

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON CATALYSIS. II.¹ DEHYDRATION AND ADDITION REACTIONS OF ETHYL ALCOHOL: THE FORMATION OF ACETAL AND MERCAPTANS²BY FRANCOIS A. GILFILLAN³

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The results described in the following paper were obtained in an investigation made to determine the comparative activity of the oxides of silicon, thorium, titanium and tungsten in inducing certain catalytic dehydration and esterification reactions with ethyl alcohol in the vapor phase and at comparatively high temperatures.

Ethyl alcohol subjected to dehydration in the vapor phase, may give rise to either or both of two products. With certain catalysts, and at lower temperatures, ether is produced, while under all other conditions a more complete dehydration occurs, with the production of ethylene.

This dehydration was first observed by Priestley⁴ while passing alcohol vapors through an earthen tube heated to redness. But it remained for Deimann⁵ to observe the catalytic action of the tube itself in this dehydration, and to separate and identify the gases formed. He found that alcohol vapors passing over heated alumina or silica were converted into ethylene, while those passing over heated glass, lime or talc produced none of this gas. The presence of a certain amount of hydrogen in the ethylene was also reported.

Berthelot⁶ found that ethyl alcohol could be passed over pumice below 500° without undergoing any decomposition, and Nef⁷ found a similar behavior up to 625°. Sabatier and Mailhe⁸ reported the use of thoria as a catalyst in 1908 and found that this oxide at 340° gave 50% more ethylene than did alumina. In addition to its greater activity it reacted exclusively as a dehydrating agent⁹ and was not rendered inactive by overheating. The recent work of Kramer and Reid¹⁰ shows that under certain conditions, thoria may also exercise an appreciable dehydrogenation on alcohols. And these same investigators have shown, furthermore, that the activity of thoria may be impaired by overheating, which fact has likewise been confirmed by the writer.

¹ Paper I by Johnson and Brown, *Proc. Nat. Acad. Sci.*, **7**, 75 (1921).

² This paper is constructed from a dissertation presented by Francois Arch Gilfillan in June, 1921, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. (Treat B. Johnson.)

³ This work was done under a special grant which was generously contributed by the Calco Chemical Company of Bound Brook, N. J. The writer desires to acknowledge at this time his appreciation of this assistance and to express his thanks to this company for its interest in his work.

⁴ Priestley, *Phil. Trans. Roy. Soc.*, **73**, 429 (1783), "Experiments and Observations on Air," Vol. 1, p. 200 (Birmingham, 1790).

⁵ Deimann, van Troostwyk, Bondt, and Louwrenburgh, *Crell. Ann.*, **1795**, II, pp. 312 and 430.

⁶ Berthelot, "Traité de chimie organique," **1872**, p. 164.

⁷ Nef, *Ann.*, **318**, 200 (1901).

⁸ Sabatier and Mailhe, *Compt. rend.*, **147**, 108 (1908).

⁹ Sabatier and Mailhe, *Ann. chim. phys.*, [8] **20**, 341 (1910).

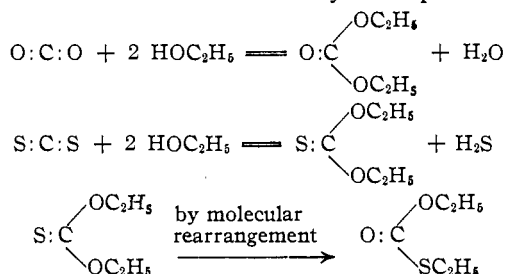
¹⁰ Kramer and Reid, *THIS JOURNAL*, **43**, 880 (1921).

Crystalline titanium dioxide, according to Sabatier and Mailhe,¹¹ shows no catalytic influence on the vapor of primary alcohols at temperatures up to 400°, but the amorphous form of this oxide is an active catalyst⁸ and at 320° ethylene is formed. Engelder passed¹² absolute alcohol over amorphous titanium oxide at 490° and obtained a gas which contained 23% more ethylene than that obtained by Sabatier at a temperature 90° lower. He also observed the formation of ethane, the proportion of which in some cases was as high as 55% of the total gas. Titanium oxide, therefore, acts simultaneously as a dehydrating, dehydrogenating, and hydrogenating catalytic agent.

