0	13.8	13.8	13.8	13.9	13.9	14.4	15.6	16.4	16.6	16.8	18.0
50.......	15.4	13.9	13.9	13.8	13.8	13.9	14.1	14.6	16.0	17.0	17.9	17.5	20.5
60.......	15.1	13.8	13.8	13.8	..	..	14.2	15.0	16.6	17.8	..	..	23.0
70.......	14.9	13.8	..	13.8	13.8	14.0	..	..	17.1	18.3	..	..	..
80.......	..	13.8	13.9	13.8	..	14.0	14.5	15.4	17.6	18.8	..	19.4	..
90.......	14.6	13.8	..	..	13.8	14.1	..	..	18.3	19.4	19.6	..	..
100.......	14.5	13.8	13.9	..	..	..	14.7	..	..	..	..	..	..
120.......	14.3	..	13.9	..	14.0	14.2	15.7	16.3	..	..	21.0	21.4	..
150.......	14.0	..	..	..	..	14.4	16.3	17.3	..	..	21.9	23.0	..
180.......	14.0	..	..	..	..	..	..	..	..	..	..	25.0	..

Degree of completeness calculated from minimum titration, per cent.:

58.0 59.9 59.9 60.4 59.9 59.9 59.8 58.0 55.8 53.8 53.8 51.8 42.6

In this table the results of titrations at different temperatures and time intervals are given. It will be seen that there is a decrease in acidity with lapse of time, a minimum being reached more quickly at higher temperatures, and that above 60° this decrease is followed by an increase in acidity, most marked at the highest temperatures; as will be shown this increase is probably due to the ether reaction. The time required for minimum acidity to be reached ranged from 150 minutes at 20° to 10 minutes, or less, at 70° and higher temperatures. This speed of reaction makes unnecessary the much longer time generally recommended for the preparation of ethyl-sulfuric acid and its salts; indeed, a longer time actually decreases the yield owing to other reactions.

The table also shows that the degree of completeness of the reaction when minimum acidity was reached was 58% at 20°, practically constant at about 60% from 30 to 70°, and then decreased to 42.6% at 140°. For temperatures from 70° upwards these figures probably involve an increasing error due to the formation of ether, as will be discussed later.

TABLE II.

Time, min.	Temperature.	Titration, cc.	Degree of completeness, %.
150	20°	14.0	58.0
70	30	13.8	59.9
40	40	13.9	58.9
20	50	13.8	59.3
15	60	13.9	58.3
10	70	14.0	58.0
5	80	14.1	56.9
5	90	14.2	55.8
5	100	14.3	54.8
5	110	14.4	53.8
5	120	14.6	51.8
5	130	14.8	49.7
5	140	15.2	45.7

This table gives the results of another series of experiments intended to confirm the previous figures obtained for the completeness of the reaction after time intervals shown by preceding experiments to be sufficient for the minimum acidity to be reached. A reasonably close agreement with the results in Table I was obtained, as will be seen from the following table:

TABLE III.

Temperature, deg.	Degree of completeness calculated from minimum acidity (%).		
	Table I.	Table II.	Average.
20	58.0	58.0	58.0
30	59.9	59.9	59.9
40	59.9	58.9	59.4
50	60.4	59.3	59.8
60	59.9	58.3	59.1
70	59.9	58.0	58.9
80	58.9	56.9	57.9
90	58.0	55.8	56.9
100	55.8	54.8	55.3
110	53.8	53.8	53.8
120	53.8	51.8	52.8
130	51.8	49.7	50.7
140	42.6	45.7	44.1

Rate of Hydrolysis.—To determine whether hydrolysis—a reversal of the original esterification—occurred to an appreciable extent after dilution with water and before the titrations were completed, within about five minutes, samples were titrated 30 minutes, 2 hours, and 24 hours after dilution, and gave exactly the same results.

This is in harmony with the experience of Zaitschek,[1] who found the esterification much quicker than the saponification, and with that of Penniman, Randall, Miller, and Enslow,[2] who found that equilibrium

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[1] *Z. physik. Chem.*, **24**, 1 (1897).

