REACTIONS OF ETHYL ALCOHOL

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I. INTRODUCTION

Ethyl alcohol is capable of undergoing several of the general types of reaction under a variety of conditions. Partial dehydration with the formation of ethyl ether is one of the simplest reactions, while complete dehydration produces ethylene.

$$2\ C_2H_5OH = (C_2H_5)_2O + H_2O$$
$$C_2H_5OH = C_2H_4 + H_2O$$

Ethyl alcohol is also readily dehydrogenated to acetaldehyde and possibly to a ketene under certain influences.

$$C_2H_5OH = CH_3CHO + H_2$$
$$C_2H_5OH = CH_2CO + 2\ H_2$$

The oxidation reaction produces a variety of products involving, in the initial stages, acetaldehyde and acetic acid, while under more vigorous conditions several other products are possible, with carbon dioxide and water being the ultimate products of complete oxidation.

$$2\ C_2H_5OH + O_2 = 2\ CH_3CHO + 2\ H_2O$$
$$C_2H_5OH + O_2 = CH_3COOH + H_2O$$
$$C_2H_5OH + 3\ O_2 = 2\ CO_2 + 3\ H_2O$$

The majority of these reactions have been fairly well investigated, but certain problems remain to be solved and many other variations in reaction conditions are yet to be studied. This review of the literature on the subject of these reactions will serve as an indication of the work that has already been completed, and perchance will also point the way to other interesting researches.

II. THE DECOMPOSITION OF ETHYL ALCOHOL

1. Pyrolysis

The simplest method of decomposing ethyl alcohol involves the passage of vapor through heated tubes. In early researches Berthelot (12) noted the occurrence of acetylene among the products of the thermal decomposition of ethyl alcohol. Somewhat later he reported (14a) that at around 500°C. in a glass tube, alcohol was decomposed in two ways; dehydration with the formation of ethylene and water, and dehydrogenation yielding acetaldehyde and hydrogen. Further decomposition of these products, involving polymerization and decomposition of ethylene and partition of the aldehyde into methane and carbon monoxide, resulted in complex secondary reactions.

Maquenne (66) made a more detailed study of these reactions and compared results at dull red and at bright red heat as shown in table 1. It will be observed that ethane is present in considerable quantities; most of the subsequent observers reported methane as the main saturated hydrocarbon.

Nef (78) studied the thermal decomposition in the range from 590° to 640°C. and found both hydrogen and ethylene to be the main products. Acetaldehyde and crotonaldehyde were identified by their odor. The gaseous products also contained considerable quantities of carbon monoxide and methane; this indicated a dehydrogenating action followed by a secondary decomposition of the aldehyde. The ratio of ethylene to hydrogen indicated that the dehydration reaction was considerably less than dehydrogenation.

Ipatiev (51) observed that the passage of alcohol through a glass tube heated at 660–700°C. induced practically no reaction, but the utilization of an iron tube at 710–750°C. gave a variety of products which included acetaldehyde, paraldehyde, hydrogen, carbon monoxide, methane, and 3 per cent of carbon. A later paper (52) discussed the dehydrating and dehydrogenating reactions and observed that the secondary decomposition of acetaldehyde increased with a rise in temperature. The passage of alcohol through a glass tube at 800–830°C. indicated that only 20 per cent of the reactant formed ethylene and the remaining 80 per cent was dehydrogenated, while one-third of the aldehyde produced was further decomposed. When a platinum tube was employed the decomposition occurred at a much lower temperature, and over 85 per cent of the alcohol reacted to form hydrogen and acetaldehyde, the latter being almost completely decomposed to methane and carbon monoxide.

TABLE 1

Pyrolysis of alcohol

PRODUCTS	DULL RED HEAT	BRIGHT RED HEAT
	per cent	*per cent*
Carbon dioxide	0.5	0.5
Carbon monoxide	22.1	26.4
Unsaturated	23.5	13.7
Ethane	13.8	13.6
Hydrogen	40.1	45.8

A more recent paper by Peytral (84) indicated that the passage of alcohol through a platinum tube at 1150°C. induced 70 per cent dehydrogenation and 30 per cent dehydration.

2. Catalytic decomposition

The decomposition of ethyl alcohol at high temperatures in the presence of various catalysts has been carefully investigated.

Greene (48) found that if alcohol was dropped on hot zinc chloride the products were numerous and varied. In addition to hydrogen chloride, several other substances were identified, including ethylene, ethane, hydrogen, water, acetaldehyde, and ethyl ether. Oils which were attributed to the polymerization of ethylene were also obtained. Hydrogen and ethylene were present in nearly corresponding quantities. The ether was formed by dehydration, but no suggestion was advanced for the source of the ethane.

In 1880 Jahn (58) found that the products obtained on passing alcohol over zinc dust at dull red heat were almost exclusively hydrogen, methane, and carbon monoxide. However, at a temperature of 300–350°C. the products included both hydrogen and ethylene. Somewhat later Keiser and Breed (60) stated that magnesium and iron glowed when heated in alcohol vapor. In both cases a large volume of gas was produced which consisted of 11 per cent of methane, 0.5 per cent of carbon monoxide, 14 per cent of unsaturated hydrocarbons, and 73 per cent of hydrogen when magnesium was used. With heated iron the products included 8 per cent of carbon monoxide, 13 per cent of methane, 0.5 per cent of carbon dioxide, 4.0 per cent of unsaturated hydrocarbons, and 63.8 per cent of hydrogen.

Ipatiev (52), continuing his work on the thermal decomposition of ethyl alcohol, observed that the presence of zinc in the reaction tubes lowered the temperature necessary for decomposition. The ratio of ethylene to aldehyde varied with the amount of zinc employed. Rods of zinc at 620–650°C. produced very little ethylene but about 80 per cent of aldehyde which was practically undecomposed. With zinc dust at 550°C. the dehydration and dehydrogenation reactions were about equal, with some of the water produced by the former decomposing to increase the hydrogen content of the exit gas. Brass containing 33 per cent of zinc gave results very similar to the zinc rod.

