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A study on the catalytic decomposition of ethyl alcohol in the presence of magnesium oxide

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A STUDY ON THE CATALYTIC DECOMPOSITION OF ETHYL ALCOHOL
IN THE PRESENCE OF MAGNESIUM OXIDE

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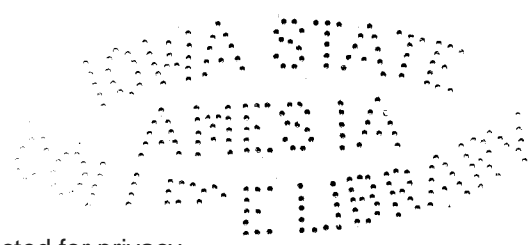
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To Vladimir N. Ipatieff, the pioneer in the use of pressure in catalytic and non-catalytic chemical reactions and an enthusiastic leader in the field today, belongs the credit of having suggested the field of study; to Dr. F. E. Brown, appreciation for advice and encouragement during the course of the investigation.

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INTRODUCTION

As a result of many researches the functions of catalysts have been clarified, and some theoretical principles have been established leading to the prediction of an efficient catalyst for any reaction thermodynamically possible. These results serve to further the interest in catalytic research.

A catalyst does not contribute energy to a reacting system, since the catalyst emerges from the reaction without loss or chemical change. Herein lies one of the principal practical advantages of the catalytic agent, since it ensures that in the presence of minimal amounts of catalyst, large quantities of the reacting substance may be transformed. The advantages of a catalyst lie in its ability to increase the rate of a given reaction or, as is usually the case, to lower the temperature at which the reaction will occur at a desirable rate, and to direct the reaction along a particular path when several paths are available.

In many instances the catalyst for a particular synthesis has been determined by a study of the catalytic decomposition of the desired product. That this study is expedient is amply illustrated by the methanol synthesis, in which the isolated experiments of Sabatier and Ipatieff on the catalytic decomposition of methanol served as a guide in the search for catalysts to be used in its synthesis.

Experimental facts throughout the literature illustrate the efficacy of some catalysts to induce the decomposition of organic compounds in several directions, while other catalysts produce decomposition in only one direction. To group them under headings of dehydrogenation or dehydration requires a chemical study of all the reactions that may occur in any given case; then and only then may conclusions be drawn as to a proper classification.

As an example of a catalyst incorrectly classified, mention may be made of the work of Sabatier and Mailhe (1), in which magnesium oxide is listed as a dehydrogenating catalyst which produced aldehyde decomposition from ethyl alcohol, because at 360° C. traces of hydrogen are found. As has been so ably demonstrated by Ipatieff (2) in the butadiene decomposition of ethyl alcohol, the liberation of hydrogen is no proof that aldehyde decomposition has taken place. Thus, more data are necessary before a final decision may be drawn.

The purpose of this research is to arrive at suitable conclusions concerning the effect of using magnesium oxide as a contact agent in the decomposition of alcohol. To do that it is necessary to study the reaction experimentally under the greatest possible variety of conditions, under gradients of temperature, pressure and space velocity, with due

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1. Sabatier and Mailhe, Ann. chim. phys., (8) 20, 289-352 (1910).
 2. Ipatieff, J. prakt. Chem., 67, 420-422 (1903).

consideration being placed on the nature of the tube used to hold the catalyst. This study requires the use of high-pressure equipment, since the course of catalytic reactions and the nature of the final product may be modified or changed by the physical factor of pressure for any given temperature.

This investigation traces the influence of magnesium oxide on the decomposition of ethyl alcohol under the following conditions: high and atmospheric pressures, low-space velocity, and the lower temperatures at which the decomposition takes place.

It is quite evident that there is still much to be done to this most interesting decomposition under the influence of magnesium oxide at other temperatures, pressures, and space velocities before its use either alone or with promoters is definitely known.

HISTORICAL RÉSUMÉ

Catalytic Decomposition of Alcohol Under Atmospheric Pressure.

Previous to Ipatieff's work, observations had been recorded on the decomposition of ethyl alcohol in the presence of extraneous substances, but no suggestion had been made that these different materials caused the decomposition of the alcohol in a specific manner to produce different products. Notable among the earlier recorded observations were those of Diemann, Troostwyk, Lauwrenburg, and Bondt (3). They showed that at high temperatures and in the presence of kaolin the gas obtained from the decomposition of alcohol was predominately ethylene. Other investigators had recorded separate, but discordant, observations on the decomposition of alcohol. Deuman (4) reported the presence of a gas which burned with a slightly luminous flame when alcohol vapor was passed through a glowing tube. Marchand (5) reported the finding of aldehyde, gas, and carbon by passing ethyl alcohol through a glowing

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3. Deimann, van Troostswyk, Lauwrenburg, and Bondt, Ann. Physik, 2, 201-215 (1799).
 4. Ipatieff, "Aluminiumoxyd als Katalysator in der organischen Chemie," Akademische Verlagsgesellschaft M.B.H., Leipzig, p. 13. 1929.
 5. Marchand, J. prakt. Chem., 15, 1-16 (1838).

porcelain [a fired mixture of kaolin ($H_2Al_2(SiO_4)_2H_2O$) and feldspar ($KAlSi_3O_8$)] tube. Berthelot (6) detected small amounts of aldehyde and hydrogen in the products resulting from the passage of alcohol through a glowing porcelain tube packed with pumice; Sassure (7) did not observe the formation of aldehyde in similar experiments. Nef (8) observed two simultaneous reactions in the decomposition of alcohol by heat in which hydrogen and water were eliminated, with a preponderance of the former.

Because of the paucity of data recorded in the literature no conclusion could be drawn as to whether the decomposition of ethyl alcohol was specific or haphazard, and one could not conclude that alcohol decomposed into aldehyde and hydrogen under the sole influence of heat, because the slight formation of aldehyde might have been due to the oxidation of alcohol by the oxygen of the air in the apparatus at the start of the experiment, or secondly, the carbon which is always formed from alcohol at high temperatures in the presence of pumice might have acted as a catalyst for the decomposition of alcohol. In spite of these difficulties, attempts were made to write the equation for the decomposition of alcohol at high temperatures. However, it was Ipatieff's work in 1900 that first drew scientific attention to the efficacy of

6. Berthelot, Ann., 81, 108-117 (1852).

7. Ipatieff, "Catalytic reactions at high pressures and temperatures," The Macmillan Co., New York, p. 1. 1936.

8. Nef, Ann., 318, 137-230 (1901).

a catalyst to influence the course of a decomposition, because, as first noted by Ipatieff (9), the products obtained from the decomposition of alcohol depended upon the tubes used in this pyrolytic reaction. Other investigators had failed to attach any significance whatsoever to the particular materials of which the tubes used in the experiments were made.

Ipatieff (10) began his study of pyrolytic and catalytic reactions with the decomposition of alcohols and found that upon the passage of ethyl alcohol in the form of vapor through a hard glass tube at 700° C. the alcohol simply distilled over through the tube without appreciable loss in weight. Minimum amounts of gas were liberated. As the temperature increased, the decomposition of alcohol became apparent by the liberation of gas and the formation of acetaldehyde. At 800° to 850° C. decomposition became energetic. Bertholet and Jungfleisch (11) reported a temperature of 500° C. as the initial temperature for ethanol decomposition in contrast to the much higher temperature given by Ipatieff for comparable experimental conditions. These discordant results might have been due to differences in time of contact or differences in methods of

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9. Ipatieff, Ber., 34, 596-600 (1901).
 10. Ipatieff, Ber., 34, 3579-3589 (1901).
 11. Bertholet and Jungfleisch, "Traité élémentaire de Chimie organique," 1886, 2nd Ed., Vol. 1, p. 256; through Marek and Eahn, "The catalytic oxidation of organic compounds in the vapor phase," The Chemical Catalog Co., Inc., New York, p. 39, 1932.

temperature measurement. Experimental data by Ipatieff indicated that the amount of alcohol decomposed depended not only on the temperature of the non-catalytic decomposition, but also on the length of time the vapors were subjected to the temperature of the heated part of the tube. Therefore, to make experiments comparable, the vapor velocity was so fixed that equal quantities of alcohol passed through the tube per unit of time; some 150 grams of alcohol were distilled over in an hour.

Ipatieff found that when 140 grams of ethyl alcohol were passed through a glass tube at 800° to 820° C., 50 grams decomposed. The greater part of that decomposed was converted into hydrogen and acetaldehyde. The acetaldehyde at higher temperatures decomposed further into simpler gases. He determined the amount of aldehyde obtained in the decomposition in the form of aldehyde ammonia. From the weight of the crystalline aldehyde ammonia the yield of aldehyde was calculated. Altogether nine grams of aldehyde were obtained. Analysis of the gas gave the following results: 11.5 per cent ethylene, 18.9 per cent carbon monoxide, 26.2 per cent methane, and 41.3 per cent hydrogen. After the removal of ethylene the gases contained 21.8 per cent carbon monoxide, 41.6 per cent hydrogen, and 31.3 per cent methane.

Ipatieff (10) determined the amount of alcohol which was dehydrated to form ethylene and water. One hundred forty grams of alcohol were passed through the glass tube at 820°

to 830° C.; 59 grams decomposed. The gas obtained by the decomposition was passed through a flask containing bromine; 45 grams of ethylene bromide were obtained. Assuming that all the ethylene obtained originated from the decomposition of alcohol directly into ethylene and water, one might judge that about 12 grams of alcohol should have been decomposed in a manner indicated by the equation $C_2H_5OH \rightarrow C_2H_4 + H_2O$. The other 47 grams of alcohol might have undergone decomposition according to another reaction, $C_2H_5OH \rightarrow H_2 + CH_3CHO$, to give about two grams of hydrogen and 45 grams of aldehyde. However, the experiment showed only 17 grams of aldehyde, the remaining 28 grams of aldehyde decomposing at the above-mentioned temperature chiefly into carbon monoxide and methane according to the equation $CH_3CHO \rightarrow CO + CH_4$. Such a reaction should therefore yield ten grams of methane and 18 grams of carbon monoxide. If these weights of gases are converted to volumes under standard conditions, a mixture of these three gases in the proportion stated would have the following composition: 43 per cent hydrogen, 30 per cent methane, 27 per cent carbon monoxide. The composition actually found was 41.6 per cent hydrogen, 31.4 per cent methane, 24.5 per cent carbon monoxide. The composition of the gaseous mixture actually found agreed, therefore, quite closely with that of the composition of the gas mixture calculated on the basis of an assumed course of decomposition. Such an agreement justifies the equations given. Furthermore, from Ipatieff's

results only about one-third of the aldehyde originally formed did not have sufficient time to decompose, the remainder having split into carbon monoxide and methane. It was found that the higher the temperature of the decomposition of the alcohol the more aldehyde should have been formed, but because of the higher temperature a greater amount of aldehyde decomposed. This fact was shown by an equalization of volumes in the gaseous mixture of hydrogen, carbon monoxide, and methane. On the other hand, the lower the temperature of the decomposition of the alcohol the greater the amount of aldehyde remained, and the greater was the percentage of hydrogen in the gaseous mixture. Consequently the approximate course of the pyrogenetic decomposition of the alcohol may be judged from the composition of the gas formed, and, accordingly, Ipatieff concluded from his experiments on the pyrogenetic decomposition of alcohol at temperatures above 700° C. in a hard glass tube, that there are two kinds of decomposition: first, alcohol into aldehyde and hydrogen, and second, alcohol into ethylene and water, with no trace of carbon formation in the tube in spite of the high temperature. The latter fact, according to Ipatieff's estimation, is very important, because if carbon were formed, one could not speak of two kinds of decomposition of alcohol under the sole influence of heat, as carbon separating at the beginning of the reaction might act as a catalyst later on and thereby change the course of the decomposition of alcohol.

Continuing his studies, Ipatieff (10) found the pyrogenetic decomposition of alcohol in a platinum tube to be the same as that in a glass tube, but the reaction occurred at a lower temperature than that in the glass tube. In these experiments, the ethyl alcohol was passed through a platinum tube heated to a temperature of 660° C. Of 100 grams of alcohol, 70 grams decomposed. From the ethylene bromide formed it was calculated 10 grams of alcohol decomposed into ethylene and water, and the remaining 60 grams into aldehyde and hydrogen. Of the aldehyde considered to be formed about five grams were absorbed by ammonia, and the remaining 55 grams were considered to have decomposed into carbon monoxide and methane. The observed composition of the gas coincided quite well with the calculated data of the gaseous composition resulting from the above assumed decomposition; the calculated composition was 34.2 per cent hydrogen, 32.9 per cent carbon monoxide, 32.8 per cent methane; the observed composition was 36.4 per cent hydrogen, 31.7 per cent carbon monoxide, 32.3 per cent methane. From the sequence of experiments Ipatieff concluded that about one-seventh of the alcohol decomposed in a platinum tube to form ethylene and water, and the other six-sevenths into acetaldehyde and hydrogen. Furthermore, he observed as before that the higher the temperature of decomposition the nearer will be an approach to equality in the resulting volumes of hydrogen, carbon monoxide, and methane. Besides these main reactions other side reactions were observed, as

in the case of the glass tube, notably the formation of small amounts of formaldehyde. Ipatieff therefore concluded from his experiments on the decomposition of alcohol in a platinum tube that decomposition started at about 540° C. These experiments indicated that platinum was a catalyst in the decomposition of ethyl alcohol, because under the same temperature conditions the decomposition was three times as great in platinum as in glass tubes.