The yellow oxide of tungsten, WO₃, is reduced at 350° by the vapors of alcohol. This blue oxide, as observed by Sabatier and Mailhe¹³, is an energetic dehydrating catalyst toward alcohols.⁹

It is well known that esterification can be promoted by certain catalysts, especially by sulfuric acid, but it was not until 1911 that catalytic esterification in the vapor phase was accomplished. For this purpose titanium dioxide has proved a much better catalyst than thoria.¹⁴ Even the weak acid hydrogen sulfide may be made to react with alcohols under the influence of catalysts of dehydration. This was first applied by Sabatier and Mailhe¹⁵ in 1910 with thoria, and the same agent has recently been employed for the same reaction by Kramer and Reid.¹⁰

The main purpose of the present research was to extend this work on esterification by catalysis, and to determine whether or not carbonic esters might be produced by the interaction of ethyl alcohol in the vapor phase with carbon dioxide and carbon disulfide. The chemical changes that were of immediate interest to us may be expressed as follows.



The catalysts employed in our work were pumice, thorium oxide, titanium oxide, and the blue oxide of tungsten, and the results of the investigation are described in detail in the experimental part of this paper. The researches on the study of catalysis will be continued.

Experimental Part

The Heating Unit.—The electric furnace in which all of our experiments were conducted was constructed from an alundum tube 61 cm. long and 4cm. internal diameter. This was wound with a spiral of Nichrome ribbon 13.7 meters in length, the ribbon being 3 mm. wide and

¹¹ Sabatier and Mailhe, *Compt. rend.*, **146**, 1377 (1908).

¹² Engelder, *J. Phys. Chem.*, **21**, 689 (1917).

¹³ Ref. 8, p. 17.

¹⁴ Sabatier and Mailhe, *Compt. rend.*, **152**, 496 (1911).

¹⁵ Sabatier and Mailhe, *ibid.*, **150**, 1217 (1910).

0.25 mm. thick The reaction tube was of fused silica, 90 cm. long and 16 mm. internal diameter. This tube extended through the alundum tube, and asbestos and magnesia were stuffed at each end into the space between the tubes, so that the silica tube, surrounded by a dead air space, extended through the alundum tube without touching it at any point.

Reagents.—The pumice used was a clean, granular product, in pieces of about the size of peas. This was used alone, and also as a support for the other catalytic agents employed.

Four contact masses were prepared from thorium nitrate, in order to observe the effect of method of preparation on the activity of this oxide. In the first instance, pumice was impregnated with a solution of 200 g. of thorium nitrate in 200 cc. of water. One-half of the pumice was dried at 100° and then ignited in a crucible at red heat for 3 hours. This charge, containing 36 g. of thoria, will be designated as Thoria A. The second portion of the impregnated pumice, without previous drying, was suspended in concentrated aqueous ammonia for several hours, then dried at 100°. This charge, prepared by precipitation of the hydroxide on the surface of the pumice, will be designated as Thoria B.

Two contact masses of thoria were prepared by direct precipitation of the hydroxide by treating a solution of the nitrate with ammonia, washing the precipitate until free from ammonia, and then drying it at 130°. One-half of this precipitate was mixed with enough impregnated pumice from Thoria B to bring the total thorium oxide content up to 60 g. This charge will be designated as Thoria C. The last contact mass, prepared and mixed with the impregnated pumice in the same manner, and containing 120 g. of thorium oxide, will be designated as Thoria D. The titanium oxide in portions of 60 g. was mixed with clean pumice before using as a catalyst. The tungsten oxide catalyst was prepared by mixing the yellow oxide of 99.23% purity with clean pumice and reducing with alcohol vapors at 350° to the blue oxide, W_2O_6 . The re-oxidation of this material to the yellow oxide was avoided by excluding air.

The alcohol used throughout the work varied in strength from 98.26% to 99.83%. The carbon disulfide employed was purified by treatment with anhydrous copper sulfate, agitating with mercury, and finally redistilling. The product then boiled constantly at about 46.3°.