The utilization of graphite as the catalyst made the reaction proceed almost completely to the formation of unsaturated hydrocarbons with ethylene produced only in small quantities (53). Ipatiev (54) also reported that the passage of alcohol through a glass or copper tube filled with powdered graphite or silica at 600°C. induced practically no reaction, but that the presence of alumina, which acted as a powerful catalyst, promoted the formation of ethylene in large quantities, giving a 98 per cent yield at 350°C. Platinum at 610–630°C. acted quite differently, decomposing only about 23 per cent of the alcohol of which 17 per cent formed acetaldehyde while the remaining 6 per cent was dehydrated; practically all of the aldehyde was further decomposed. Metallic copper was unsatisfactory, but finely divided copper, which had been freshly reduced by alcohol, dehydrogenated 10 per cent of the alcohol at 620°C. Lead and nickel oxides behaved in a similar manner. Metallic zinc became active at 520°C. and at 540–550°C. it dehydrogenated the alcohol almost completely, the production of ethylene being negligible. The use of china clay at 500°C. converted the alcohol completely to ethylene (55).

Ehrenfeld (33) investigated the decomposition of alcohol at high temperatures over carbon, aluminum, and magnesium. He found that when alcohol vapor is passed over carbon, heated to dull redness, it is decomposed into equal volumes of methane, carbon monoxide, and hydrogen. At a lower temperature ethane is obtained; this he believed to be a primary product. Over aluminum the products are ethylene and water, the latter producing hydrogen at dull red heat. At lower temperatures there is also an indication of dehydrogenation, while at bright red heat this is the predominating reaction. At yellow heat there commenced the secondary decomposition of carbon monoxide, but ethylene and water were still evident in the products, together with hydrogen, methane, and carbon monoxide. Ipatiev (56) called attention to the fact that Ehrenfeld was not the first to use aluminum as a dehydrating agent. Ehrenfeld also reported that magnesium behaved very much like aluminum with an increase in the production of hydrogen. From this work he concluded that the relative proportions of reactions depended upon the specific nature of the substance over which the alcohol was passed.

A much more recent paper by Ipatiev and Kluikvin (57) discussed the simultaneous catalytic action of iron and aluminum at high temperatures and pressures. They reported that the heating of alcohol to 530–540°C. for six hours produced a variety of compounds, including polymerized ethylene, ketones, and aldehydes, as well as 16–20 per cent of carbon dioxide.

Prior to the thorough investigations of the catalytic decomposition of ethyl alcohol at relatively low temperatures, several investigators reported on the action of metals and their compounds upon alcohol. Deville and Debray (29) studied the action of rhodium, iridium, and ruthenium in the presence of an alkali, and found hydrogen and an acetate to be the products. In 1876 Gladstone and Tribe (45) stated that aluminum has no effect upon alcohol even when the two are boiled together for some hours. However, the addition of iodine gave hydrogen and aluminum ethylate which on heating decomposed to alumina, alcohol, and some ethylene.

Simon (100) noted the production of alcoholates when ethyl alcohol was treated with lithium or magnesium chlorides. About the same time Destrem (28) reported that barium oxide and calcium oxide combined with ethyl alcohol when heated up to 275°C., but that at 300°C. decomposition occurred with the barium oxide producing equal volumes of hydrogen and ethylene. In the case of lime no hydrocarbon was produced but a light liquid with an aromatic odor was recovered. Forcrand (41) investigated the action of alcohol on calcium carbide at 180°C. and noted acetylene, methane, and ethylene as well as calcium ethoxide to be the products.

The rigorous investigations of the influence of metallic catalysts upon ethyl alcohol date from the researches of Sabatier and coworkers. This work has been summarized in Sabatier's treatise (94) and will not be discussed further, except to show the action of metallic catalysts. These results are presented in table 2, given by Rideal and Taylor (92) and summarizing work of Sabatier and Mailhe. The figures refer to the percentage of ethylene in the ethylene-hydrogen mixture produced by the passage of alcohol vapor over the catalyst mass at 350°C.

Since these classical researches, however, a great number of more recent results have been published to elucidate the mechanism of catalysis, to determine optimum decomposition conditions, to compare catalytic activity, to examine promoter effects, and to study the influence of catalyst preparation upon its subsequent activity. Among these should be mentioned the investigations of Adkins and coworkers (1), Palmer and Constable (81), Armstrong and Hilditch (3), Rideal (91), Brown and Reid (20), Alvarado (2), Cremer (27), and Engelder (34).

TABLE 2

Action of metallic catalysts

CATALYST	ETHYLENE FORMED	
	per cent	
ThO_2	100	Dehydration catalysts
Al_2O_3	98.5	
W_2O_3	98.5	
Cr_2O_3	91	Mixed dehydration and dehydrogenation catalysts
SiO_2	84	
TiO_2	63	
BeO	45	
ZrO_2	45	
U_3O_8	24	
Mo_2O_5	23	
Fe_2O_3	14	
V_2O_3	9	
ZnO	5	
MnO_2	0	Dehydrogenation catalysts
SnO	0	
CdO	0	
Mn_3O_4	0	
MgO	0	
Cu	0	
Ni	0	

It should be noted that there are two possible reactions involving dehydration of ethyl alcohol, the first of which yields ethyl ether and the second ethylene. While ether is readily produced with metallic catalysts under certain conditions, it is more readily prepared by the classical method of Williamson (113), utilizing concentrated sulfuric acid. It has also been reported that phosphoric and arsenic acids may be used to replace sulfuric acid in this reaction (17). Many other substances have been suggested for the catalytic decomposition of ethyl alcohol, but this work has been reviewed elsewhere in detail (94).