Ipatieff's (12) experiments on the decomposition of alcohol in a porcelain tube indicated that decomposition proceeded the same way as in the glass tube. In the same series of experiments he observed that, when alcohol was passed through a tube made of pure red copper at a temperature of 780° to 800° C., he obtained approximately the same percentage products as he did in a glass tube; thereby he concluded that pure red copper was not a catalyst for the decomposition of alcohol. His experiments with alcohol carried out in an aluminum tube and in a glass tube filled with pulverized aluminum, with both absolute and 96 per cent alcohol, showed no decomposition when heated to a temperature of 600° C.

Ipatieff (9, 10, 12) was impressed with the enormous influence of iron on the decomposition of alcohol at high temperatures; it was the first catalyst which he discovered for the dehydrogenation of alcohol. He observed that if the vapors of primary alcohols (in this case ethyl alcohol) were

12. Ipatieff, Ber., 35, 1047-1057 (1902).

passed through an iron tube or through a glass tube containing iron filings an energetic decomposition of alcohol into aldehyde and hydrogen ensued at a temperature of 460° to 480°C. Increases in the temperature of this catalytic reaction increased its velocity, and at certain temperatures the aldehyde which was formed started to decompose, principally into saturated hydrocarbons and carbon monoxide. In some cases, the experiments showed that part of the aldehyde decomposed to give small amounts of olefins. The presence of olefins might have been explained, however, by the decomposition of a saturated hydrocarbon into olefins and hydrogen, and the presence of saturated hydrocarbons by the reduction of carbon monoxide to methane in the presence of catalytic iron. Carbon deposits were noted on the surface of the iron, the amounts depending on the temperature of the reaction. The lower the temperature of the decomposition of the alcohol in the presence of iron the more regularly the aldehyde decomposition proceeded, with the liberation of a gas consisting chiefly of hydrogen. The above conclusions were drawn from the following experiments: 192 grams of alcohol were passed through an iron tube at 700° C., 144 grams decomposed, 20 grams of aldehyde were formed, and 27 grams of carbon were obtained. Under the same conditions, when he used 195 grams of alcohol at 600° C., only 23 grams of alcohol decomposed, and 12 grams of aldehyde and three grams of carbon were obtained. The gas analysis in the first case was 0.8 per cent ethylene, 21.1

per cent carbon monoxide, 12.1 per cent methane, 65.9 per cent hydrogen, and in the second case 5.3 per cent ethylene, 10.9 per cent carbon monoxide, 10.9 per cent methane, 71.9 per cent hydrogen.

Because of the formation of carbon in these particular experiments Ipatieff believed that part of the decomposition was probably due to the carbon formed. To answer the question whether carbon would produce such decomposition of alcohol, alcohol was passed through a glass tube containing carbon which was free from iron. At 700° C. from 134 grams of alcohol, 17 grams were decomposed, and four grams of aldehyde were obtained. The carbon did not increase in weight. An analysis of the gas gave the following results: 3.6 per cent unsaturated hydrocarbons, 23.2 per cent carbon monoxide, 49.8 per cent hydrogen, and 22.3 per cent methane. Thus it appeared that iron was the cause of the separation of carbon during the decomposition of alcohol. When a minimum amount of iron was mixed with the carbon, and 136 grams of alcohol passed through the tube containing the mixture at 600° C., 17 grams of aldehyde were produced and the carbon gained 4.5 grams in weight; nine grams of ethylene bromide resulted when the exit gas was passed into bromine, indicating that the decomposition is the same as in the iron tube. Ipatieff concluded from these experiments that iron was an energetic catalyst for the decomposition of alcohol and that it appeared to cause the separation of carbon.

Ipatieff carried out an experiment to determine whether the carbon separation in the presence of iron was due to the decomposition of alcohol or of aldehyde. In this experiment 131 grams of paraldehyde were passed through an iron tube at 600° C., 120 grams were decomposed, and 17 grams of carbon were obtained. The composition of the gas was as follows: three per cent ethylene, 42.6 per cent carbon monoxide, 38.5 per cent methane, 17 per cent hydrogen, showing that the chief products of the decomposition of acetaldehyde in the presence of iron are methane and carbon monoxide. Because of the large carbon deposition in this experiment, it was concluded that the carbon obtained in the decomposition of ethyl alcohol was primarily due to the decomposition of aldehyde in the presence of catalytic iron. Senderens (13) stated that when alcohol vapors were passed over amorphous carbon some formaldehyde was produced. The gas from the reaction contained 54.7 per cent methane, 38.5 per cent ethylene, 4.5 per cent carbon monoxide, and 4.8 per cent hydrogen. This high percentage of methane and low percentage of hydrogen and carbon monoxide differed materially from Ipatieff's results just mentioned.

Ipatieff (10), in order to determine which metals produced decomposition of alcohol, conducted a whole series of experiments, noting the effect of other metals which might produce catalytic decomposition. Among those tried were

13. Senderens, Comp. rend., 144, 381-383 (1907).

magnesium, aluminum, cadmium, tin, copper, lead, bismuth, antimony, manganese, nickel, and zinc. From a comparative study of the action of metals, he found that at a temperature of 600° C. the vapor of alcohol did not suffer any change by coming into contact with copper, aluminum, lead, tin, bismuth, antimony, and magnesium; but by passage through manganese and nickel a decomposition occurred similar to that with the iron catalyst. Of the metals tried metallic zinc was found to be the best catalyst for decomposing alcohol into aldehyde and hydrogen. Larger yields of aldehyde were noted in contradistinction to the iron catalyst, because zinc seemed to be less active than iron in decomposing the newly formed aldehyde into saturated hydrocarbons and carbon monoxide. Also, only traces of carbon formation were observed. Ipatieff cites the following experiment to bring forth this view: 145 grams of ethyl alcohol were passed, at the rate of 150 grams per hour, through a glass tube containing 137 grams of pure zinc in granular form, and heated to a temperature of 620° to 650° C.; 35 grams of alcohol were decomposed and 27 grams of aldehyde were obtained, a yield which corresponds to about 80 per cent of the alcohol decomposed. Less than a gram of ethylene was formed, an amount which indicated that zinc is an excellent catalyst for producing a high yield of aldehyde, because this catalyst does not decompose the product further into carbon monoxide and methane.

Sabatier and Senderens (14, 15) showed that reduced nickel promoted the catalytic decomposition of alcohol into aldehyde and hydrogen, but that reduced nickel even at low temperatures, 178° C., decomposed the aldehyde further into carbon monoxide and saturated hydrocarbons. Bouveault (16) also converted alcohol into aldehyde and hydrogen by copper or nickel catalysts at 200° to 350° C. and obtained a 90 per cent yield of aldehyde. At higher temperatures the aldehyde decomposed, and dehydration to ethylene also took place. Later Armstrong and Hilditch (17) reported a 35.7 per cent yield of aldehyde from alcohol in the presence of a nickel catalyst at 240° or 260° C. Earlier Ipatieff (12) pointed out that this property of reduced nickel, which promotes the formation of saturated hydrocarbons, makes this metal unsuitable for the decomposition of alcohol into aldehyde.

Ipatieff also showed the influence of the dispersion of the metal catalyst on the course of the decomposition of alcohol by the use of zinc dust. His data indicated that about one-half of the alcohol decomposed into ethylene and water, and the other one-half into aldehyde and hydrogen. In earlier experiments, Jahn (18) decomposed alcohol, using zinc

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14. Sabatier and Senderens, Comp. rend., 136, 983-986 (1903).
 15. Sabatier and Senderens, Ann. chim. phys., (8) 4, 391-488 (1905).
 16. Bouveault, Bull. soc. chim., (4) 3, 119-124 (1908).
 17. Armstrong and Hilditch, Proc. Roy. Soc., 97A, 259-264 (1920).
 18. Jahn, Ber. 13, 983-990 (1880).

dust as a catalyst at temperatures from 300° to 350° C., obtaining chiefly ethylene and water. In another experiment using a temperature of about 600° C., he obtained, in addition to these products, considerable quantities of aldehyde and hydrogen.

Ipatieff (10) showed also that the zinc alloy with copper, namely brass (33 per cent zinc and 67 per cent copper), decomposed alcohol near temperatures of 600° C. Carbon deposits were slight, being less than one per cent.

Ipatieff (10, 12) conducted a series of experiments on the decomposition of alcohol in the presence of metallic oxides, showing particularly that oxides take part in the catalytic decomposition of alcohol. Experimentally, he showed that practically no decomposition occurred when he passed alcohol over molten tin heated to from 660° to 700° C. However, when he placed tin oxides in the tube, an energetic decomposition took place at 650° to 660° C. He carried out the same experiment with copper and copper oxide, and found that red copper was not a catalyst for the decomposition of alcohol. Sabatier and Senderens (15, 19) showed that copper oxide reduced by the dehydrogenation of alcohols into finely dispersed copper containing copper oxide was a catalyst.

From the results of his experiments on the decomposition of alcohol in the presence of metals and metallic oxides, Ipatieff (12) drew the following conclusions:

19. Sabatier and Senderens, Comp. rend., 136, 738-741 (1903).

1. If a metal is a catalyst in the aldehydic decomposition of alcohol, its oxide usually possesses the same properties although it is not capable of being reduced to finely divided metal; for example, zinc and zinc oxide are both excellent catalysts.

2. The catalytic activity of the metal and its oxide seems to be related to the position of the element in the periodic system of elements. The metals arranged according to their increasing ability to form the aldehydic decomposition of alcohol are as follows: chromium, manganese, iron, cobalt, nickel, copper, and zinc, the order of which is the same as their increasing atomic numbers. In this series chromium causes only slight decomposition at high temperatures, manganese and iron are good catalysts, cobalt and nickel are very reactive, and reduced copper and metallic zinc are the best catalysts for the decomposition of alcohol.

3. The ability of the metals to decompose the catalytically formed aldehyde into saturated hydrocarbons and carbon monoxide increases in the series of catalysts--manganese, iron, cobalt, and nickel. The reduced copper and zinc causes no decomposition.

4. Metals and metallic oxides of high molecular weight induced the two types of alcoholic decomposition, dehydrogenation and dehydration. However, dehydrogenation was not observed with tungsten and uranium oxides.

Armstrong and Hilditch (17), studying the decomposition of ethyl alcohol in the presence of copper, obtained a yield

of from 90 to 95 per cent acetaldehyde at 300° C. They found that the presence of water improved the yield of acetaldehyde; that as the temperature was raised the yield of aldehyde was considerably lessened, although the amount of alcohol decomposed and the volume of hydrogen produced were much increased; that at higher temperatures the yield of aldehyde was improved by the use of alcohol containing a larger proportion of water; that when anhydrous alcohol was used, the yield of aldehyde even at 300° C. was considerably decreased. Small quantities of n-butyric aldehyde, crotonic aldehyde, and ethyl acetate were also obtained in all their experiments.

Again attention must be called to the differences in the catalytic activity of one and the same metal under different conditions of physical aggregation. Thus, for example, electrolytic copper is not effective as a catalyst in the dehydrogenation of alcohol, whereas copper prepared in other ways may be extremely active (20, 21, 22, 23, 24). Sabatier and Senderens (25, 26) reported that finely divided copper was preeminent among the metals in its ability to facilitate the formation of aldehyde from alcohol; but Ipatieff reported

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20. Constable, Proc. Roy. Soc., 110A, 283-301 (1926).
 21. Palmer, Proc. Roy. Soc., 98A, 13-26 (1920); 99, 412-425 (1921).
 22. Gauger, J. Am. Chem. Soc., 47, 2279-2282 (1925).
 23. Adkins, J. Am. Chem. Soc., 44, 2175-2186 (1922).
 24. Legg and Adam, British Patent 166,249, Sept. 3, 1919. C. A. 16, 801 (1922).
 25. Sabatier and Senderens, Ann. chim. phys., (8) 4, 319-432, 433-488 (1905).
 26. Sabatier, Ber., 44, 1984-2001 (1911).

the activity of reduced copper weakened greatly with use, and that it was never possible to obtain as large a yield of aldehyde with copper as with zinc. In his experiment, freshly reduced copper decomposed alcohol into hydrogen and aldehyde between the temperatures of 420° and 450° C. The activity, however, decreased, and an increase in temperature was required up to 530° or 570° C.

Milligan and Reid (27) used the oxides of cerium for the dehydrogenation of ethyl alcohol, the dioxide being more active than the trioxide, but less stable. Large amounts of carbon dioxide were also formed. The addition of small amounts of manganese oxide to ceria increased its activity, according to Anisimov (28).

Sabatier and Mailhe (1) found that magnesia, prepared by heating magnesium hydroxide below 400° C., exercised very little catalytic action on primary alcohols. A small amount of gas, which was almost pure hydrogen, was obtained when ethyl alcohol was passed over magnesia at 380° C.

It has been stated that when ethanol is passed over magnesium oxide supported on wood charcoal at a temperature of 420° to 430° C., butanol, ethyl acetate, and acetaldehyde are obtained. When manganese carbonate or zinc oxide is used on wood charcoal at a temperature of 450° C., butanol and aldehyde are obtained. An activated magnesium oxide catalyst

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27. Milligan and Reid, J. Am. Chem., 44, 202-205 (1922).
28. Anisimov, J. Gen. Chem., (U.S.S.R.), 7, 1931 (1937),
C. A. 32, 33 (1938).

can be prepared when precipitated magnesium hydroxide is heated at 400° C. (29, 30).