The Dehydration of Ethyl Alcohol

Pumice was found to have no catalytic effect on alcohol at 400°. When passed through the tube at the rate of 30 g. per hour, the recovery represented from 99% to 100% of the weight of the original alcohol used, and an analysis showed the presence of only a trace of acetaldehyde. The presence of carbon dioxide exerted no influence on the reaction, even when the temperature was raised to 500°.

As stated above, several catalytic masses of thoria were employed, the first of these, Thoria A, being prepared by ignition of pumice impregnated with thorium nitrate. Three experiments with this material at temperatures between 250° and 350°, and at rates of flow varying between 22 g. and 70 g. per hour, showed recovery between 98% and 100% of alcohol containing a trace of aldehyde, which, however did not appear when air was displaced from the apparatus by carbon dioxide. Quite different results were obtained by use of the other thoria masses, prepared

without calcining. Thoria C showed at 250° a 92% recovery of alcohol, 90% at 300°, and 77% at 400°. In each instance some aldehyde was shown to be present. Thoria D was used in 5 experiments. At 300°, a recovery of 97% was observed when the rate of passage was 40 g. per hour, but when the rate was lowered to 20 g. per hour, only 93% was recovered. At 350° the same recovery was observed, but at 360°, only 68% was recovered. The catalytic mass was then heated to low redness in the furnace for 18 hours, after which three experiments were performed, in the presence of carbon dioxide. At 325° only a trace of ethylene was obtained, and 98% of the alcohol was recovered. At about 425°, from alcohol passing over the catalyst at the rate of only 15 g. per hour, 82% was recovered.

Results of the above investigation are shown graphically in Fig. 1, in which the curve Thoria A represents catalyst prepared by calcination.

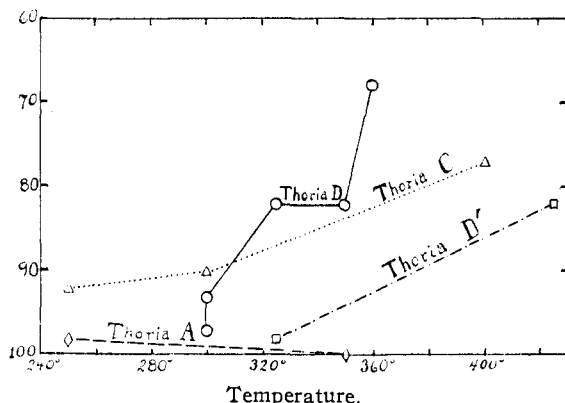


Fig. 1.—Inactivation of thoria by calcination.

The curves Thoria C and Thoria D represent the action of the two samples of catalyst prepared by precipitation, while curve Thoria D' depicts the activity of the corresponding catalyst after having been heated to low redness for 18 hours. It is evident that, contrary to the statement of Sabatier,¹⁶ the catalytic action of thoria is greatly diminished by calcination, or even by prolonged heating at a lower temperature. As would be expected, the amount of catalyst present does influence the rate of activity, as likewise does the rate of passage of the alcohol.

Titanium oxide gave results quite different from those given by thorium oxide. Alcohol passed through the furnace at the rate of 25 g. per hour gave at 325°, 350°, and 355°, a recovery of 98% by weight of alcohol containing small amounts of unidentified substances. When carbon dioxide was passed through with the alcohol at 262° and at 300°, all of

¹⁶ Sabatier, "Die Katalyse," Akad. Verlagsgesellschaft M. B. H. in Leipzig, 1914, p. 170.

the alcohol was recovered unchanged. At 350° and 355°, there was a slight evolution of ethylene, and 98% of the alcohol was recovered. In each of the 7 experiments which were conducted over this catalyst, the recovered alcohol contained a trace of impurity, which decolorized bromine water and gave a slight turbidity when the alcohol was diluted with water. This was soluble in ether but on evaporating the solvent there remained behind an insufficient quantity of material for identification. The above results indicate that the titanium dioxide used in our work had practically no dehydrating effect upon ethyl alcohol, and also that it does not accelerate a reaction between the alcohol and carbon dioxide.

The blue oxide of tungsten was found to be the most active of the 4 catalysts investigated, and in the following table are recorded the results of 7 experiments with this oxide. In each experiment 100 g. of alcohol was used and the vaporization was at the rate of about 20 g. per hour.