3. Decomposition by electrical means

The influence of several forms of electrical discharge upon ethyl alcohol has been reported by various workers. The use of the silent electric discharge as a means of inducing reaction has been most widely studied in this field. In 1884 Maquenne (66) reported results with a variation of pressure and compared the products obtained with those of the thermal decomposition previously mentioned. The results are given in table 3.

TABLE 3

Decomposition of ethyl alcohol by the silent electric discharge

PRODUCTS	AT 2 MM. PRESSURE	AT 100 MM. PRESSURE
	per cent	*per cent*
Carbon dioxide	2.2	0.5
Carbon monoxide	11.0	14.7
Acetylene, ethylene	14.0	1.1
Ethane	30.1	21.6
Hydrogen	42.6	62.1

Berthelot (13) investigated this same phenomenon in an atmosphere of nitrogen and found that hydrogen, carbon dioxide, and a solid substance with the composition $C_{10}H_{20}N_4O_5$, were the final products of the reaction. In the initial stages of the decomposition ethane and carbon monoxide were also formed, but these gradually disappeared as the reaction progressed. Lob checked both of these results and found in the simpler case that the main products, among a great variety formed, were butyric acid, acetaldehyde, and formaldehyde (63). In the presence of nitrogen he found that the silent discharge produced ammonium formate and hexamethylenetetramine in appreciable quantities (64). More recently Poma and Nesti (87) refluxed the alcohol through two coaxial tubes and produced the discharge between an internal armature of plated silver and an external net of iron.

In this case the gaseous products consisted of 2.2 per cent of carbon dioxide, 4.4 per cent of carbon monoxide, 9.0 per cent of ethylene and acetylene, 26.0 per cent of methane and ethane, and 59.0 per cent of hydrogen.

The effect of electrical oscillations upon ethyl alcohol has been given by de Hemptinne (50) who obtained carbon monoxide, carbon dioxide, hydrogen, ethane, and methane as products. Recent results of Muller (74) discussed the action of an electric arc struck between an iron cathode and a carbon anode beneath the surface of ethyl alcohol. One liter of alcohol was sparked for five hours and produced 1200 liters of gas and 108 cc. of condensate; most of this latter was alcohol but it also contained 12 cc. of acetaldehyde and 2.5 cc. of acetylenes. One point worthy of note was the identification of a small amount of butadiene among these acetylenes. The products also included some free carbon, which could have come from the electrode, and a small amount of tar. An analysis of the gases produced indicated acetylene 7–9.9 per cent, ethylene 6–6.9 per cent, saturated hydrocarbons 6.8–20.4 per cent, carbon monoxide 20.4–23.8 per cent, and hydrogen 46.2–49.9 per cent. Fowler and Mardles (42) investigated the passage of an electric discharge which took the form of a hissing flame through alcohol in the vapor state. These workers identified hydrogen, methane, acetylene, and other unsaturated hydrocarbons, along with traces of carbon, as the products of this reaction.

Berthelot and Gaudechon (14) found that ethyl alcohol in quartz tubes was decomposed by radiations from an unscreened mercury vapor lamp, while somewhat similarly Bates and Taylor (10) worked out the action of excited mercury atoms on alcohol. The decomposition proceeded by way of the intermediate formation of acetaldehyde, indicating that the final products would include hydrogen, carbon monoxide, and methane.

A study by Moens and Juliard (71), of chemical reactions in the gaseous phase under the influence of high frequency electromagnetic fields, revealed the fact that ethyl alcohol was readily decomposed.

From these results of various workers it may be seen that the reactions induced in ethyl alcohol by heat or physical phenomena are both dehydrogenating with the formation of hydrogen and acetaldehyde, and dehydrating with the production of ethylene and water. In a large number of cases these initial derivatives undergo secondary reactions with the formation of various products. A large number of derivatives have been reported which would not be expected from the known reactions of ethyl alcohol, and in the majority of cases their origin is unexplained.

III. THE CATALYTIC OXIDATION OF ETHYL ALCOHOL

There are three general methods of oxidizing alcohol catalytically and two other methods which have been suggested which probably owe their activity to catalytic influences.

The oxidation of ethyl alcohol by the action of enzymes is well known, while the catalytic activity of various metals in promoting the air oxidation of alcohol, and the photochemical autooxidation of alcohol in a homogeneous system by organic compounds have also been investigated.

The other two methods involving electrolytic oxidation and oxidation by means of ozone have been studied with and without catalysts, and it seems quite probable that catalytic influences are at work in both cases.

1. Enzymatic oxidation

The action of enzymes in the oxidation of ethyl alcohol to acetic acid has been very thoroughly examined. Several comprehensive reviews of the reaction have been published, consequently the details will not be discussed here.

There is one point, however, which seems somewhat controversial and should be indicated, namely, the formation of aldehydes in this reaction. Mathieu (68) stated that the aldehyde produced in wines was due to contact with air without the action of organisms. The reaction was apparently accelerated by the presence of oxidizable substances such as sulfur dioxide, ferrous sulfate, ferrous oxide, or manganous oxide. It was also observed that direct sunlight had a similar effect, while vessels made of green glass also favored the oxidation.

These results have not been fully confirmed and in several cases it has been reported that the photochemical oxidation of alcohol is negligible, as will be shown later.

Trillat and Santon (106) also believed that acetaldehyde was not a normal product of the fermentation of alcohol but that its formation was due to the oxidation of alcohol by air. Verification of this premise was obtained by Palmore (82), who found that if ethyl alcohol, free of aldehyde, was saturated with carbon dioxide, there was no appreciable formation of aldehyde even after standing for two and one-half years.

A statement by Voisenet (111) that formaldehyde was a normal product of the oxidation of ethyl alcohol whether the reaction was promoted by physical, chemical, or biological means, seems to have been neither refuted nor corroborated in connection with enzyme reactions. This aldehyde has been fairly frequently observed, however, in the products of oxidation by other methods.