Müller (31) decomposed alcohol in a novel way. An electric arc from iron and carbon electrodes was played under the surface of 1.1 liters of alcohol in a copper vessel attached to a copper reflux condenser, for five hours. The products of the reaction were:

1. Forty-eight cc. of condensate, boiling point above 12° to 15° C., containing 44 cc. alcohol and four cc. of acetaldehyde.

2. Sixty cc. of condensate, collected at -40° to -30° C., which in addition to alcohol contained eight cc. of acetaldehyde and 2.5 cc. of acetylenes. From the latter was isolated about 0.5 to 1.0 gram butadiyne, $\text{HC}\equiv\text{CC}\equiv\text{CH}$, to every liter of alcohol decomposed. It polymerized above 0° C.

3. One thousand two hundred liters of gas from which the 108 cc. of the condensate in 1 and 2 were taken. The remaining gas analyzed as follows: 46.2 to 49.9 per cent hydrogen, 20.4 to 23.8 per cent carbon monoxide, 6.8 to 20.4 per cent paraffins, 6.0 to 9.6 per cent ethylene, and 7.0 to 9.9 per cent acetylene.

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29. Consortium für Elektroch. Ind., French Pat. 648,169 (1927).
Marek and Hahn, "Catalytic Oxidation of Organic Compounds in the Vapor Phase." The Chemical Catalog Co., New York, p. 57. 1932.
30. Marine Chemicals Co., Ltd., French Patent 812,575, May 12, 1937. C. A. 32, 1059 (1938).
31. Müller, Helv. Chim. Acta, 8, 821-825 (1925).

To summarize briefly, during the pyrogenetic decomposition of alcohol under the influence of catalytic agents, chiefly aldehyde and hydrogen were formed. In addition to this reaction, there was considerable decomposition of the alcohol into ethylene and water; especially was this noticeable in glass and platinum tubes. As noted previously, in experiments conducted by Ipatieff (10) and Jahn (18), the decomposition of alcohol in the presence of zinc dust at 550° C. proceeded equally well in the two directions. In some of his experiments to determine whether iron or carbon was the actual catalyst in the aldehyde decomposition of alcohol at 600° C., Ipatieff used a graphite tube containing a necessary binder (kaolin). Beyond all expectations, an entirely different reaction seemed to take place. The exit gas on bubbling through bromine yielded pure ethylene bromide. The liquid remaining in the receiver consisted only of water, undecomposed alcohol, and a slight trace of aldehyde; from these results he concluded that there was a new catalyst in the graphite mass which produced a specific decomposition of alcohol into olefin and water. A study of the component parts of the graphite tube led Ipatieff (32) to the opinion that it was alumina. Earlier observations by four Dutch chemists, Deimann, van Troostwyk, Lauwerenburg, and Bondt (3) indicated this possibility, but they gave no indication of the temperature required, the yield of ethylene, or the

32. Ipatieff, Ber., 35, 1057-1064 (1902).

manner of experimentation. In his experiments, Ipatieff found that pure graphite free from iron did not catalyze the decomposition of alcohol into ethylene and water at 600° C. To determine further the question as to which of the ingredients of the graphite was the catalyst in the olefin decomposition of alcohol, silicic acid and alumina were also studied at high temperatures. In the experiments carried out with powdered silica heated to 650° C., from 150 grams of alcohol used, slightly more than 140 grams remained undecomposed; but when alumina was used instead of silica the alcohol was readily decomposed into olefin and water. A quantitative decomposition into these substances was obtained by regulating the rate of flow of the alcohol into the catalyst tube, and the temperature of the alumina catalyst. In more detail, these experiments concerning the decomposition of alcohol were carried out as follows: several blank experiments were run in which alcohol was passed through glass and copper tubes under the same conditions as were to be used in the decomposition of alcohol in the presence of alumina. When 100 grams of ethyl alcohol were passed through a glass tube at a temperature of 610° to 630° C. for 70 minutes, the air being first displaced by nitrogen, 10 grams of alcohol decomposed. With alumina in a copper tube, ethyl alcohol began to decompose into ethylene and water at 360° C., the optimum temperature being from 420° to 450° C. That no decomposition into aldehyde and hydrogen took place was proved

by a special experiment in which the original air present was swept out by carbon dioxide; 100 grams of ethyl alcohol were passed in one hour over 12 grams of alumina heated to a temperature of 380° C. The gas obtained was 97.7 per cent ethylene, determined as ethylene bromide. About one gram of divinyl tetrabromide was also formed. The liquid which collected in the receiver during the reaction consisted of water and unchanged alcohol free from even a trace of aldehyde. This experiment seemed to indicate that the alumina under the conditions of the experiment promoted only the ethylene decomposition of ethyl alcohol, and only when air was present in the apparatus was acetaldehyde formed. In experiments conducted at ordinary pressure with alumina in either the iron or copper tube, Ipatieff (33) noted that ethyl ether was formed in significant amounts only at the lower temperatures of decomposition. Sabatier and Mailhe (1) substantiated these findings. Furthermore, Ipatieff showed that at lower pressures an iron tube with alumina promoted pure ethylene decomposition up to temperatures of about 450° to 460° C., but above these temperatures iron began to function catalytically, promoting aldehyde decomposition, and at a temperature of about 520° C. the ethylene and aldehyde decompositions were about equal in rate.

Ipatieff (33) observed that not every sample of alumina was a good catalyst for the dehydration of alcohol, some

33. Ipatieff, Ber., 37, 2986-3005 (1904).

samples requiring a temperature of 360° to 400° C., others a temperature of 500° to 550° C. Some samples yielded a product containing only from 50 to 60 per cent olefin, the remaining being carbon monoxide, hydrogen, and methane. Experiments led Ipatieff to conclude that the requirement necessary for catalytic activity was that alumina must contain a minimum amount of water of hydration, corresponding somewhat to the formula $AlOOH$. And thus, when alumina is prepared for catalytic work by precipitation and drying, it should not be heated too strongly, that is, not above 400° C. The properly prepared product dissolves easily in hydrochloric or sulphuric acid, and also in concentrated sodium hydroxide solutions.

Senderens (34) found that precipitated silica or moderately calcined alumina dehydrated alcohol, giving pure ethylene. If the calcination of alumina is strong and long continued, the catalytic power is less active and tends to change in character, so that it dehydrogenates only part of the alcohol.

Alexander, Horn and Munro (35, 36), investigating the catalytic dehydration of ethyl alcohol by alumina, found that the water content of the catalyst affected not only its activity but also the course of the reaction. For the particular aluminum oxide used, there was one optimum water

34. Senderens, Bull. soc. chim., (4), 3, 197-202 (1908).

35. Alexander, Horn and Munro, Can. J. Research, 15, 438-446 (1937).

36. Munro and Horn, Can. J. Research, 12, 707-710 (1935).

content for the production of ethylene.

Ipatieff (2, 33) showed that, when ethyl alcohol was passed through a copper tube containing alumina which had been strongly ignited, the decomposition temperature of the alcohol was higher, and the ethylene produced was not pure, being contaminated with carbon monoxide, methane, and hydrogen. The exit gas, when passed through bromine at 0° C., formed ethylene bromide, and a certain amount of a high boiling product which proved to be butadiene tetrabromide. Ipatieff carefully investigated this formation of butadiene from ethyl alcohol and was led to the discovery of a new pyrolytic reaction of ethanol. When ethyl alcohol was passed over powdered aluminum at 600° C., a special sort of decomposition took place; besides acetaldehyde and ethylene, there was a considerable amount of diolefin, butadiene, formed. Contact time and temperature played an important part in this reaction as regards the yield of butadiene. Lebedev (37) later patented a method for the production of butadiene by heating alcohols at 400° C. in the presence of a dehydrating catalyst and a dehydrogenating catalyst, such as zinc oxide and aluminum oxide.

Pease and Yung (38) obtained appreciable quantities of diethyl ether as well as ethylene from ethyl alcohol in the presence of alumina at 275° and 300° C., the amount of alcohol

37. Lebedev, British Patent 331,482, Jan. 30, 1929. C. A. 25, 115 (1931).

38. Pease and Yung, J. Am. Chem. Soc., 46, 390-403 (1924).

decomposed attaining a maximum corresponding to about 65 per cent conversion. The maximum yield of ether obtained was 60 per cent at 250° C., while the alcohol was completely dehydrated to form ethylene at 350° C. The presence of water vapor and ethylene diminished somewhat the efficiency of the catalyst to dehydrate alcohol. Clark, Graham, and Winter (39), however, reported a yield of 81 per cent ether when alcohol was passed at the optimum rate of flow (15 to 20 cc. per hour) over alumina in a pyrex tube at 250° C. Alvarado (40), investigating the results of Pease and Yung, and those of Clark, Graham, and Winter, studied the catalytic dehydration of ethanol by alumina at 269°, 300°, and 354° C. He obtained a yield of 82.2 per cent ether at 269° C.; 73.5 per cent at 300° C.; and 55 per cent at 354° C.; and he thereby confirmed the higher value given by Clark, Graham, and Winter.

Alvarado concluded that dehydration of alcohol is at least a two-step process; first the production of ether, and second the dehydration of ether to ethylene. Data obtained by Kearby (41) in his studies on the dehydration of ethyl alcohol in the presence of different alumina catalysts confirm the hypothesis that ether is an intermediate product in

39. Clark, Graham, and Winter, J. Am. Chem. Soc., 47, 2748-2753 (1925).

40. Alvarado, J. Am. Chem. Soc., 50, 790-792 (1928).

41. Kearby, Chem. Age (London), 37, 427-428 (1937).

ethylene formation from alcohol. In contrast, Adkins and Perkins (42) concluded, from evidence obtained in their experiments on the dehydration of alcohols in the presence of alumina, that the formation of ethylene takes place directly from the alcohol and not by way of the ether, for although ethyl alcohol in contact with alumina gives the same rate of production of ethylene at 400° C. as ether, this is not true for butyl alcohol and its ether, nor do ethyl alcohol and ether undergo dehydration at equal rates if catalysts other than alumina are used.

Engelder (43), studying the effect of added water on the dehydration of alcohol, found that the presence of water in the alcohol was unfavorable to dehydration, and when present in large amounts induced dehydrogenation.

Coris (44) investigated the effect of temperature, rate of flow of the liquid over the catalyst, and the concentration of the alcohol on the decomposition of ethyl alcohol in the presence of alumina. At 420° to 450° C., 68.9 per cent alcohol was practically all decomposed, but with alcohol containing more than 50 per cent water unsatisfactory results were obtained.

Bliss and Dodge (45) studied the dehydration of alcohol

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42. Adkins and Perkins, J. Am. Chem. Soc., 47, 1163-1167 (1925).
 43. Engelder, J. Phys. Chem., 21, 676-704 (1917).
 44. Coris, Chimie et Industrie, 11, 449-452 (1924).
 45. Bliss and Dodge, Ind. Eng. Chem., 29, 19-25 (1937).

and the hydration of ethylene, using alumina, alumina mixed with tungstic acid, sulfuric acid, phosphoric acid, potassium hydroxide, aluminum borate, and aluminum sulfate. They found that all the catalysts, if not given special activation treatment continuously, diminished in activity. The addition of two per cent of tungstic oxide or phosphoric acid to alumina increased its initial activity.

Senderens (46) carried out a series of investigations on the catalytic activity of alumina and aluminum salts in the ethylene and water decomposition of alcohol. Such catalysts as aluminum phosphate, aluminum silicate, and anhydrous aluminum sulfate all gave practically pure ethylene, but the speed of dehydration was different. Later he found that sodium bisulfite yielded olefins at lower temperatures than alumina or aluminum salts.

Jatkar and Watson (47) studied the effect of alumina, basic aluminum sulfate, aluminum sulfate, chrome alum, and potassium alum as catalysts for the preparation of ether from alcohol. They found that potassium alum was the most efficient catalyst. At 225° C., which was the optimum temperature, 75 per cent of the alcohol was converted into ether. They observed no appreciable decomposition of alcohol into ethylene at temperatures below 270° C. Mailhe and Godon (48)

46. Senderens, Ann. chim. phys., (8) 25, 449-529 (1912).

47. Jatkar and Watson, J. Soc. Chem. Ind., 45, 168-170 (1926).

48. Mailhe and Godon, Bull. soc. chim., 25, 565-568 (1919); 27, 121-126 (1920).

stated that alum gave pure ether at 175° C. with no formation of ethylene or aldehyde.

After Ipatieff's discovery of the catalytic properties of alumina, Sabatier and Mailhe (1, 49, 50) also carried out experiments on the decomposition of alcohol with other oxides. They found that thorium oxide and the blue oxide of tungsten were very good for this purpose, and concluded that thorium oxide was the best catalyst for the ethylene decomposition of alcohol, claiming that aluminum oxide soon lost its activity. However, Ipatieff (32) points to the industrial application of alumina for the preparation of ethylene, and Engelder (43) stated that alumina is a very rugged catalyst, and that, because of its cheapness, it is the best catalyst for commercial dehydration. Brown and Reid (51) studied the action of the blue oxide of tungsten, alumina, thorium, and silica gel in the dehydration of alcohols at 220° to 500° C. and found that alumina and the blue oxide of tungsten gave the largest yields of ethylene from ethyl alcohol.