Temperature ° C.	Recovered alcohol G.	Purity %	Absolute Alcohol recovered G.
275	94	96	90
300	86	87	75
325	82	85	70
360	72	77	55
250	97	98	95
300	82	88	72
350	62	67	42

The last 3 experiments were conducted with a stream of carbon dioxide passing through the tube with the alcohol during the dehydration.

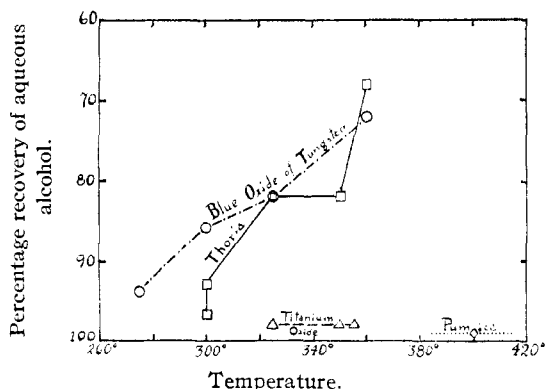


Fig. 2.—Dehydration of ethyl alcohol by various catalysts.

In Fig. 2 are shown curves indicating the amounts of aqueous alcohol recovered when 100 g. of absolute alcohol was led over the various catalysts at different temperatures. Pumice showed no activity at 400°. Titanium dioxide was without action up to 355°, the highest temperature

employed, while thoria and the blue oxide of tungsten decomposed alcohol at temperatures of 300° or lower. A comparison of these two catalysts is shown in Fig. 3, where the curves are plotted from data covering experiments in which the recovered aqueous alcohol was analyzed to determine its content of absolute alcohol. From Figs. 2 and 3, it is apparent that at lower temperatures the catalytic activity of the blue oxide of tungsten is greater than that of thoria, although at higher temperatures they approach the same value.

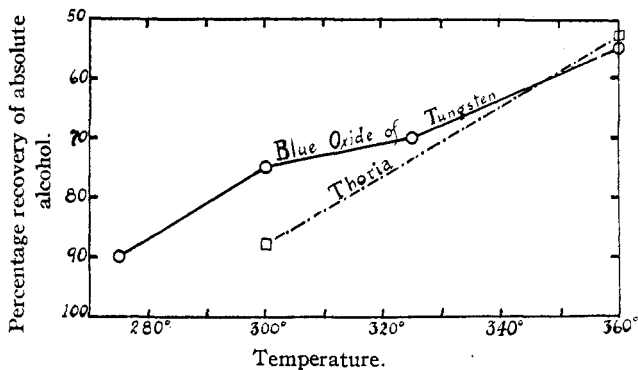


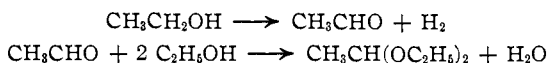
Fig. 3.—Destruction of absolute alcohol.

In operating with any of the above catalysts and ethyl alcohol, the main product of dehydration was ethylene. No trace of ether was detected in any of the experiments, but small traces of other products were found. In almost every instance acetaldehyde was shown to be present. The amounts of this material were quite small at the lower temperatures, but when the temperature reached 360° , appreciable amounts were produced by each catalyst, including thorium dioxide, despite the statement of Sabatier that thoria is exclusively a catalyst of dehydration.

It has been stated that no ether was produced in any of the experiments conducted, but in certain cases when thoria or the blue oxide of tungsten was employed, there was produced from alcohol a very small amount of an unidentified liquid boiling between 30° and 40° . This liquid was lighter than water and immiscible with it. It did not dissolve in alkali, reduce ammoniacal silver solution, interact with phenylhydrazine, nor decolorize bromine water. It burned with a colorless flame, and had a peculiar musty odor.