2. *Electrolytic oxidation*

In 1875 Renard (88) investigated the electrolysis of ethyl alcohol which had been slightly acidified with dilute sulfuric acid. Hydrogen gas was liberated at the cathode, but the oxygen which might have been evolved at the anode was consumed in the oxidation reactions of alcohol. As the products of a 48 hour run under these conditions the following were identified,—acetaldehyde, ethyl formate, ethyl acetate, and a small amount of acetal. There was also a very small quantity of another substance present which was called ethylidine monoethylate, $C_2H_5OCH(OH)CH_3$. A later paper (89) noted that after a considerable time formic acid, acetic acid, and oxygen were evolved in appreciable quantities at the anode. Separating the electrodes with a porous partition effected no change in the end products.

Bartoli and Papasogli (9) studied this electrolytic activity in an alkaline solution and found large quantities of aldehyde produced; this aldehyde polymerized quite readily as far as a resin. A small yield of acetic acid was also obtained. These workers used carbon electrodes which were slightly disintegrated with the formation of a deposit of carbon.

Askenasy, Leiser, and Grunstein (4) followed Renard's method, using platinum gauze electrodes and an acidulated solution. It was observed that ethyl acetate was the first product formed, but the yield diminished considerably as the action continued. A quantity of acetaldehyde was also obtained. The most efficient temperature range was between 30° and 40°C., when yields of acetic acid from 77–93.8 per cent were obtained. The current yield was about 75 per cent. It should be noted that these workers added chromic sulfate as an oxygen carrier to assist the reaction catalytically.

Muller and Miro (75) advanced a mechanism to account for the presence of large quantities of hydrogen and methane as the products of the electrolysis of ethyl alcohol from alkaline solution.

In addition to these results on the electrolytic oxidation, the effect of the silent electric discharge on the oxidation of ethyl alcohol was studied by Comanducci (25). It was observed that acetaldehyde was the main product when ethyl alcohol and oxygen were placed together under the influence of the discharge.

3. Ozonization

The oxidizing action of ozone on alcohol was first noticed by Boillot (16), who observed that the passage of ozonized air or ozonized oxygen into ethyl alcohol induced reactions forming acetic acid, formic acid, and, apparently, small quantities of acetic ether. Wright (115) investigated these reactions more thoroughly, using five different methods to promote the formation of acetic acid. When alcohol vapor and ozone were passed through a flask at 180°C., the yield amounted to 1.6 per cent of the alcohol, while if the reactants were passed through a porcelain tube at 200–250°C. only 0.8 per cent of acid was formed. Ozone was then passed into cold alcohol and the solution shaken for 10 to 12 hours; the acid content of the products amounted to 0.3 per cent. The product obtained on passing ozone through boiling alcohol contained 1.18 per cent of acid; passing ozone through boiling alcohol in a flask fitted with a reflux condenser, so that the condensed liquid was continually subjected to the action of the gas, gave a slightly higher yield of 1.22 per cent of acetic acid.

It was also noted that water had a very appreciable influence on the reaction, acting as a strong diluent, but the degree of inhibition was dependent upon the conditions of the reaction.

Renard (89) stated that the action of ozone was similar to that of electrolytic oxygen, while Otto (80), in a paper discussing the reactions of ozone, made the observation that acetaldehyde and acetic acid were the essential products of the reaction between ozone and ethyl alcohol.

4. Catalytic oxidation

The oxidation of ethyl alcohol by air or oxygen in the presence of catalysts has been fairly widely examined with a variety of catalysts. In 1867 Calvert (21) investigated the action of pure oxygen on ethyl alcohol by passing alcohol vapor over carbon containing absorbed oxygen. Acetic acid was the main product. Later, work by Senderens (97), who also used oxygen absorbed on animal charcoal, indicated that with alcohol vapor at 400°C. the gaseous products consisted of 0.5 per cent of carbon dioxide, 35.5 per cent of ethylene, 4.5 per cent of carbon monoxide, 54.7 per cent of methane, and 4.8 per cent of hydrogen. Formaldehyde was also formed, and its destruction might produce carbon monoxide and hydrogen. Senderens stated that the action of the carbon was purely catalytic and that it did not act as a reducing agent. To prove this he passed oxygen and alcohol over siliceous sand, pumice stone, magnesia, and dicalcium phosphate, and obtained results in agreement with his work on carbon.

Sabatier also reports the work of Woog (114) who discovered that coal, heated in air to 300°C., is a good oxidation catalyst when used at 150–300°C., this activity being partly due to the iron oxide present in the ash. This latter supposition was confirmed by results obtained on the addition of ferric oxide to the coal. The products obtained from ethyl alcohol consisted essentially of acetaldehyde and acetic acid.

The direct oxidation of alcohol by air, using platinum or platinum black as a catalyst, was first observed by Mulder (73) in 1883. The action is unusually vigorous and when platinum black is used the alcohol is quite easily ignited. The products of the reaction, using either form of platinum, are acetic acid and acetaldehyde. The use of platinum wire electrically heated to various temperatures was investigated by Trillat (105). The oxidation proceeded readily even when the temperature of the platinum was as low as 225°C., and the products of such a reaction included 16.8 per cent of acetaldehyde and 2.3 per cent of acetal. It was also observed that aldehyde was formed even in the absence of air. The use of platinum for the production of formaldehyde from ethyl alcohol and oxygen has been patented (83). The platinum should be heated to redness and the flow of reactants adjusted to prevent complete combustion. The vapors must be cooled rapidly to obtain satisfactory yields of formaldehyde.

Recently Muller and Schwabe (76) studied the oxidation of aqueous ethyl alcohol in the presence of sodium hydroxide and acetic acid using platinum, palladium, and rhodium powder as catalysts at 20°C. The essential point of study in this case was the mechanism of such a reaction, and it is compared with that of acetic acid and formic acid.