Senderens (52, 53) carried out a series of experiments with such substances as silica, silicates, alumina, calcium sulfate, aluminum sulfate, phosphorus, and phosphates. He found that amorphous phosphorus decomposed alcohol at 215° to

49. Sabatier and Mailhe, Bull. soc. chim., (4) 1, 107, 341, 524 (1907).

50. Sabatier and Mailhe, Comp. rend., 150, 823-826 (1910).

51. Brown and Reid, J. Phys. Chem., 28, 1077-1081 (1924).

52. Senderens, Comp. rend., 144, 1109;1111 (1907).

53. Senderens, Bull. soc. chim., (4) 1, 687-696 (1907).

240° C., giving a gas containing 95 per cent ethylene, but that, because it is so variable and difficult to purify, it is not satisfactory for the production of ethylene. He found, however, that certain phosphates, especially aluminum phosphate, were excellent catalysts for the production of ethylene and that anhydrous calcium sulfate had very little catalytic power (54). The activity of these catalysts was diminished by the presence of such substances as sodium chloride, sodium carbonate, and sodium sulfate (54).

Ipatieff (55) claims that the initial temperature of the decomposition of alcohol with phosphorus is not below 250° C., the decomposition being more rapid at 330° to 360° C., but that it is in general slower at this temperature than alumina at 420° C. To raise the temperature of phosphorus above 360° C. is considered dangerous, and there is some distillation of yellow phosphorus at this temperature. Nef (56) observed the formation of olefins when alcohol was decomposed in the presence of phosphorous pentoxide. Balarew (57) has stated that the catalytic action of phosphorous pentoxide in the splitting off of water from ethyl alcohol and ether depends upon its capacity to unite with alkyl hydrates and oxides.

54. Senderens, Bull. soc. chim., (4) 3, 633-638 (1908).

55. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, p. 78. 1936.

56. Nef, Ann., 318, 1-57, 137-230 (1901).

57. Balarew, J. prakt. chem., 104, 368-377 (1922).

Brooks (58) reported that ethylene could be prepared in excellent yields by passing a mixture of alcohol and steam over kaolin at 400° to 500° C. Kaolin and active clay have also been used by other investigators to produce ether from alcohol; active clay gave a yield of 60.2 per cent ether (59).

Neff (56) earlier had shown that pumice, when used in the catalytic decomposition of ethyl alcohol, was a catalyst, decomposing the alcohol into olefins, aldehydes, and other substances. He obtained seven cc. of distillate when 30 cc. of absolute ethyl alcohol were passed over pumice at 590° to 640° C. for three hours. This distillate contained 4.75 cc. alcohol and 1.5 cc. water. Acetaldehyde and crotonaldehyde were recognized by their odor. There were formed 12.6 per cent ethylene and 29.4 liters of other gases with the following composition: 35.5 per cent hydrogen, 35.6 per cent methane, and 26.9 per cent carbon monoxide. The fact that nearly molar proportions of these three substances appeared indicated the almost complete secondary decomposition of acetaldehyde.

Gilfillan (60) investigated the activity of pumice alone and of various oxide catalysts supported on pumice for the dehydration of ethyl alcohol. Pumice alone exerted no appreciable action at 400° C. The method of preparation of the

58. Brooks, Chem. Met. Eng., 22, 629-633 (1920).

59. Hori, Oike, and Mukusima, J. Agr. Chem. Soc. Japan, 15, 483-495 (1939). C. A. 34, 4725 (1940).

60. Gilfillan, J. Am. Chem. Soc., 44, 1323-1333 (1922).

thoria catalyst determined to a great extent its activity. Thoria prepared by precipitation was found to be far more active than a similar catalyst produced by calcining the nitrate. A precipitated thoria catalyst began to dehydrate alcohol at about 300° C. The blue oxide of tungsten, prepared by heating the yellow oxide to 350° C. in alcohol vapor was more active than thoria at temperatures up to 320° C., but above this temperature the activity of the two catalysts became about equal. Titanium oxide was found to be relatively inactive even at 350° C. Under certain conditions thoria acted to a slight extent as a dehydrogenation catalyst, a fact also reported by Kramer and Reid (61). Gilfillan did not obtain ether with any of these catalysts. Baskerville (62) earlier had reported that no ether was formed from alcohol when a thoria catalyst was used even at temperatures as low as 250° C. Levi (63), working with thorium oxide catalysts prepared in seven different ways, reported that thorium oxide was an energetic catalyst for the formation of ethylene from ethyl alcohol, and that no appreciable difference was found in the catalytic action of the different catalysts.

Adkins and Lazier (64) found that the activity of catalysts varies greatly with the method of preparation. A zinc

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61. Kramer and Reid, J. Am. Chem. Soc., 43, 880-890 (1921).
62. Baskerville, J. Am. Chem. Soc., 35, 93-96 (1913).
63. Levi, Atti accad. Lincei, (5) 2, 419-422 (1925). C. A.
20, 1018 (1926).
64. Adkins and Lazier, J. Am. Chem. Soc., 46, 2291-2305
(1924); 47, 1719 (1925); 48, 1671-1677 (1926).

oxide catalyst may be so modified that it will give from four to six times as much dehydrogenation as dehydration of ethanol. They also found that in the presence of zinc oxide catalysts the proportion of dehydration to dehydrogenation was practically independent of the temperature when the temperature range was 340° to 440° C. Ordinary iron oxide gave a gaseous product with ethanol that contained from 20 to 25 per cent hydrocarbons at 400° C., but an oxide made from alkyl ferrites gave no more hydrocarbons than did copper. Two distinct types of nickel are produced by reduction with alcohol, and with hydrogen. These types have quite different powers in the dehydrogenation of alcohol, and in their ability to break the carbon to carbon linkages. The true catalyst is not a nickel oxide but metallic nickel. Adkins and Lazier stated that the spacing of the active points on a nickel catalyst is a matter of fundamental importance, as in the case of non-reducible oxide catalysts. One of the marked characteristics of all nickel catalysts is their pronounced ability to break the carbon to carbon linkages.

Taylor (65) has stated that the presence of sulfate ions will cause an increase in the dehydration ratio in the case of predominantly dehydrogenating catalysts, such as uranium oxide, molybdenum oxide, ferric oxide, and vanadium oxide, and that alkali ions will favor dehydrogenation. To investigate

65. Adkins and Millington, J. Am. Chem. Soc., 51, 2449-2460 (1929).

this, Adkins and Millington (65) studied the effect upon the ratio of dehydration to dehydrogenation of ethanol, of adding small amounts of various acidic and basic oxides to zinc oxide. They concluded that the direction of the shift in the ratio of two competing reactions is not dependent upon the acidity or basicity of the promoter, and that both the direction and amount of change in the ratio is specific for the alcohol and the catalyst.

In various reactions involving the decomposition of alcohol over catalysts, varying percentages of carbon dioxide were obtained, and invariably when carbon dioxide appeared in appreciable quantities in the gaseous products of the reaction, a brown, odorous, unsaturated oil, or resinous material, was also obtained. Numerous explanations have been advanced for the formation of the carbon dioxide and of the ethane which has also been obtained in certain cases. None of the proposed mechanisms, however, is free from objections. Adkins and Lazier (66) use the formation of ketene and the subsequent reaction of ketene with the other products of the reaction as an explanation for the formation of carbon dioxide.

To account for the presence of ethane in the ethanol decomposition, Engelder (43) supposes the simultaneous dehydration and dehydrogenation reactions followed by the hydrogenation of the ethylene formed over a suitable catalyst.

66. Lazier and Adkins, J. Phys. Chem., 30, 895-898 (1926).

Adkins (67) proposes another reaction to account for the ethane, in which the alcohol breaks down into aldehyde, ethane, and water. Boomer and Morris (68), in their work, favor Adkins' conception as the logical one, but do not attempt to explain the high percentages of carbon dioxide, the small amounts of brown oil, and the acid nature of the condensate, in their decomposition of ethanol over their copper-chromium catalyst supported by silica gel.

Catalytic Decomposition of Ethyl Alcohol
Under High Pressure.

From the beginning of his studies on the catalytic decomposition of alcohol at high temperature and ordinary pressures, Ipatieff (12) was also interested in studying the possibilities of these reactions in a closed system. Secondly, he was interested in determining whether these dehydrogenation catalysts could be used to catalyze the reverse reaction of hydrogenation. Coincidentally, as Ipatieff was discovering the dehydrogenation of alcohols, Sabatier and Senderens were discovering the catalytic hydrogenation of aromatic hydrocarbons, thus substantiating partially the existence of catalytic reversibility, the validity of which at that time was beclouded because of certain difficulties; for example,

67. Taylor, J. Phys. Chem., 30, 145-171 (1926).

68. Boomer and Morris, Can. J. Research, 2, 384-387 (1930).

the reduced nickel of Sabatier and Senderens had excellent properties for the hydrogenation of the aromatic nucleus but was shown by Ipatieff (9, 10) to be worse than iron as a dehydrogenation catalyst for producing aldehyde from alcohol. To account for this discrepancy and others, Ipatieff (33, 69) resorted to a series of experiments conducted under pressure, because pressure is one of the most influential of physical factors in many chemical processes, causing reactions to occur which in all probability would not occur at ordinary pressures, or if at all, would proceed very slowly. Furthermore, high pressures may slow up some reactions which might take place readily at ordinary pressures. Because of these factors, Ipatieff observed the influence of pressure on some catalytic reactions to determine whether the characteristic activity of a catalyst at atmospheric pressure was maintained completely or partially when the reaction caused by it occurred under higher pressure. The effect of pressure was not introduced sooner into the study of catalytic reactions because of the experimental difficulties involved; notable among these were the construction of an apparatus which could be heated to 600° C. or above while under several hundred atmospheres of pressure, the development of means of measuring continuously the pressure developed within the apparatus throughout the experiment, and a means of slowly discharging any gaseous products at the end of the experiment. These

69. Ipatieff, Ber. 37, 2961-2985 (1904).

difficulties were surmounted, and Ipatieff's first experiments were made with alcohol at temperatures above the critical temperature. Consequently, this substance was in the vapor state and would thereby seem to represent the dissociation of a gaseous body by the catalytic effect of a solid body.

In his experiments involving the decomposition of ethyl alcohol in an iron tube an energetic decomposition took place, the velocity of which depended upon the temperature. A comparison of the results with those obtained at atmospheric pressure indicates that in the transition from atmospheric to elevated pressure the decomposition is fundamentally the same, but under high pressure a higher temperature is required to bring about the aldehydic decomposition. Also, in a closed apparatus it was found that the decomposition of alcohol proceeds more complexly because of side reactions caused by the development of high pressures, the pressure opposing the complete decomposition of alcohol and probably increasing the limit of those side reactions which may or may not take place, or are not observed at low pressures.

In a series of experiments Ipatieff (69) found that the decomposition of alcohol under high pressure in an iron tube seemed to start about 450° C. and proceeded very slowly to certain limits. From the gas analysis there was evidence that besides this aldehydic decomposition there was also a decomposition of the acetaldehyde because of the formation of a large amount of hydrocarbons, chiefly methane.

This was quite different from the decomposition of ethyl alcohol at 450° C. under ordinary pressures, in which only a small quantity of methane was noticed. Comparative studies of the gases formed in these and other experiments led to the conclusion that with the increase in pressure the gaseous products became richer in saturated hydrocarbons and poorer in hydrogen, the percentage of carbon monoxide increasing up to a certain limit and then dropping off. This change in gas composition, dependent upon temperature and pressure, was partially explained by the aldehydic decomposition into a saturated hydrocarbon and carbon monoxide. However, other factors seemed to indicate that a reaction took place between the gaseous products under the influence of the catalyst.

Experiments conducted by Sabatier and Senderens (70) showed that carbon monoxide and carbon dioxide were easily reduced to methane by hydrogen under the catalytic action of nickel. Other metals probably bring this about at a lower temperature. Consequently, because of the composition of the gaseous products of the decomposition of alcohol in the presence of iron under high pressures, iron also seemed to be a catalyst for this reduction.

The liquid product obtained from the decomposition of alcohol in the presence of iron at the high temperatures and pressures studied usually consisted of two layers, the lower

70. Sabatier and Senderens, Comp. rend. 134, 514-516, 689-691 (1902).

layer being aldehyde, water, and undecomposed alcohol, and the upper layer a transparent oil with a boiling point range from 70° C. to above 250° C. Ipatieff (71) assumed this layer to be polymers of ethylene, and to test this assumption conducted a series of experiments with ethylene under the influence of iron at high temperatures and pressure and obtained a liquid with similar properties. In general, the amount of liquid product decreased, and the percentage of saturated hydrocarbons in the gaseous products increased as the temperature increased. At a temperature of 600° C. the upper layer entirely disappeared. For any given temperature the period of heating greatly influenced the results. In experiments carried out at a temperature of 540° C. and a pressure of 226 atmospheres in which the time of heating was 95 minutes, 25 grams of liquid products were obtained. This amount decreased approximately 50 per cent when the time of heating was 420 minutes.