When operating over thoria at 325° in the presence of carbon dioxide, a 2% yield was obtained of a liquid distilling between 80° and 110° , when the temperature of the furnace was raised to 425° , this fraction constituted about 10% of the recovered material, and boiled between 80° and 95° . It was lighter than water and immiscible with it. Further examination of this material showed it to consist chiefly of acetal, mixed

with unchanged alcohol. The presence of carbon dioxide seemed to promote the formation of this product, which might result from the dehydrogenation of alcohol under the influence of thoria, yielding acetaldehyde, which could then condense with the excess of alcohol. Its complete synthesis may be expressed as follows.



The Decomposition of Carbon Disulfide

Pure, dry carbon disulfide, when vaporized over pumice or over the blue oxide of tungsten, suffered little or no decomposition. At 400° there was a slight discoloration, due to the formation of a trace of brown, resinous material. When carbon dioxide was passed through the furnace with the carbon disulfide, there was no reaction as long as the gases were perfectly dry. But if moisture was present in any amount, or if the contact mass was not perfectly dry, then hydrogen sulfide was always produced in direct proportion to the amount of water present. It was thought possible that some carbon oxysulfide might be evolved from this reaction, as had been observed by Meyer and Schuster¹⁷ at a higher temperature, but analysis of the gas failed to reveal any such reaction product.

The Interaction of Ethyl Alcohol and Carbon Disulfide

Absolute alcohol was mixed with purified carbon disulfide in the proportion of two moles of the former to one mole of the latter. When this mixture was passed over pumice at a rate varying between 20 g. and 40 g. per hour, the weight of the recovered liquid varied between 91% and 98% of that employed. In each case, the formation of hydrogen sulfide was observed, but analyses revealed no carbon oxysulfide. The hydrogen sulfide doubtless resulted from the interaction of the carbon disulfide with the small amount of water present in the alcohol. When carbon dioxide was passed through the furnace along with the vapor mixture, it exercised no appreciable influence on the course of the reaction.

When the alcohol-carbon disulfide mixture was passed over Thoria C at 300° the recovered liquid represented 82% of the weight of the original material. At 400° only about 45% was recovered. The evolution of hydrogen sulfide was much greater at the higher temperature, which temperature was also productive of a considerable quantity of ethyl mercaptan, resulting from the condensation of alcohol with the hydrogen sulfide generated. This condensation forms one mole of water, which may again react with more carbon disulfide for the further production of hydrogen sulfide, so that a trace of water in the original alcohol would suffice, theoretically, for the conversion of the entire mixture into car-

¹⁷ Meyer and Schuster, *Ber.*, **44**, 1931 (1911).

bon dioxide and ethyl mercaptan. In practice, however, only moderate quantities of mercaptan were obtained.

High-boiling liquids were obtained from this reaction, but in small quantities. Of this product, very little boiled between 100° and 160° , but the fractions between 160° and 228° were considerably larger. All fractions were specifically lighter than water in which they were insoluble. The higher fractions were partially or totally insoluble in hydrochloric acid and in potassium hydroxide solution, but soluble in benzene and in alcohol. All possess a very nauseating odor.

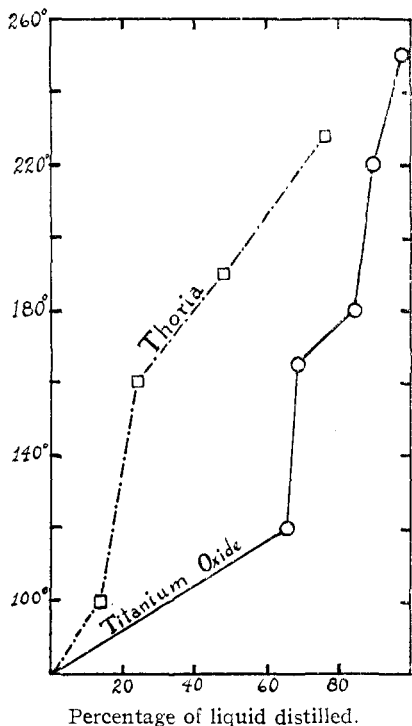


Fig. 4.—Comparative distillation of high-boiling liquids produced by the action of catalysts upon a mixture of alcohol and carbon disulfide.

The most promising feature of the titanium oxide curve is the section representing 16% of material boiling within a range of 15° between 165° and 180° ; but as there was only 10 cc. of this liquid, its purification was not attempted. Whether we are dealing here with thiocarbonate combinations remains to be established.