Duchemin and Dourlen (32), while observing the reactions of ethyl alcohol at its boiling point, noticed that with long refluxing, either alone or in the presence of a catalyst, a considerable quantity of acetic acid was produced. The catalysts tested were copper, lead, tin, and zinc; copper proved to be the most efficient of these. A possible mechanism was formulated which gave a metallic hydride and acetaldehyde as the primary products; in such a case the hydride would decompose with the existing conditions and the aldehyde would be further oxidized to acid. Copper has been more fully studied by Orloff (79) by passing air and alcohol over copper gauze. The products of this reaction were varied; acetaldehyde was the chief derivative, but carbon monoxide, carbon dioxide, saturated and unsaturated hydrocarbons, as well as small quantities of acids and ketones were also detected.

Alcohol and air were passed over finely divided copper at 260–270°C. by Mailhe and de Godon (116). It was observed that the catalyst aged, favoring aldehyde formation; 60 cc. of alcohol produced 18 grams of acetic acid and 12 cc. of acetaldehyde. Moreau and Mignonac (117) studied the action of silver on asbestos at 340–380°C. Alcohol vapor together with 50 per cent of the theoretical quantity of air was passed over the catalyst and the products mixed with more air and passed over a second catalyst. With two catalysts in series the product contained 84 per cent of acetaldehyde.

Faith and Keyes (118) have recently examined the catalytic effect of silver, copper, and nickel both in a metallic form and supported on asbestos. It was noted that metallic catalysts were more efficient, owing to a greater coefficient of heat transfer than was possible with supported catalysts. Maximum yields varied with the catalyst; at 515°C. silver gauze produced 80.6 per cent of acetaldehyde, at 512°C. copper turnings gave 78.0 per cent of aldehyde, and at 560°C. nickel gauze produced 29.6 per cent of aldehyde.

Various patents have been issued on the use of copper and silver as catalysts for the oxidation of alcohol. A few of these have been selected as indicative of the methods recommended. One patent (5) claims the use of copper discs treated to form a layer of copper acetate which on reduction leaves a very fine layer of metallic copper. Another patent (7) mentions similar discs soaked in copper or nickel nitrate which yield hydroxides on treatment with ammonium hydroxide; this form is readily reduced to the metal. Iron and chromium may be similarly formed. Both of these patents specifically refer to the formation of acetaldehyde by the oxidation process, but apparently not to the formation of acetic acid. As a later development for the same process the use of copper, nickel, chromium, or iron as catalysts has been patented (6). A similar patent protects the use of silver (47) for the air oxidation of alcohol to acetic acid and acetaldehyde in a range of 380–440°C.

As early as 1907 Naumann, Moeser, and Lindenbaum (77) observed that vanadium pentoxide was an active catalyst for the formation of acetaldehyde and acetic acid from air and ethyl alcohol. Fester and Berraz (40) studied the activity of vanadium much more thoroughly by employing vanadium pentoxide, silver and copper vanadates on silica, and silver vanadate on fuller's earth. The products of the reaction were acetaldehyde, acetic acid, and carbon dioxide, with the latter being the main product if the temperature rose to 360°C. The most satisfactory operating conditions with vanadium pentoxide produced 9–13 per cent of aldehyde and 2–5 per cent of carbon dioxide. The action of zinc oxide was similarly investigated and an optimum yield of 10.7 per cent of aldehyde and 4.8 per cent of carbon dioxide was obtained.

Hay (49) noticed that colloidal clay was a fair catalyst for the oxidation of alcohol to acetaldehyde, and a patent (38) developed along similar lines indicated that alcohol could be oxidized by the use of a catalyst consisting of finely divided clay dispersed in a fluid medium, by the addition of a deflocculating agent such as ammonia, sodium hydroxide, or sodium carbonate. The catalytic activity of such a preparation may be much further enhanced by the addition of metallic catalysts known to promote the oxidation. Somewhat similar metals are included in a patent (26) which states that ethyl alcohol may be oxidized by passage over barium oxide at a temperature of 400–500°C. The products of this reaction contain some of the higher alcohols, such as butyl alcohol, in addition to acids, esters, acetals, and aldehydes. Similarly magnesia, lime, manganese dioxide, or the alcoholates of magnesium and sodium may also be used to promote this oxidation.

Slaboszewicz (101) in 1902 made the general observation that in the oxidation of ethyl alcohol by air a large number of higher oxidation products were obtained in addition to acetaldehyde. This early observation rather anticipated the above mentioned patent. The general process of oxidation of ethyl alcohol is mentioned in a patent (67) which states that the passage of air and alcohol over a catalyst yields acetaldehyde, which may then be mixed with more air and passed over another catalyst to produce acetic acid.

Recently several workers have conducted more thorough investigations of the catalytic oxidation of ethyl alcohol, using a wide variety of catalysts and studying the reaction in the vapor or liquid phase. Simington and Adkins (99) passed alcohol mixed with air over numerous catalysts and obtained aldehydes, ketones, acids, saturated and unsaturated hydrocarbons, carbon monoxide, carbon dioxide, hydrogen, and slight amounts of esters. The quantity of hydrogen produced was usually quite small except with brasses, while zinc promoted dehydrogenation but not the oxidation of the evolved hydrogen. Plated catalysts were unsatisfactory, but it was noticed that small amounts of diluent materials had no appreciable effect upon the reaction; from this it was concluded that a large portion of the catalytic surface was active in this oxidation.

Karpov (59) also reported an extensive study of catalysts suitable for the production of acetaldehyde by the oxidation of ethyl alcohol. He tested oxidized copper, iron, and nickel gauzes, chromium trioxide, cobalt oxide, manganese tetroxide (Mn_3O_4), cupric oxide, and barium oxide deposited on asbestos, and found that those containing iron, manganese, copper, and chromium were the most satisfactory. When nickel and cobalt catalysts were used, it was noticed that some carbon was invariably formed, while with nickel and chromium catalysts a certain amount of the alcohol was oxidized to acetic acid and some of this latter in its turn was decomposed to methane and carbon dioxide. With a large excess of oxygen the products were largely formaldehyde, water, and carbon dioxide, although the time of contact was important in all cases. Optimum results were obtained when using twice the theoretical amount of air and a temperature depending upon the catalyst in use. In this latter connection nickel was effective between 170°C. and 190°C., while chromium was active over a somewhat wider range of 170–220°C.