The outstanding facts shown by the experiments conducted on the decomposition of alcohol under pressure in the presence of iron were the negligible formation of carbon and the high percentage of saturated hydrocarbons sometimes mixed with a considerable amount of carbon dioxide, in contradistinction to the observed results of carbon deposition on the walls of the iron tube above 520° C. when the experiments were conducted at atmospheric pressure. Because of the

71. Ref. 55, pp. 110-113.

absence of the formation of carbon in the decomposition of alcohol in an iron bomb under high pressure, Ipatieff indicated that the carbon which might separate during the reaction meets the hydrogen at the moment of liberation, forming methane under the influence of both pressure and catalyst.

In all the foregoing pressure experiments on the decomposition of ethyl alcohol in the presence of iron, the initial pressure in the apparatus was due to the vapor of the alcohol. In this closed system as the temperature increased, the increased pressure readings were due to the vapor of alcohol, until augmented by the pressure of the products of decomposition. The final value depended upon the temperature and the period of heating. Under these conditions in all probability other reactions besides the basic one could and did occur. To counteract any influence of this nature due to the pressure gradient, and to determine the effect of pressure on the basic catalytic action observed, Ipatieff conducted a series of experiments in which the initial pressure of the alcohol was augmented either by the products of decomposition or by an inert gas. In a number of experiments on the decomposition of alcohol using iron as a catalyst and the initial pressure being furnished by hydrogen, carbon dioxide, and nitrogen, Ipatieff drew the following conclusions: it was impossible to determine the effect of pressure on the catalytic decomposition of alcohol in the presence of iron in an atmosphere of hydrogen, for the experiments indicated

that hydrogen at a temperature above 450° C. in the presence of iron hydrogenates the products of decomposition, converting them into saturated hydrocarbons. This reduction becomes more complete the higher the temperature and the pressure. The introduction of carbon dioxide up to 50 atmospheres and nitrogen to 78 atmospheres does not influence the course of the catalytic decomposition of alcohol.

Subsequent experiments with reduced nickel as the catalyst with and without hydrogen in the high-pressure apparatus indicated that at 195° C. and under high pressure of hydrogen ethyl alcohol does not decompose, decomposition starting only when the temperature reaches 300° C. and proceeding slowly. The decomposition products are chiefly acetaldehyde and saturated hydrocarbons. The same experiments conducted in the absence of hydrogen at a temperature of 210° C. indicated that the same reaction occurs, with the exception that carbon monoxide is among the products. In neither case were olefin hydrocarbons produced. This fact is explained by the observation of Sabatier and Senderens (14) that nickel promotes the conversion of ethylene into ethane even at low temperatures. Iron and zinc do not promote this conversion to such a high degree. Consequently when alcohol is decomposed in their presence at high pressures small amounts of olefins are observed.

Although zinc oxide promotes the aldehydic decomposition of ethanol at temperatures from 300° to 400° C. and at

atmospheric pressure, Adkins and co-workers (72) reported that no aldehyde resulted when the reaction was conducted under sufficient hydrogen pressure. They obtained a complex mixture including esters of acetic, butyric, and caproic acids, and alcohols up to and higher than octyl. They used condensation reactions of acetaldehyde to account for the presence of these compounds, but no definite proof has been advanced to explain the mechanism of their formation.

In concerted efforts by Ipatieff (33, 69) on the decomposition of ethyl alcohol under high pressure in the presence of alumina, two tubes were used, copper and iron respectively. In each experiment approximately 38 grams of alcohol and from two to three grams of alumina were introduced into the tubes. The observed data in the case of the copper tube containing alumina showed that diethyl ether was the chief product when the heating period was short and the temperature was not above 490° C. With shorter periods of heating and a higher temperature both ether and ethylene were found in addition to water. Pressure increases diminished the decomposition into ethylene, forcing it in the direction of ether. If the temperature was above 500° C. together with long periods of heating, other products appear; the gaseous content became poorer in olefins and richer in saturated hydrocarbons. Again, as noted in the case of iron, page 43, the duration of heating played an important role in these

72. Adkins, Kinsey and Folkers, Ind. Eng. Chem., 22, 1046-1048 (1930).

experiments; for example, when ethyl alcohol was heated four hours at 530° C. the gas contained 12 per cent of ethylene, but when the heating period was one hour at the same temperature the gas was 78 per cent ethylene. Similar results were obtained at 560° to 570° C. In the experiments conducted above 520° C. there was always a small amount of carbonaceous residue, the quantity having increased with rise in temperature. Also, an additional product was observed in very small amounts, an unsaturated material similar to that found in the decomposition of alcohol in the presence of iron. At 620° C. the only products were carbon, water, and heavy condensation products. In these experiments a further important observation was made which seemed to indicate the formation of a condition of equilibrium between the alcohol and its decomposition products which formed at such temperatures, because on heating at 530° C. the pressure rose to a maximum and remained there. The ether formed was about 30 per cent of the theoretical amount. Other experiments conducted by Ipatieff emphasized the occurrence of an equilibrium between alcohol, aldehyde, and hydrogen at certain temperatures and pressures in the reactions catalyzed by iron, iron oxide, nickel oxide, and other substances.

When the iron tube containing alumina was substituted for the copper tube and the experiments continued under high pressure, diethyl ether and water were the sole products of the decomposition at a temperature of 400° C.

Using an activated copper catalyst, containing small percentages of magnesium and manganese oxides, Tischchenko (73) reported that under atmospheric pressure and at a temperature of 350° C., of the 50 per cent of alcohol decomposed, 11 per cent was converted to the ester and the rest to aldehyde. Under a pressure of 270 atmospheres at the same temperature, of the 50 per cent of alcohol decomposed, about 50 per cent went to ethyl acetate, 25 per cent to normal butyl alcohol, and the remainder formed acetic acid and acetaldehyde, the products having been separated by a distillation process. Other metals such as copper, iron, nickel, cobalt, either alone or mixed with oxides of other metals such as chromium, manganese, magnesium, and calcium, were catalysts for the reaction.

Frolich and Cryder (74) reported that a catalyst mixture suitable for methanol synthesis, which was composed of chromium and zinc oxides admixed with barium hydroxide or potassium oxide promoted the dehydration of ethanol to butanol in a high pressure process.

73. Tischchenko, Chem. Zentr., 1900I, 525 (1900).

74. Frolich and Cryder, Ind. Eng. Chem., 22, 1051-1057 (1930).

EXPERIMENTAL

Apparatus

The apparatus used in the decomposition of ethyl alcohol at atmospheric pressure is illustrated in Figure II. The alcohol passed from the constant flow burette A at definite rates through the mercury seal into the arm of the catalyst tube D (inside diameter 26 mm.; length 37 cm.). Upon entering the catalyst tube, the alcohol came into contact with the catalyst, which was confined in a space of 15 cm. in height, passed downward through the catalyst into the water-cooled condenser E, then to receiver F. The contact mass was supported on a small amount of pyrex glass wool, which in turn was supported by internal prong-like indentures made in the tube. At the top of the catalyst tube the alcohol vapor had a tendency to escape through the ground glass joint, which held the pyrex tube B, used for the thermo-couple wires. Counteracting the tendency of the alcohol to evaporate is a jacket, sealed to the upper end of the catalyst tube in which water circulated freely. The receiver F was maintained at a low temperature by means of ice. By the introduction of nitrogen through the three-way stopcock at the right of receiver F, the contents of the receiver were removed, when desired, through the side arm reaching to the bottom of the

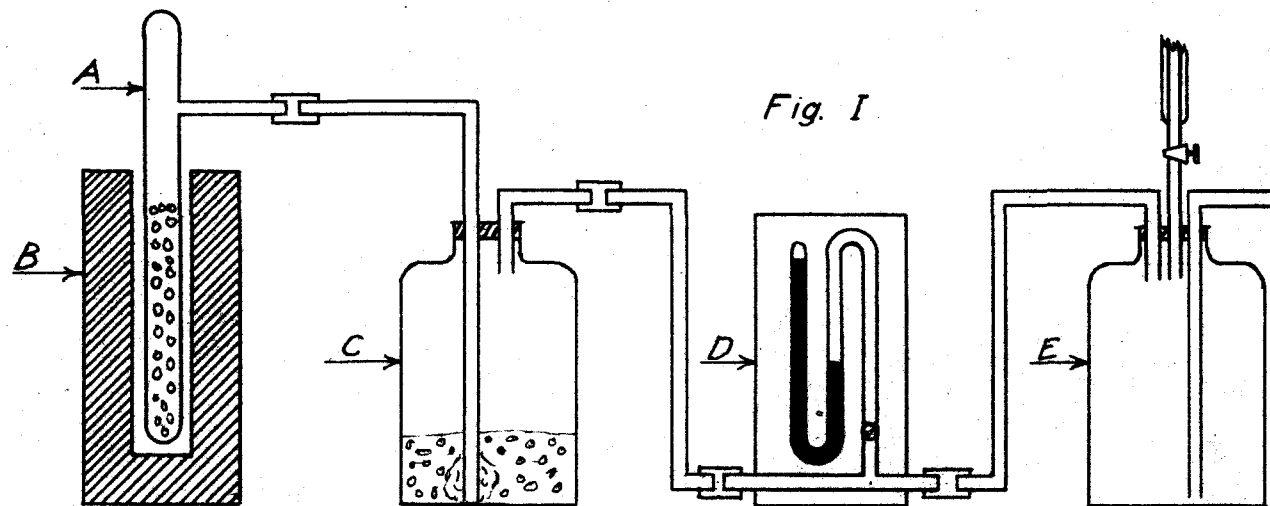
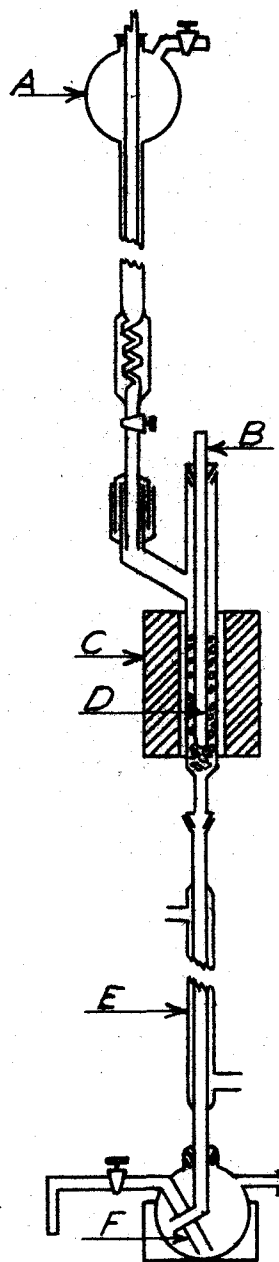


Fig. I

Fig. I. Apparatus for dehydrating the magnesium oxide.

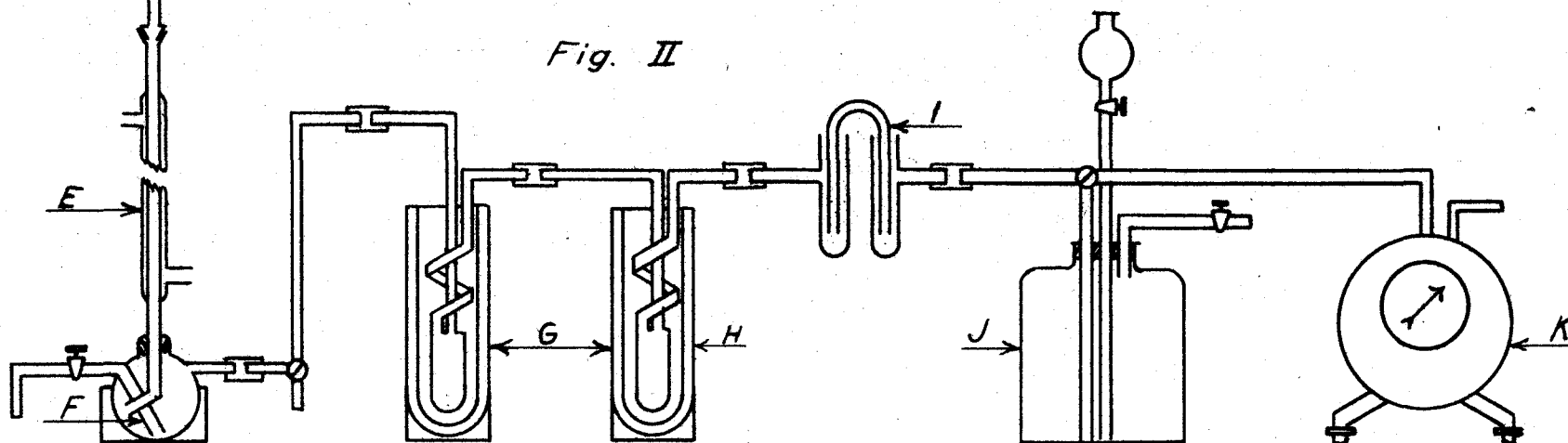


Fig. II

Fig. II. Apparatus for the decomposition of ethyl alcohol at atmospheric pressure.

receiver. The gaseous products formed during the decomposition passed from receiver F by means of glass tubing to the two spiral condensers G, placed in thermos bottles. The first spiral condenser was cooled with ice, the second condenser H, with a mixture of dry ice and acetone. The products not condensed passed through the bubbler I, then through the wet gas test meter K, and out to the atmosphere. Samples of the gas were collected intermittently during the run in the gas receiver J, which was filled with a saturated solution of sodium chloride. By the addition of the salt solution through the dropping funnel, samples for analysis were obtained by displacement of the gas in the receiver J. Flasks, tubing, catalyst chamber, condensers, and so forth, were made of pyrex glass, and the use of ground glass joints gave a certain degree of desirable mobility to the apparatus. The furnace C, mounted in a vertical manner similar to those used for combustion purposes, operated on either 110 or 220 volts. The furnace was so mounted that each half section could be swung horizontally, thus exposing the catalyst tube for inspection when desired. The temperature of the furnace was controlled through the use of a rheostat. The temperature of the catalyst was determined by the use of a thermo-couple and a Potentiometer-indicator. The chromel-alumel thermo-couple was inserted in the protective pyrex tube B, which reached to the center of the catalytic mass.