[2] *J. Ind. Eng. Chem.*, **8**, 904 (1916).

was attained only after ten hours' heating in sealed tubes in boiling water 5 g. "aromatic sulfuric acid" with 3 g. water—about equal volumes of water and the reaction mixture of alcohol and strong sulfuric acid; at this temperature equilibrium is reached in the opposite direction in less than ten minutes. Presumably at room temperature the hydrolysis would have been much slower.

It seems surprising in view of the esterification reaction being not far from one-half complete that equilibrium should be reached in 150 minutes at 20° in the esterification, while in the opposite direction there should be no appreciable progress in 24 hours at about the same temperature on the addition of a large excess of water. There is apparently some marked autocatalytic effect involved.

Formation of Ether.—As has been stated, above 70° a steady increase in acidity was found after the minimum had been reached in the first ten minutes. This can be accounted for on the assumption that ether was being produced, according to Equation G. It is evident that there would be a doubling of the acidity of the ethyl-sulfuric acid, or a return to that of the original sulfuric acid, if the ether reaction were complete. The odor of ether was observed in all those experiments showing increasing acidity.

To determine how rapidly this change took place, the usual mixture of alcohol and sulfuric acid was kept at 140° and duplicate samples were withdrawn at five-minute intervals for titration, with the following results:

TABLE IV.

Time, min.	Titration, cc.	Time, min.	Titration, cc.
5	15.2	35	17.5
10	15.6	40	18.0
15	16.0	45	19.5
20	16.4	50	20.5
25	16.7	55	21.8
30	17.0	60	23.0

If the ether formation had been complete without complications due to other reactions, the original acidity and volume of the sulfuric acid would have been restored, and the titration would have been 40 cc.

It is apparent from these results that at the higher temperatures the minimum titration figures are increasingly too high to correctly represent the degree of completeness of the esterification, and that the completeness results calculated from these are correspondingly too low. It seems probable, therefore, that the degree of completeness of the ethyl-sulfuric acid reaction at equilibrium varies little from 58 to 60% at any temperature between 20 and 100°. This shows that there is no advantage in the artificial heating of the mixture of alcohol and sulfuric acid generally employed in the preparation of ethyl-sulfuric acid and its salts, the spontaneous heating to about 70° effecting a maximum production of ethyl-sulfuric acid within 10 minutes.

Formation of Ethyl Sulfate.—When the original mixture was allowed to stand at 20° for a considerable time, after the rapid decrease in acidity due to the formation of ethyl-sulfuric acid, practically complete in 150 minutes, there was a very slow further decrease in acidity, the titration figure changing from 13.9 to 13.8 in 2 days, 13.6 in 7 days, 13.4 in 2 weeks, and 13.3 in 3 weeks. This is probably due to the formation of ethyl sulfate, according to reaction (D), or possibly that of isethionic acid or ethionic acid by reactions (E) or (F), or to all three reactions.

Isolation of Potassium Ethyl Sulfate.—The essential correctness of the assumption that the completeness of the ethyl-sulfuric acid reaction was really measured by the minimum titrations was confirmed by isolating the ethyl-sulfuric acid in the form of its potassium salt, as follows: To the mixture, after sufficient time for the minimum acidity to be reached, calcium carbonate was added as long as effervescence resulted; the calcium sulfate was then filtered out and washed; to the filtrate containing calcium ethyl sulfate potassium carbonate solution was added until the precipitation of the calcium carbonate was just complete; the filtrate from this was evaporated to dryness, and the residue of potassium ethyl sulfate was weighed. The yield corresponded in one case to a 57% completeness of reaction, as compared with 59% by the titration method for the same conditions; in another case the yield indicated a completeness of 60.9 and the titration one of 60.0%. The possibility is not excluded that the product might have included salts of isethionic and ethionic acids. In view of the work of others this seems improbable to any considerable extent.

Conclusions.

1. The reaction between equimolecular quantities of ethyl alcohol and sulfuric acid is about 58% complete when equilibrium is reached at any temperature from 20 to 100°.

2. The time necessary for the establishment of equilibrium ranges from 150 minutes at 20° to less than 10 minutes at 70° and higher temperatures.

3. The ethyl-sulfuric acid reaction is very slowly reversible on addition of water.

4. At temperatures from 70° upwards ether is formed with increasing rapidity.

5. At ordinary temperatures there is a very slow formation of ethyl sulfate (or isethionic or ethionic acid), as evidenced by a loss of 4% of the acidity in 3 weeks.

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