A specialized study on the use of the rare earth oxides as vapor phase catalysts was made by Lowdermilk and Day (65), using samarium admixed with copper. It was found that the oxide was too active to be used alone, but could be largely diluted with copper and still had a strong action. The effect of this addition on the copper was carefully examined. It was found possible to obtain a good yield of acetaldehyde, but it was necessary to regulate the temperature carefully, since the mass of catalyst and its temperature were of fundamental significance.

Day (119) recently continued this study by examining the effect of small amounts of samarium oxide on the catalytic activity of silver. At 370°C. the presence of samarium slightly decreased the yield of acetaldehyde; a catalyst containing 2.785 grams of silver and 0.0075 gram of Sa_2O_3 produced 79.5 per cent of aldehyde. Higher yields of acetaldehyde were obtained in a one-step vapor phase oxidation of ethyl alcohol than had previously been obtained by similar methods.

The most thorough study of the partial oxidation of alcohol in liquid or vapor phase is due to King, Swann, and Keyes (61) and to Snow and Keyes (102). In the first paper the formation of acetic acid from ethyl alcohol in two steps, using manganese or cobalt acetates as catalysts, was investigated. Air was bubbled through 96 per cent alcohol maintained at 50–53°C. to approximate a ratio of five moles of air to one mole of alcohol. This mixture was passed into a catalyst tube containing activated copper gauze at 310°C. At this stage 40–50 per cent of the alcohol was converted to acetaldehyde. The aldehyde was mixed with twice the theoretical quantity of oxygen and oxidized to acetic acid. The conversion to acetic acid was nearly 90 per cent of the theoretical.

The second paper reported the results obtained with about one hundred and fifty catalysts in the liquid phase. The alcohol, together with the dissolved or suspended catalyst, was placed above a porous plate and oxygen was forced through this plate into the liquid. The temperature of the system was held at 70–75°C. In all but one of the cases no acetic acid was produced and a great many catalysts were entirely inactive. Cerium oxide with alkali produced acetic acid, formic acid, aldehyde resin, and carbonic acid. The effect of pressure was studied with about forty catalysts and was found to have no appreciable influence. The extent of oxidation was limited to the formation of small concentrations of acetaldehyde, paraldehyde, and acetal. Only in the cases of some hopcalites and an alkaline cerium catalyst were acetic acid and carbon dioxide noted.

From this review of the catalytic oxidation of ethyl alcohol it will be observed that many of the points have been thoroughly studied, but that many catalysts remain to be tested, particularly at high temperatures and in one-stage oxidations. The ultimate products in nearly all cases are fairly complex mixtures and the efficiency of this process remains to be improved for commercial success in one step.

5. *Photochemical oxidation*

The influence of light on the oxidation of ethyl alcohol with or without catalysts has been reported on a few occasions. In 1886 Richardson and Fortey (90) exposed carefully purified ethyl alcohol, containing water and oxygen, to light. The work was repeated by sealing alcohol in tubes with moist oxygen. In both cases it was observed that there was a trace of peroxide at the end of a few weeks, but this was not evident after a prolonged exposure. The formation of acetic acid and hydrogen peroxide had been anticipated under these conditions. Ciamician and Silber (23) note the fact that while ethyl alcohol is not directly oxidizable by the action of light, it is capable of undergoing photochemical auto-oxidation in the presence of a small quantity of *p*-xylene. Thus, ethyl alcohol containing water and *p*-xylene in an atmosphere of oxygen was exposed to light for three and one-half months. At the end of this period the alcohol had been oxidized to acetic acid, while the xylene was also reactive producing xylylic acid.

Sernagiotto (98) also stated that alcohol is not oxidized by the action of light alone, but he found that in the presence of oxalic acid the alcohol was slowly oxidized yielding carbon dioxide, formic acid, and acetic acid. This catalytic action of organic compounds has been studied in one other instance, namely, by Cohen (24) in his investigation of the influence of ketones on the photochemical oxidation of alcohol to acetic acid. It was found that this reaction was independent of the quantity of ketone present over fairly wide ranges of concentration.

Recently Stoklasa and Bares (103), investigating the formation of acetaldehyde in plant organisms, advanced the theory that it was produced in a secondary reaction involving the partial oxidation of ethyl alcohol. It is evident from these results that there is still a fairly wide field available for the examination of the influence of organic compounds on the oxidation of ethyl alcohol. These organic catalysts offer a relatively simple method of studying homogeneous catalysis as applied to oxidation reactions.

IV. OXIDATION OF ETHYL ALCOHOL BY VARIOUS OXIDIZING AGENTS

1. Hydrogen peroxide

Various oxidizing agents have been studied to determine their action on ethyl alcohol; of these hydrogen peroxide was probably the first to be investigated. In 1877 Fairley (37) stated that peroxide solutions of 2–5 per cent have no appreciable action on 80 per cent alcohol, while in 1880 Renard (89) also observed that this oxidizing agent had no action on dilute or concentrated alcohol solutions, in an acid, alkaline, or neutral medium, even after several days standing.