Preparation of Materials

Preparation of anhydrous ethyl alcohol

The alcohol used in all the experiments on the decomposition of ethyl alcohol was prepared by the addition of four grams of metallic sodium to 400 ml. of the absolute alcohol obtained from the stockroom. When the sodium had dissolved, the alcohol was distilled (75). The fraction distilling over between 77° and 78° C. was used immediately, either in the low- or in the high-pressure experiments.

Preparation of the magnesium oxide catalyst

Dilute ammonium hydroxide was added to a hot five per cent solution of magnesium nitrate ("Reagent" grade made by the General Chemical Company of New York) until precipitation was complete. The precipitate was washed with hot water three times by decantation, filtered on a Buchner funnel, and washed with hot water until the wash water no longer gave the brown ring test for the nitrate ion. The precipitate was dried over night in an electric oven at 110° C. The oven-dried material was then transferred to a pyrex glass tube A (Figure I), which was then sealed at the top and heated in

75. Marvel, "Organic Syntheses," Vol. IV, John Wiley and Sons, Inc., New York, p. 55. 1925.

the electric furnace B at a temperature of 350° to 360° C. for 24 hours. The system during the heating was under a vacuum of approximately 15 mm. There was a decrease in weight from 28.0 to 28.5 per cent during the heating operation. The dried catalyst was crushed slightly and screened; that which passed through a three mm. screen but was retained on a two mm. screen was used in all the experiments run at atmospheric pressure. The fine particles that passed through the two mm. screen, as well as the material retained on the two mm. screen, were used in the experiments run at high pressure. The pyrex glass which was used to determine the catalytic effect of glass was prepared by crushing and screening odd pieces of pyrex tubing. Those particles which passed through a three mm. screen but were retained on a two mm. screen were used as the catalytic material.

A spectrographic analysis of the magnesium oxide catalyst showed, besides magnesium, traces of silica and iron and faint traces of copper, nickel, potassium, and calcium.

Procedure for the Decomposition of Ethyl Alcohol
at Atmospheric Pressure

When ready for an experimental run, with alcohol in the constant flow burette, the catalyst in the catalyst tube, the ice in place for the condensation of vapors, and the heating units turned on, the apparatus was flushed out slowly with nitrogen for several minutes. As the temperature of the catalyst approached the temperature to be used in the experiment, alcohol, at the desired rate, was allowed to enter the catalyst tube, and passed downward through the catalytic mass. The passage of the alcohol through the catalyst was always accompanied by a drop in temperature. The temperature of the furnace was raised to compensate for this drop. After an equilibrium between the temperature and the rate of flow was established, the first 50 ml. which passed through the catalyst were removed. Before the gaseous products were collected in the gas receiver, time was allowed for the apparatus to be swept out by the gaseous products of decomposition. The intermittent collecting of gas from the main stream of flow gave a mixture that was representative of the run. Samples of this gas to be analyzed were withdrawn from the gas receiver and analyzed in a gas analysis apparatus (76); this gas was passed successively through

76. United States Steel Corporation, "Method of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Gases," 3rd ed., Carnegie Steel Co., Pittsburgh, Pa. 1927.

potassium hydroxide (360 grams per liter) to remove the carbon dioxide; through fuming sulfuric acid to remove unsaturated hydrocarbons; through alkaline pyrogallol (12 grams pyrogallol and 84 grams potassium hydroxide per liter) to absorb the oxygen; and lastly through an acid solution of cuprous chloride (75 grams cuprous chloride and 600 ml. hydrochloric acid per liter) to absorb the carbon monoxide. The gas was then passed through a tube containing cupric oxide, heated to a temperature of 290° to 300° C., to remove the hydrogen, and the saturated hydrocarbons in the residual gas were determined when the gas was passed at the rate of one ml. per minute into the combustion pipette which contained a measured amount of oxygen.

At the conclusion of some of the experiments, the liquid product collected in the first receiver was immediately fractionated, and the different fractions subjected to a qualitative analysis to determine their class; then appropriate derivatives were made. In other experiments the liquid product collected in the first receiver was mixed with an equal volume of water. The mixture separated into two layers. After separation by means of a separatory funnel, the upper layer was washed with water until the volume became constant, then dried over anhydrous calcium chloride and distilled. The oxygen-containing compounds extracted by the water were salted out with sodium carbonate, dried with anhydrous sodium carbonate, and distilled. The fractions resulting

from the distillation were subjected to a qualitative analysis, and derivatives made when possible. The contents from the spiral condensers were removed after each run and characterized.

Discussion of Results for the Decomposition of
Ethyl Alcohol at Atmospheric Pressure.

In reactions carried out under the influence of a catalyst the time of contact of the reacting material with the catalyst may influence the nature of the products or the temperature at which the products are formed. In these studies the temperatures were low and the contact period was long, as shown by the low rate at which the alcohol was allowed to enter the catalyst tube (Table I).

It is difficult to estimate the influence of the walls of the catalyst tube on the decomposition of alcohol. Consequently blank experiments were run to determine the effect of glass. The results are shown in Tables I and II. The liquid product obtained in the experiments 3-C-8 to 4-C-1 inclusive was predominately alcohol. For example, a fractional distillation of the liquid product from 3-C-8 (volume 695 ml., 542 grams) gave only one fraction, b.p. 77-80° C. (690 ml.). The distillation of the liquid product from experiment 4-C-8 (478 ml., 376 grams) gave the following fractions: (1) to 70° C., 5 ml.; (2) 70-77° C., 35 ml.; (3) 77-78° C., 430 ml. Fraction 1 contained acetaldehyde and alcohol. The liquid found in the ice trap was also acetaldehyde, characterized as the 2,4-dinitrophenylhydrazone (mixed m.p., 164° C.). The liquid product obtained in experiment 4-C-1 was not distilled, because in the

Table I

Catalytic Decomposition of Ethyl Alcohol at Atmospheric Pressure.

Expt. No.	Catalyst	Temp. ° C.	Rate ml. per hour	Alcohol		Liquid Products				Gas Produced	
				Vol. l.	Wt. g.	Receiver 1		Ice trap Vol. ml.	dry ice trap Vol. ml.	Vol. l.	Temp. ° C.
						Vol. l.	Wt. g.				
3-C-8	Pyrex glass	480	20	700	546	695	542	0	0	very little	
4-C-5	Pyrex glass	488	18	500	390	480	384	1.5	0	0.7	25
4-C-8	Pyrex glass	602	20	500	390	478	376	13.0	0	3.0	27
4-C-1	Pyrex glass	676	45	500	390					50.7	31
3-C-1	24 g. MgO	365	18	500	390	430	335	0	0	5.4	30
2-C-4	22 g. MgO	440	22	400	312	362	300	0	5	25.3	22
2-C-3	22 g. MgO	450	20	400	312	335	284	0	18	42.7	24
5-C-1	21 g. MgO	453	15	400	312	306	258	0	20	43.6	28
2-C-5	22 g. MgO	457	20	400	312	305	261	0	21		
5-C-2	23 g. MgO	455	20	400	312	340	287	0	20	43.2	25
5-C-3	23 g. MgO	455	18	400	312	325	278	0	20	45.7	23
5-C-4	same	448	21	400	312	360	304	0	17	32.4	23
5-C-5	same	446	18	400	312	335	287	0	10	33.3	25
5-C-6	same	453	23	400	312	360	298	0		24.4	25
6-C-1A	same	455	20	400	312	325	272	0		24.5	25
6-C-1B	same	448	20	400	312	345	289	0		29.4	23
6-C-2	same	445	26	400	312	370	310	0		28.1	23

Table II

Analysis of the Gas Produced by the Catalytic Decomposition of Ethyl Alcohol
at Atmospheric Pressure.

Expt. No.	CO ₂ (%)	C _n H _{2n} (%)	O ₂ (%)	CO (%)	H ₂ (%)	C _n H _{2n} + 2 (%)
4-C-3	0.2	13.2	0.1	15.3	52.7	Not determined.
4-C-1	0.4	15.8	0.3	16.2	42.2	
3-C-1	1.6	10.0	0.1	0.6	85.2	
2-C-4	1.4	15.2	0.0	1.6	77.0	
5-C-1	3.5	11.1	0.3	2.3	80.7	
5-C-2	2.8	11.1	0.3	2.0	81.5	
5-C-3	2.3	10.6	0.9	2.4	81.8	
5-C-4	1.6	10.6	0.1	1.1	84.2	
5-C-5	1.7	11.2	0.1	1.3	81.7	
5-C-6	2.0	10.4	0.1	1.6	83.1	
6-C-1A	2.0	11.3	0.3	0.7	81.4	
6-C-1B	1.6	11.2	0.3	1.3	81.2	
6-C-2	1.7	13.7	0.1	1.4	81.0	

experiments involving magnesium oxide as the catalyst the temperatures were decidedly below that used in this experiment.

In some of the experiments in which magnesium oxide was used, the liquid product obtained in receiver 1 was immediately fractionated. A representative idea of the fractions obtained may be drawn from experiment 5-C-2, in which the liquid product (340 ml., 287 g.) yielded the following fractions: (1) 30-56° C., 7 ml.; (2) 56-65° C., 7 ml.; (3) 65-72° C., 17 ml.; (4) 72-74° C., 7 ml.; (5) 74-77° C., 8 ml.; (6) 77-80° C., 187 ml.; (7) 80-90° C., 45 ml.; (8) 90-116° C., 27 ml.; (9) 116-118° C., 10 ml.; (10) 118-124° C., 2 ml.; (11) residue 22 ml. The identification of individual substances in these fractions was extremely difficult; however, the fractions were classified according to their solubility in the following solvents: water, ether, five per cent sodium hydroxide, five per cent hydrochloric acid, five per cent sodium bicarbonate, cold concentrated sulfuric acid, and 85 per cent phosphoric acid. They were further classified with the following reagents: Tollen's reagent, five per cent bromine in carbon tetrachloride, two per cent permanganate, and Fuchsin-aldehyde reagent.

The individual experiments showed that from 45 to 55 per cent of the original alcohol was decomposed. However, upon fractional distillation of the liquid product, little information could be obtained as to the composition of the different fractions, because of incomplete separation and the

small volume of some of the fractions. Therefore, more liquid product was prepared in as nearly an identical manner as possible and fractionated. The corresponding fractions were combined and refractionated. This second fractionation gave a better separation and made it possible to identify several compounds formed in the decomposition. The fractions with the largest volumes obtained from this second fractionation were collected at the following temperatures: (1) below 58° C., (2) 68-75° C., (3) 75-80° C., (4) 86-92° C., (5) 98-103° C., (6) 103-118° C., (7) greater than 118° C.

With the exception of fraction 3, which was principally alcohol, all the fractions were soluble in ether, very slightly soluble or insoluble in water, insoluble in sodium hydroxide, sodium bicarbonate, and hydrochloric acid. All the fractions were soluble and formed color in sulfuric acid (sp. gr. 1.84) and in phosphoric acid.

Fraction 1 decolorized bromine with slight evolution of hydrogen bromide. It also decolorized potassium permanganate and reacted positive toward Fuchsin-aldehyde reagent and Tollen's reagent. This fraction contained some alcohol and acetaldehyde, characterized as the 2,4-dinitrophenylhydrazone (mixed m.p. 163-164° C.).

Fraction 2 decolorized bromine with evidence of hydrogen bromide formation and also potassium permanganate solution. It reacted positive to Fuchsin-aldehyde reagent and Tollen's reagent. This fraction contained besides alcohol,

n-butyraldehyde, characterized as the 2,4-dinitrophenylhydrazone (mixed m.p. 122-123° C.).

Fraction 3, which was predominately alcohol, always contained traces of aldehyde.

Fraction 4 decolorized large amounts of bromine very rapidly with no evidence of hydrogen bromide formation and also a potassium permanganate solution. However, the fraction gave a slight test with Fuchsin-aldehyde reagent and Tollen's reagent.

Fraction 5 decolorized bromine with no evidence of hydrogen bromide, reacted with potassium permanganate, and gave a negative test with the aldehyde reagents. This fraction was found to contain some water along with methyl n-propyl ketone, characterized as the 2,4-dinitrophenylhydrazone (mixed m.p. 140-141° C.).

Fraction 6 decolorized potassium permanganate and bromine without the formation of hydrogen bromide, and reacted with metallic sodium. This fraction was found to contain n-butyl alcohol, characterized as the 3,5-dinitrobenzoate (mixed m.p. 64-65° C.).

Fraction 7 reacted with bromine and potassium permanganate. Large amounts of this fraction did not completely dissolve in sulfuric acid (sp. gr. 1.84).