The blue oxide of tungsten shows a very different behavior from that of thoria and titanium oxide. At 265° there was very little reaction during vaporization of the mixture of alcohol and carbon disulfide. A small

Titanium oxide, in the light of its inactivity toward ethyl alcohol, gave surprising results when used as a catalytic mass with mixtures of alcohol and carbon disulfide. The rate of passage through the furnace varied between 13 g. and 18 g. of liquid per hour. At 225° the liquid recovered represented 94% of the weight of the original amount used. At 300° this value dropped to 84%, and at 355° and 360° the recovery represented 50% and 46%, respectively, of the original weight. Large quantities of hydrogen sulfide were evolved in each experiment and the yield of pure ethyl mercaptan at 360° with this catalyst was about 10%.

High-boiling liquids were produced in the presence of this catalyst, similar to those produced with thoria, but the yields were very much smaller. The distillation of fractions above 80° from these two products is shown graphically in Fig. 4.

amount of hydrogen sulfide was evolved, but the 91% of recovered liquid contained no reaction product that could be isolated. At 300° there was an 89% recovery of liquid, which contained a trace of mercaptan, while a mixture of hydrogen sulfide and ethylene was evolved. When the temperature was raised to 325°, gaseous evolution increased, and the recovered liquid represented 80% of the original weight, and contained only a small amount of mercaptan. At 360° there was vigorous evolution of ethylene and hydrogen sulfide, and 66% by weight of the liquid was recovered. This material separated into two layers, a phenomenon not observed with the other catalysts. This shows the pronounced dehydrating action of this catalyst, in that enough water was produced to throw the carbon disulfide out of the alcoholic solution. Production of mercaptan by this

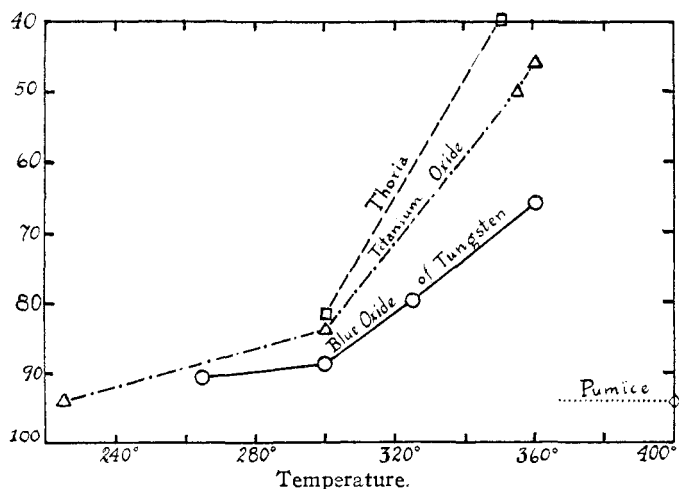
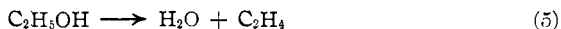
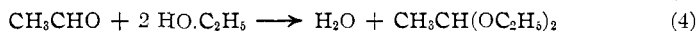
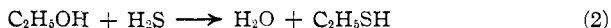
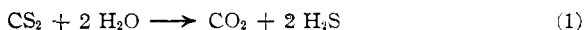


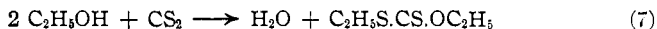
Fig. 5.—Gaseous products of the action of various catalysts upon a mixture of carbon disulfide and ethyl alcohol.

catalyst was far inferior to that by thoria and titanium oxide, but the ethylene production was much greater. The presence of carbon dioxide seemed to exert no influence on the course of the reaction.

Comparison of the activity of these four contact catalysts is not an easy matter. It has been however, shown that the following 5 reactions occur.



There are also numerous other possible reactions, including the formation of thio-esters, as indicated in the following equations.



In Fig. 5 is shown the production of gas from mixtures of alcohol and carbon disulfide passing over catalysts at various temperatures. (Equations 1, 3, 5). Pumice, as would be expected, is quite inert; but titanium dioxide, which has been shown to exert almost no catalytic influence on ethyl alcohol alone (Equations 3 and 5), shows the formation of a large amount of volatile products. This may be due, then, to the formation of hydrogen sulfide (Equation 1), which supposition is confirmed by the relatively large production of mercaptan, as shown in Equation 2.