Following these negative results it was discovered that the oxidation of alcohol by hydrogen peroxide depended upon the presence of an iron salt. Fenton and Jackson (39) found that the addition of ferric or ferrous acetates catalyzed the reaction, but that the production of acetaldehyde was negative, the entire product being acetic acid. Considerably later Doroshevskii and Bardt (31), while examining the effect of charcoal on the oxidation of ethyl alcohol, found that it was dependent on the presence of ferrous salts such as chloride, sulfate, or oxalate. If ferrous sulfate and hydrogen peroxide were added to alcohol, it was noted that the oxidation proceeded readily with the formation of acetic acid and acetaldehyde, but when ferrous oxalate was employed as the catalyst, the reaction proceeded almost completely to the formation of acid. Oxidizing the ferrous salt to the ferric state seemed to inhibit its activity to a certain extent. It was also remarked that dilute solutions were more readily oxidized than pure alcohol. Chauvin (22) observed that the action of peroxide on ethyl alcohol was greatly influenced by 0.01 per cent of manganese acetate, while the products of this oxidation using only 1 per cent of peroxide contained aldehyde, ester, and traces of higher alcohols.

The most thorough study of this reaction is due to Walten and

Christiansen (112). It was found that the conversion of alcohol to acid was practically quantitative but was dependent on several factors. Acids seemed to retard the velocity of the reaction with the order of this effectiveness being acetic, nitric, hydrochloric, and sulfuric acids if each were present in equivalent concentration. The velocity of reaction was proportional to the concentration of the catalyst and also increased with an increase in hydrogen peroxide. Iron salts were found to be effective, whether present in the ferric or the ferrous state; this effectiveness was said to be due to the immediate oxidation of ferrous salts to ferric salts. A mechanism which involved the intermediate formation of a ferric acid was postulated. It was also noted that in some cases the reaction went to the products of complete oxidation, carbon dioxide and water. A large number of metals and salts were investigated to determine their promoter action, but the results in most cases were negative; sodium vanadate and potassium chloroplatinate were the only compounds showing activity, but even in these cases the conversion was relatively small. Some of these results have been confirmed by Rosenthaler (93) on the oxidation of ethyl alcohol by hydrogen peroxide in the presence of ferrous sulfate.

2. Potassium permanganate

The oxidation of ethyl alcohol by the action of potassium permanganate was first reported by Morawski and Stingl (72) who found that the alcohol was oxidized to acetic acid. The acid in turn combined with excess of the permanganate to produce potassium acetate and a brown unidentified precipitate was formed.

Doroshevskii and Bardt (31), working under these conditions, found that with the inclusion of ferrous salts as catalysts in the oxidation of ethyl alcohol by potassium permanganate, the results varied with the catalyst selected. If ferrous sulfate was employed the oxidation stopped with the formation of acetaldehyde, but if ferrous oxalate was used as the catalyst, the product was a mixture of aldehyde and acetic acid. These latter results confirm the higher oxidizing activity of hydrogen peroxide over that of potassium permanganate.

According to Benedikt and Neudorfer (11), Benedikt and Zsigmondy were the first to observe that in the presence of alkaline potassium permanganate, ethyl alcohol was oxidized to oxalic acid. Using a 2 per cent solution of alcohol, however, these workers were unable to obtain more than a 64 per cent conversion to oxalic acid.

Evans and Day (35) studied the action of alkaline permanganate in a much more detailed manner. An aqueous solution of the oxidizing agent, together with varying quantities of potassium hydroxide, was added to ethyl alcohol to completely reduce the permanganate; the products were analyzed for carbon dioxide, acetic acid, and oxalic acid. The results varied with the hydroxide concentration. The yields of the products were plotted against potassium hydroxide concentration, and it was found that the oxalic acid curve was parallel to the potassium hydroxide from 150 grams of potassium hydroxide up; the carbon dioxide curve was parallel above 175 grams of potassium hydroxide and acetic acid above 225 grams. It was later reported (36) that under the same conditions, at temperatures of 25°, 50°, and 75°C., the product in neutral solution was acetic acid; however, over the same temperature range and an alkalinity from 0.415 gram to 340.8 grams of potassium hydroxide the products were varied, as already mentioned. If the temperature was raised to 100°C. at a potassium hydroxide concentration of 0.415 gram per liter the product was acetic acid, but raising the concentration from this minimum to 340.8 grams per liter changed the products to carbon dioxide and oxalic acid. As a conclusion to this work it was stated that the yield of acetic acid decreased and that of carbon dioxide and oxalic acid increased with an increase in alkalinity to the maximum effect. An increase in temperature produces much the same effect but to a smaller extent. Increasing alkalinity or temperature increases the rate of oxidation to an optimum without influencing the relative amounts of the products.

In a fairly recent series of papers Tronov and coworkers have discussed the mechanism of this reaction. The first paper (107) used an aqueous solution of $KMnO_4$, of $KMnO_4$ and KOH, or of $KMnO_4$ and H_2SO_4, in either equivalent quantities or with an excess of alcohol. The reaction proceeded readily and it was observed that alkaline permanganate reacts about one hundred times faster than in neutral solution. The acid permanganate was not active. A second paper (109) reported more fully on the velocity of this reaction. It seemed to follow the equation for a second order reaction until large amounts of the reaction products had accumulated. The influence of neutral salts, such as potassium chloride, sodium chloride, potassium nitrate, sodium nitrate, potassium perchlorate, potassium sulfate, and sodium carbonate was examined later (108). It was stated that when a standard alkaline permanganate was used, the acceleration of the reaction by these salts was directly proportional to their concentration. The nature of the cation was apparently of minor importance.

The effect of calcium permanganate has been noted by McDermott (69), who threw this substance on a porous plate saturated with ethyl alcohol and observed brilliant scintillation followed by a steady glow. Aldehyde and acid were detected by their odor. Donath (30) studied the action of manganese dioxide upon alcohol vapor and found that with temperatures varying from 150–360°C. the products were carbon dioxide, acetone, and small quantities of higher boiling compounds. If the manganese dioxide was soaked in sodium hydroxide it was even more effective for this oxidation.