In some experiments the liquid product obtained in receiver 1 was not immediately fractionally distilled; for example, in experiment 2-C-5 the entire content of receiver 1

(305 ml., 261 g.) was extracted with water. The top oil layer was washed several times with water, dried over anhydrous calcium chloride, and this material (22ml., 19 g.) fractionated. The following fractions were obtained: (1) 60-61° C., 4 ml.; (2) 92° C., 6 ml.; (3) greater than 92° C., 16 ml. (brown). This same procedure was followed in several other experiments, and the corresponding fractions mixed together. A classification of the fractions showed them all to be positive towards ether, sulfuric acid, phosphoric acid, bromine in carbon tetrachloride, and two per cent potassium permanganate. Fractions 1 and 2 were also positive towards Fuchsin-aldehyde reagent and ammoniacal silver nitrate.

Fraction 1 (b.p. 60-61° C.), besides containing acetaldehyde contained unsaturated hydrocarbons, as shown by the fact that it decolorized bromine in carbon tetrachloride without the formation of hydrogen bromide.

Fraction 2, was refluxed with a water suspension of silver oxide to remove the aldehyde, then filtered and distilled. The distillate (b.p. 98-103° C.) was salted out with sodium carbonate and found to contain methyl n-propyl ketone, characterized as the 2,4-dinitrophenylhydrazone (mixed m.p. 140-141° C.).

A small amount of fraction 3 (b.p. greater than 92° C.) reacted very readily with bromine in carbon tetrachloride without the formation of hydrogen bromide, and seemed to be completely soluble in sulfuric acid (sp. gr. 1.84), but a

larger amount upon treatment did not completely dissolve. Therefore, compounds other than unsaturated ones must have been present.

The portion extracted by water from the receiver 1, experiment 2-C-5, was saturated with sodium carbonate. The oxygen-containing compounds which separated out were dried over sodium carbonate and fractionated. From approximately 273 ml. of solution the following fractions were obtained: (1) up to 65° C., 5 ml.; (2) 65-69° C., 6 ml.; (3) 73-76° C., 10 ml.; (4) 77-79° C., 141 ml.; (5) 80-83° C., 9 ml.; (6) 86-90° C., 10 ml.; (7) 90-92° C., 53 ml.; (8) 94-100° C., 48 ml.; (9) greater than 100° C., 10 ml. The same procedure was followed in several other experiments, and the corresponding fractions mixed together and refractionated.

Fractions 1 and 2 were mixed together and refluxed with freshly prepared silver oxide to remove acetaldehyde, filtered, and then distilled. The distillate which came over between 50° and 60° C. contained acetone, characterized as the 2,4-dinitrophenylhydrazone (mixed m.p. 126-127° C.). The silver salt formed was analyzed for silver.

Anal. calcd. for silver acetate: Ag, 64.6. Found: Ag, 64.8.

Fraction 3 gave a positive test with the aldehyde reagents, reacted slightly with bromine, and decolorized potassium permanganate slowly. This fraction was refluxed with silver oxide to remove the aldehyde, filtered, and the

filtrate distilled. Acetone, as well as water and ethyl alcohol, was found to be present.

Fraction 4, predominately alcohol, contained traces of aldehyde.

Fraction 5, reacted readily with metallic sodium. To determine whether alcohol other than ethyl was present, the 3,5-dinitrobenzoate was prepared (mixed m.p. 91-92° C.). The result showed that ethyl alcohol was the only alcohol present.

Fractions 6 and 7 rapidly decolorized large amounts of bromine and potassium permanganate, and gave a slight reaction towards the aldehyde reagents.

Fraction 8, slightly yellow in color, was soluble in ether but insoluble in water, sodium hydroxide, sodium bicarbonate, and hydrochloric acid. It dissolved with a red coloration in sulfuric acid and phosphoric acid, and decolorized bromine and potassium permanganate very rapidly.

The material contained in the dry ice trap, approximately 20 ml., (experiment 2-C-5) was found to be soluble in ether, insoluble in water, sodium hydroxide, sodium bicarbonate, and hydrochloric acid; it reacted and formed color with sulfuric acid and phosphoric acid; it reacted readily with bromine and potassium permanganate solutions, and gave a positive test with the Fuchsin-aldehyde reagent. This material was found to contain some acetaldehyde, characterized as the 2,4-dinitrophenylhydrazone (mixed m.p. 163-164° C).

Because of the appearance of a white precipitate when bromine was added to the material, the entire content of the dry ice trap in similar experiments was treated with a solution of bromine in sodium bromide. During the addition the substances were kept at low temperatures. A white crystalline precipitate was formed, filtered, and recrystallized from alcohol (m.p. 115° C.). The percentage of bromine was determined by the Parr bomb method.

Anal. Calcd. for 1,2,3,4-tetrabromobutane: Br, 85.54.
Found: Br, 85.83.

From another sample of this material, the addition product of maleic anhydride was prepared (m.p. $103-104^{\circ}$ C.). Therefore this material was 1,3-butadiene.

In experiments 5-C-3 to 6-C-2 inclusive, Table I, the same catalyst was used under continuous operation until 2184 grams of alcohol had passed through. The experiment was discontinued when carbon began to be deposited in considerable quantities, because carbon acts as a dehydrating agent. The amount of liquid product in the dry ice trap totaled 100 ml.

Procedure for the Decomposition of

Ethyl Alcohol at High Pressure.

The apparatus used in these high pressure studies was the Parr Hydrogenation bomb, model B30, manufactured by the Parr Instrument Company, Moline, Illinois. In the investigation the bomb was used without a glass liner; hence the internal volume was approximately 480 ml., and the charging capacity 200 ml. The ethyl alcohol and contact agent used were prepared in exactly the same manner as those used in the low pressure study. In this work there were two series of experiments, the decomposition of alcohol with and without a contact agent. All the experiments were carried out in essentially the same manner. One hundred ml. of alcohol were introduced into the cylinder, which was made of 18-8 stainless steel. In the experiments in which the contact agent was used, the magnesium oxide was either intimately ground with the alcohol or added separately along the side of the cylinder. After the material was introduced, the head of the cylinder was carefully replaced, and the cylinder was tested for leaks by means of nitrogen. If no leaks developed, the cylinder was flushed once more with nitrogen, placed into the electrically heated furnace and brought to the desired temperature as rapidly as possible, then held there for a considerable length of time. At stated intervals during the heating period and after the temperature became constant,

pressure readings were taken. Then the apparatus was allowed to cool, usually over night. Before the liquid contents of the cylinder were removed, the pressure reading at room temperature was recorded, and the gas released and measured through a wet gas flow meter. At intervals during the metering several samples of gas for analysis were taken. It was noticed that the composition of the first samples in which the gas was under high pressure when collected was different from that of the last samples taken. Consequently the average percentage composition for that experiment was recorded. In later experiments, more representative samples were obtained by collecting the entire volume of gas in one container, through the displacement of a saturated sodium chloride solution, and then withdrawing samples from this container for the gas analysis. In others, a smaller gas collector was filled with a saturated sodium chloride solution and the gas allowed to enter it intermittently; then a sample was removed from this container for a representative gas analysis of the experiment.

In Tables III, IV, and V are given the results of these experiments, and in Graph I are a number of curves that show the course of decomposition. To obtain these curves the pressures developed during the period of heating were plotted as ordinates against time, in minutes, as abscissae. As noted, each table and curve represents the data of either one or the average of several experiments carried out under

as nearly identical conditions as possible; for example, 1-C-92 represents the average of four experiments performed at a temperature of 452° C., in the presence of five grams magnesium oxide, heated at the same rate and held at the same temperature for identical lengths of time. The gas analysis for 1-C-92 indicates the limits observed in these four experiments.

When all the gas had been completely expelled, the liquid contents were removed and filtered if necessary, dried with anhydrous sodium sulfate and subjected to a fractional distillation immediately, unless there was a separation into two layers. From these respective fractions, by means of qualitative analysis, some idea of the nature of the products was obtained. If two layers occurred, a separation was made by means of a separatory funnel; the upper brown layer was washed several times with water, dried with anhydrous sodium sulfate and subjected to a fractional distillation; the lower layer was fractionally distilled without previous treatment.

Discussion of Results for the Decomposition of
Ethyl Alcohol at High Pressure.

The characteristics of the decomposition of alcohol in a closed system are conveniently studied by the time-pressure plots first advocated by Ipatieff (69), and due consideration is paid to his interpretation. At the beginning of the experiment the pressure gauge indicates only the vapor pressure of alcohol at various temperatures. At the temperature at which the decomposition of alcohol begins the pressure gauge shows the sum of the vapor pressure of the remaining undecomposed alcohol plus the vapor pressure of the decomposition products. As the temperature increases, the decomposition products are responsible for a greater part of the total pressure. If the increase in the vapor pressure of alcohol, above critical temperature, follows the simple gas law and if no decomposition of the alcohol takes place, the increase in pressure is proportional to the temperature. Each pressure reading, therefore, corresponds to a definite temperature, irrespective of the time of heating. However, if decomposition occurs, this relationship between pressure and temperature no longer holds. Although an idea can be obtained as to the course of the decomposition by this relationship, it seems more advantageous to trace the course of the decomposition by means of a pressure-time plot, which not only delineates the course of the reaction but gives

some idea as to its rate. When a comparison is made between the increase in pressure that results when a catalyst is introduced into the reaction with that when the catalyst is omitted, some idea concerning the accelerating action of the catalyst can be obtained. The most characteristic value of the course of decomposition is not the average pressure increase per unit of time, but the maximum increase denoted by $(dp/dt)_{max}$, because it belongs to that period of decomposition which is affected least by side reactions.

In the decomposition of alcohol the curves that are obtained when the pressure is plotted against time consist of three branches: the first branch represents chiefly the vapor pressure of the ethyl alcohol; the second branch of the curve represents the pressure due to the decomposition of the alcohol (this is the most characteristic part of the curve, and its shape is different for different maximum temperatures, because the acceleration of the decomposition of the alcohol depends upon the catalyst and the temperature); the third branch of the curve begins where the curve becomes parallel to the abscissa, a fact which indicates that the maximum pressure reached in the decomposition of the alcohol and the establishment of equilibrium in the gaseous products of decomposition have been reached.

It is interesting to observe the results of a series of experiments represented by the data in Tables III and IV and in Graph I. When 100 ml. (78 grams) were heated in the high

Table III

Decomposition of Ethyl Alcohol Under Pressure.

1-C-80, curve 1			1-C-84, curve 2			1-C-92, curve 3		
Catalyst 5 g. MgO			Catalyst 5 g. MgO			Catalyst 5 g. MgO		
Time Min.	T. C.	P. lbs.	Time Min.	T. C.	P. lbs.	Time Min.	T. C.	P. lbs.
0	25	0	0	24	0	0	27	0
20	178	200	20	184	220	15	142	50
50	361	1460	50	365	1500	50	350	1400
80	479	2440	80	455	2240	80	404	1900
110	497	3200	110	474	2800	110	450	2440
130	497	3280	140	476	3200	140	453	3040
			170	474	3500	210	454	3500
			185	478	3620	290	455	3800
						330	455	3860
						400	455	4000

Table III (continued)

1-C-88, curve 4			1-C-79			1-C-68, curve 7		
Catalyst 5 g. MgO			Catalyst 5 g. MgO			Catalyst 5 g. MgO		
Time Min.	T. C.	P. lbs.	Time Min.	T. C.	P. lbs.	Time Min.	T. C.	P. lbs.
0	24	0	0	24	0	0	26	0
20	154	50	50	392	2000	15	184	200
30	220	400	70	392	2080	45	310	1160
60	358	1500	175	392	2100	75	344	1460
90	438	2100	275	396	2120	120	356	1520
150	444	2550	375	396	2140	210	356	1520
210	446	2800	605	396	2160	300	356	1520
260	446	2980	680	396	2190	405	356	1520
365	446	3240	725	396	2190			
395	446	3320						
520	446	3480						
590	446	3560						
620	444	3590						

Table III (continued)

1-C-69, curve 8			1-C-76, curve 5			1-C-77, curve 6		
Catalyst 10 g. MgO			Catalyst none			Catalyst none		
Time Min.	T. C.	P. lbs.	Time Min.	T. C.	P. lbs.	Time Min.	T. C.	P. lbs.
0	30	0	0	29	0	0	28	0
15	216	360	70	374	1640	60	332	1320
45	296	1040	170	395	1840	90	368	1580
75	338	1380	345	392	1920	135	392	1740
130	348	1440	480	392	2000	200	394	1800
190	348	1440	610	392	2040	285	394	1820
250	358	1440	730	395	2080	360	394	1840
325	361	1440				450	394	1860
515	361	1440				510	394	1880
						660	394	1940
						765	394	1960
						855	394	2000

Table IV
Catalytic Decomposition of 78 grams Ethyl Alcohol Under High Pressure.

Expt. No.	Curve No.	Time Min.	Temp. Max. C.	Catalyst	Pressure		Liquid recovered		Gas produced liters	temp. C.
					Max. lbs.	Final after cooling lbs.	ml.	g.		
1-C-76	5	730	395	none	2080	150	90		5.35	24
1-C-77	6	855	394	none	2000	80	92		4.20	25
1-C-68	7	405	356	10 g. MgO	1520		93		3.00	28
1-C-69	8	515	361	10 g. MgO	1440		91		3.80	28
1-C-79		725	396	5 g. MgO	2190	300	72	51.9	10.55	27
1-C-88	4	620	446	5 g. MgO	3590	690	51	36.9	22.07	24
1-C-92	3	400	455	5 g. MgO	4000	790	53	38.5	28.39	22
1-C-84	2	185	478	5 g. MgO	3620	620	57	41.5	21.85	25
1-C-80	1	150	497	5 g. MgO	3280	520	65	47.5	17.83	24

Table V.