The blue oxide of tungsten has been shown to be a much more active dehydrating agent toward ethyl alcohol alone than the other catalysts employed, and yet the amount of volatile products from the mixture is, according to Fig. 5, much less than was produced by thoria or by titanium oxide. This fact would indicate that the blue oxide of tungsten functioned in a series of reactions which produced a maximum of water and a minimum of gaseous products. Or it may be possible that a reaction occurred between these gaseous products, whereby they were transformed into non-volatile compounds. Whether or not any ethyl esters of carbon disulfide were formed, as indicated in Equations 6 and 7, was not proved. A small amount of high-boiling material was found in almost every experiment, but a sufficient quantity of this material was never obtained to permit the isolation of any pure compound.

Summary

1. Alcohol vapors alone, or in the presence of carbon dioxide, may be passed over pumice at 500° without undergoing appreciable decomposition.
2. By strongly calcining thoria, or by prolonged heating at a lower temperature, this oxide may be inactivated for dehydration of ethyl alcohol.
3. Thoria is not exclusively dehydrating in its action upon ethyl alcohol. Under certain conditions a considerable amount of aldehyde is produced by dehydrogenation.
4. The titanium oxide employed as a catalyst effected practically no dehydration of ethyl alcohol at temperatures up to 355°.
5. The blue oxide of tungsten at lower temperatures is a much more active catalyst for the production of ethylene than is thoria, but at higher temperatures they are practically of equal efficiency.
6. No ether was produced from alcohol in the presence of any of the catalysts.
7. By operating over thoria in the presence of carbon dioxide, a considerable quantity of acetal was formed from ethyl alcohol.
8. Pure, dry carbon disulfide, when vaporized over pumice or over the

blue oxide of tungsten, suffers no decomposition at temperatures up to 400°. A trace of moisture, however, causes decomposition and the evolution of hydrogen sulfide.

9. In the presence of any of the three metallic oxides employed as catalysts, a mixture of absolute alcohol and carbon disulfide produced considerable quantities of ethyl mercaptan. Titanium dioxide, which had been almost without action upon alcohol alone, proved the most active catalyst for this esterification. This new method may be advantageous for the synthesis of certain mercaptans.

10. From alcohol and carbon disulfide, amounts of high-boiling liquids were obtained, but in quantities too small for identification. We obtained no other evidence of the formation of esters of thiocarbonic acids by interaction of alcohol and carbon disulfide.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE BUREAU OF STANDARDS OF THE DEPARTMENT OF COMMERCE]

ABIETIC ACID AND CERTAIN METAL ABIETATES¹

BY LAWRENCE L. STEELE

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Introduction

Abietic acid is the name most commonly given to the crystalline material made by treating ordinary rosin with alcohol or other organic solvents. Many years ago Maly² expressed the view that rosin was essentially the anhydride of abietic acid, but his idea has not been generally accepted. Recently Knecht and Hibbert³ have presented strong evidence in favor of the anhydride theory for rosin. From the assumption that rosin is an acid anhydride, a new method for the preparation of abietic acid has been developed by which a pure product can be made more easily and in larger yield than by the older published methods. Some physical and chemical data of the product will be given together with a description of the preparation of several metallic abietates with their analyses for metal content.

Methods for the Preparation of Abietic Acid

The method of Maly⁴ has been used extensively for preparing abietic acid. Rosin is heated with 70% alcohol, whereby after some hours it partly dissolves and partly crystallizes. The impure crystals are treated in the same way with dil. alcohol a number of times and finally repeatedly recrystallized from strong alcohol. The method is tedious and the yield of pure product is very low.

¹ Published by permission of the Director of the Bureau of Standards.

² Maly, *Ann.*, **149**, 244 (1869).

³ Knecht and Hibbert, *J. Soc. Dyers Colour.*, **35**, 150 (1919).

⁴ Maly, *J. prakt. Chem.*, **86**, 111 (1862).