3. Potassium dichromate

Early in 1891 Frankland and Frew (43) noticed that when ethyl alcohol was heated with potassium chromate and sulfuric acid in a sealed jar for seven hours at 100°C., over 98 per cent of the alcohol was converted to acetic acid. Much later Plotnikov (85) tested ammonium chromate and chromic oxide as oxidizing agents on ethyl alcohol. The reaction velocity was the same with both substances and the extent of reaction was proportional to the alcohol concentration. A later paper (86) reviewed the photooxidation of organic compounds by dichromates and reported the formation of acetaldehyde and a brown precipitate of unknown composition from ethyl alcohol.

Schwarz (96) confirmed this photochemical oxidation of alcohol by potassium dichromate. It was found that the product was essentially acetaldehyde, while the dichromate was changed to a brown unidentified substance. The actual production of aldehyde was considerably lower than the theoretical yield calculated from the quantity of dichromate removed, but the residual substance made a complete determination of the discrepancy rather difficult. It was also observed that the reaction velocity increased with time, indicating an autocatalytic activity on the part of the reaction products.

This photochemical activity of the dichromate ion was further investigated by Bowen and Bunn (18). From these results the chromate ion in neutral or alkaline solution was found to be photochemically quite inactive toward the alcohol. The results of Plotnikov on the activity of ammonium chromate were explained by assuming a partial hydrolysis to the dichromate. The photochemical reaction with the acid dichromate ion and ethyl alcohol produced acetaldehyde without any precipitate. In neutral solution the dichromate ion also gave aldehyde but an unknown precipitate was formed. A later paper by Bowen and Yarnold (19) compared the quantum efficiencies of the $HCr_2O^-{}_7$, $Cr_2O_7^{--}$, and $HCrO_4^-$ ions and indicated that only the first of these three is photoactive. The latest paper in this series by Bowen, Peacocke, and Wellburn (120) reported measurements on the rate of photochemical oxidation by potassium dichromate in light of two different wave lengths and at hydrogen ion concentration varying from 10^{-4} to 10^{-7}. The results can be quantitatively accounted for on the assumption that the photoactive ion was $HCrO_4^-$ and that CrO_4^{--} ion also present acted as an inner filter. The results of Bowen and Yarnold were apparently based on the acceptance of incorrect equilibrium constants in dichromate solutions. However these results may be explained qualitatively by the appearance of HCr_2O_7 ions at the higher hydrogen ion concentration used in their experiments.

Tronov and Lukanin (107) observed that the oxidation of ethyl alcohol by chromium trioxide may be represented by a second order equation. The activity of chromium trioxide was increased one hundred times in sulfuric acid solution; the reaction went to completion under these conditions, while in neutral solution only 30 per cent of the available oxygen was utilized. Tronov, Udodov, and Chizhova (110) also stated that alcohol was readily oxidized by chromium trioxide. These workers studied the action of 39 or 67 per cent nitric acid on alcohol and found it to be even more active than chromium trioxide.

In this latter connection Trifonow (104) investigated the effect of pernitric acid on alcohol and found that it oxidized the latter almost completely to acetaldehyde.

4. Miscellaneous agents

A study of the vapor phase oxidation of ethyl alcohol in air, as part of a general survey on the oxidation of fuel vapors in air, has recently been given by Mardles (121). Two methods involving both flow and static closed bulb systems were studied. The temperature of initial combustion was above 450°C. Oxidation proceeded slowly and only a small amount of acetaldehyde was produced, which was in support of Mardles combustion theory.

A large number of other substances which oxidize ethyl alcohol have been investigated. The action of bleaching powder on alcohol was reported by Schmitt and Goldberg (95) in 1879. These compounds reacted spontaneously after a lapse of 7 to 10 minutes; acetaldehyde and acetal distilled off, together with a greenish yellow oil which was believed to be ethyl hypochlorite. Goldberg (46) studied the effects of diluting the alcohol with water. In equivalent amounts of water and alcohol there was no diluent effect in evidence, but above this ratio the water acted as an inhibitor. The presence of chloroform among the products was noted with these diluted reactants.

Bhaduri (15) investigated the action of chlorine peroxide on alcohol. In this work a mixture of ethyl alcohol and sulfuric acid was added dropwise to an aqueous solution of potassium chlorate. The reaction was slow initially, but became violent as the reactants were warmed. The distillate was essentially ethyl acetate, but tests for acetaldehyde and chloroform were obtained, while traces of chlorinated derivatives were found in the residue.

Letellier (62) reported that an ammoniacal solution of cupric oxide oxidized ethyl alcohol almost completely to acetaldehyde at 180°C. The action of Fehling's solution at various temperatures was investigated by Gaud (44). The reactants were heated in sealed tubes at 100°C. When alcohol was in excess both acetaldehyde and acetic acid were produced, while if the solution was in excess, acetic acid was the sole product. There was no reaction at room temperature, but above that a precipitate of cuprous oxide was formed in all cases. At 240°C. the products were still more varied and included cuprous oxide, cupric acetate, carbon dioxide, and acetic acid.

Two other interesting results have been recorded. Mittra and Dhar (70), while working on the effect of sodium sulfite and ferrous hydroxide on ethyl alcohol, observed that oxidation occurred quite readily, with the formation of acetaldehyde and carbon dioxide. The action of phosphorus pentoxide was much as would be expected, as shown by Balarew (8). Various esters of orthophosphorous acid were formed, and although the action was essentially dehydration, it was noticed that the yield of ethylene from the reaction was dependent on the stability of the esters produced.

V. CONCLUSION

In this review the general reactions of ethyl alcohol under a wide variety of conditions have been reported. In many cases there is evidence of much greater complexity in the reactions than might be expected; consequently derivatives have been isolated which were not anticipated. It is evident that certain reactions have been fully studied, but equally apparent that many of the reactions herewith reported merit further investigation.

Although ethyl alcohol is one of the simplest alcohols there are many possible reactions which have been neglected, possibly because of a lack of such information as this review has conveyed.

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