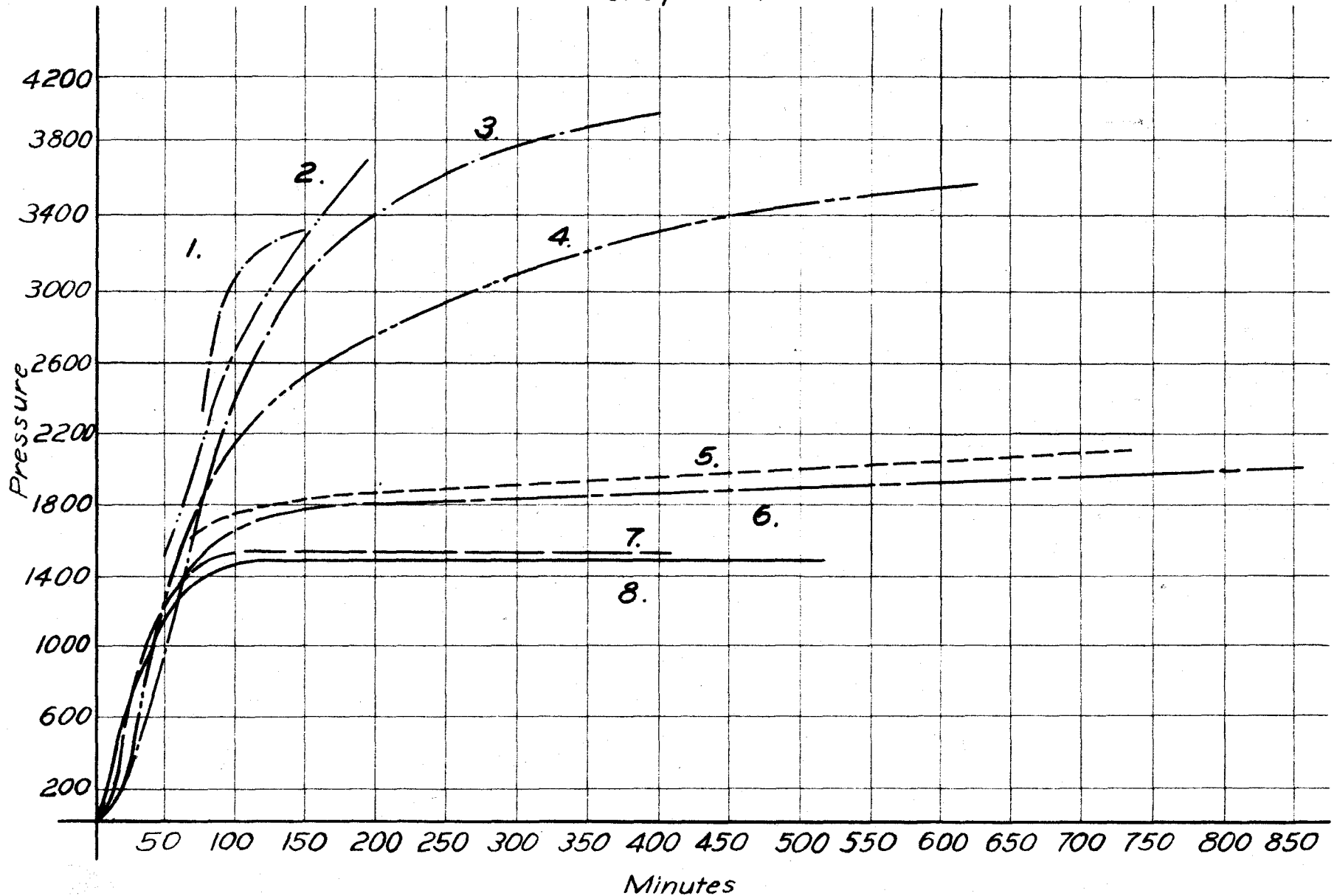
Analysis of the Gas Produced by the Catalytic Decomposition of Ethyl Alcohol Under High Pressure.

Expt. No.	CO ₂ (%)	C _n H _{2n} (%)	O ₂ (%)	CO (%)
1-C-76	2.2	20.3	0.1	7.2
1-C-77	2.2	22.2	0.1	5.0
1-C-68	1.5	16.5	0.1	1.3
1-C-69	1.5	17.5	0.1	1.5
1-C-79	7.4-8.0	6.1-6.5	0.0-0.0	5.6-7.1
1-C-88	12.5-13.4	2.9-3.2	0.0-1.0	4.0-4.3
1-C-92	12.7-13.3	2.8-2.9	0.1-0.4	4.6-4.7
1-C-84	6.8- 7.3	3.0-4.1	0.2-0.3	8.1-8.9
1-C-80	4.8- 6.0	3.8-5.6	0.1-1.0	9.9-11.0

Table V (continued)

Expt. No.	H ₂ (%)	C _n H _{2n} + 2 (%)	CH ₄ (%)	C ₂ H ₄ (%)
1-C-76	28.8	29.1	2.1	27.0
1-C-77	27.3	27.0	2.7	24.2
1-C-68	45.4	28.2		
1-C-69	47.5	27.6		
1-C-79	53.9-54.1	16.9-17.2	3.0-2.1	13.9-15.1
1-C-88	39.9-40.8	31.5-31.1	2.7-2.8	28.4-28.6
1-C-92	37.5-38.3	35.0-36.9	4.7-6.4	30.3-30.5
1-C-84	41.6-46.2	27.3-31.8		
1-C-80	41.8-45.8	24.5-29.3		

Graph No. 1



Graph No. I. Time-pressure curves for the decomposition of ethyl alcohol.

pressure apparatus to different temperatures, first with and then without a catalyst, curves 5 and 6, Graph I, and experiments 1-C-76 and 1-C-77, Tables III, IV, and V, show that a slight decomposition of alcohol occurs at 394° C. because of the catalytic action of the walls of the container. A fractional distillation of the combined recovered liquids (182 ml.) gave the following fractions: (1) 25-74° C., 1.0 ml.; (2) 74-77° C., 9.5 ml.; (3) 77-80° C., 150 ml.; (4) 80-83° C., 11.5 ml. Fractions 1 and 2 contained considerable amounts of acetaldehyde, characterized as the 2,4-dinitrophenylhydrazone (mixed m.p. 164-165° C.). Fraction 2 was refluxed with freshly prepared silver oxide to remove the acetaldehyde, and after filtering was distilled, the distillate being principally alcohol. The silver salt was analyzed for silver.

Anal. Calcd. for silver acetate: Ag, 64.6. Found:
Ag, 64.3.

Fraction 4 contained small amounts of ethyl methyl ketone, characterized as the 2,4-dinitrophenylhydrazone (mixed m.p. 115-116° C.).

However, if the results of these experiments are compared to the average of two other experiments (designated by 1-C-79, Tables III, IV, and V) carried out at approximately the same temperature, it is noticed that under the influence of magnesium oxide a more energetic decomposition occurs, as evidenced by the larger volume of gas. Furthermore, from the gas analysis one observes an outright tendency of the

magnesium oxide to decrease the percentage of the ordinary gaseous unsaturated hydrocarbons, but this decrease in unsaturated hydrocarbons does not necessarily mean that magnesium oxide favors dehydrogenation with aldehyde formation, because in all the experiments conducted above this temperature there was formed a noticeable amount of an unsaturated, yellowish, oily material which separated out on the surface of the liquid and was insoluble in water. Later experiments showed that this material was probably a mixture of saturated and unsaturated hydrocarbons.

Curves 7 and 8, Graph I, and experiments 1-C-68 and 1-C-69, in which a larger amount of magnesium oxide was used, show the slight decomposition below 396° C., the large volume of liquid recovered being principally alcohol with traces of acetaldehyde. Three ml. of liquid (b.p. up to 77° C.) were obtained, and upon characterization with ammoniacal silver nitrate and 2,4-dinitrophenylhydrazine proved to be acetaldehyde.

Experiment 1-C-80, Tables III, IV, and V, and curve 1, Graph I, represent the average data of four experiments used for the purpose of determining the character of the gaseous products before the maximum pressure had been reached. In all cases the catalyst became slightly gray in color and increased approximately one gram in weight. The other experiments, 1-C-84, 1-C-88, 1-C-92, Tables III, IV, and V, and curves 2, 3, and 4 in Graph I, represent the average data

of four experiments conducted at different temperatures to indicate the course of decomposition. As shown by the data presented in Table IV, the quantity of liquid products obtained depended upon the temperature of the decomposition. In some experiments there was a separation into two layers (a brown upper layer and a colorless lower layer); in other experiments, particularly those conducted at lower temperatures, a single brown-colored liquid was obtained. This liquid, however, on being treated with water separated into two layers, an insoluble brown layer, and a colorless layer, which upon salting out with sodium sulfate separated into two layers. The upper layer was distilled. In the other experiments where the decomposition was slight, only a colorless liquid remained in the container.

In the four experiments represented by 1-C-88, Tables III, IV, and V, and curve 4, Graph I, from 100 ml. of alcohol there were obtained, on the average, 51 ml. of liquid product, separating into two layers, the clear lower layer averaging 17.5 ml. (15.8 grams), and the upper layer 32.5 ml. Shaking of the upper layer with water removed the water soluble products, reducing the volume on an average of 6 ml. Upon fractional distillation, the insoluble portion remaining (26 ml.) showed that it did not consist entirely of hydrocarbons, because a carbon-hydrogen analysis did not total above 80 per cent, a result which indicated the presence of oxygen. Traces of acetaldehyde and the presence of

unsaturated compounds were also observed in all fractions up to b.p. of 90° C. However, an average of 7 ml. of brownish oily liquid with a b.p. greater than 90° C. remained; this liquid showed its unsaturated nature by decolorizing a two per cent permanganate solution and reacting with bromine in carbon tetrachloride without any evidence of hydrogen bromide. It turned darker upon exposure to air. The substance did not dissolve completely in sulfuric acid (sp. gr. 1.84). A carbon and hydrogen analysis was made.

Anal. Calcd. for C_nH_{2n} ; C, 85.7, H₂, 14.3. Found: C, 83.4, H₂, 15.6. Therefore the liquid was probably a mixture of saturated and unsaturated hydrocarbons.

The lower colorless layer, approximately 70 ml. (about 17.5 ml. per experiment), was subjected to a fractional distillation. A separation and an analysis of these products were extremely difficult because of the small range of boiling points, the similarity of properties or the formation of mixtures. However, an idea of the fractions and their respective boiling-point range may be obtained from the following: (1) to 56° C., 3.4 ml.; (2) 56-69° C., 3.4 ml.; (3) 69-76° C., 7.2 ml.; (4) 77-79° C., 29.8 ml.; (5) 81-86° C., 6 ml.; (6) 87-90° C., 7 ml.; (7) above 90° C., 6 ml. The distillation loss of the product, about 7 ml., is due partly to the presence of acetaldehyde, which persistently appears in the fractions up to and including fraction 5, as shown by the reduction of ammoniacal silver oxide. Fraction 6

showed considerable unsaturation, decolorizing a two per cent permanganate solution and a solution of five per cent bromine in carbon tetrachloride, with no evidence of the formation of hydrogen bromide. Fraction 7 was an oil-like material, brown in color.

SUMMARY

1. A study of the decomposition of ethyl alcohol was made with and without magnesium oxide as a contact agent under the following conditions: low temperatures, long contact time, atmospheric pressure.

2. Studies of the same decomposition were made with and without magnesium oxide as a contact agent in a closed system under high pressure in an 18-8 stainless steel bomb.

3. Because of the different materials used in the construction of the catalyst chambers, a fair comparison of the two studies cannot be drawn.

4. When the experiment was conducted at atmospheric pressure, the decomposition of alcohol began slightly below 365° C. in the pyrex glass tube containing magnesium oxide. Under high pressure in the presence of magnesium oxide in the 18-8 stainless steel container, the decomposition began at a temperature slightly below 392° C.

5. Between 45 and 55 per cent of the alcohol decomposed in the presence of magnesium oxide at atmospheric pressure in the temperature range 440° to 460° C. Under the conditions of high pressure in a closed system, within the same temperature range, 60 to 70 per cent of the alcohol decomposed.

6. From the liquid product obtained in the decomposition of alcohol at low pressure, the following substances were identified: undecomposed alcohol, acetaldehyde, acetone, butyraldehyde, methyl n-propyl ketone, butyl alcohol, and 1,3-butadiene. Other substances, seemingly present but not identified, were unsaturated in nature. In the liquid product obtained in the high pressure experiment the only oxygen-containing compounds identified were undecomposed alcohol and acetaldehyde. Experimental facts indicated the presence of saturated as well as unsaturated hydrocarbons.

7. The gaseous product of decomposition obtained at low pressure was predominately hydrogen, 80 to 85 per cent. The gaseous product obtained at high pressure was from 40 to 55 per cent hydrogen.

8. Time-pressure curves were plotted, showing the course of decomposition of alcohol under high pressure.