THE OXIDATION OF THE GASEOUS PARAFFIN HYDROCARBONS

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1. INTRODUCTION

The gaseous paraffin hydrocarbons are a veritable treasure house as a source of material for transformation into derivatives of great utility. The quantity of gaseous paraffin hydrocarbons which is produced is of astronomical magnitude. They are available in tremendous quantities in natural gas, and are also produced in quantity from crude oil, in the cracking of oils, in the

TABLE 1

*Available supplies of commercial fuel gases and their content of gaseous paraffin hydrocarbons**

GAS	VOLUME	METHANE	ETHANE	PROPANE	BUTANE
	cubic feet	*per cent*	*per cent*	*per cent*	*per cent*
Natural gas†	1,750,000,000,000	85	9	3	1
Coke oven gas‡	639,644,000,000	28	12	1	
Gas from refining of crude oil§	240,000,000,000	61	21	12	4
Coal and water gas¶	210,743,000,000	13	3	0.3	
Cracked gas from pressure distillation of heavy oils**	200,000,000,000	55	18	5	2
Carburetted water gas¶	112,186,000,000	13	3	0.3	
Oil gas¶	24,289,000,000	40	15		
Coal gas¶	7,411,000,000	31	1.0		
Propane and butane in natural gasoline calculated to gas volume††	15,995,750,000				
Propane and butane in unblended refinery gasoline, straight run and cracked calculated to gas volume ‡‡, §§	15,865,500,000				

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* The gas analyses were approximated by G. A. Burrell from results of his observations.

† Hopkins, United States Bureau of Mines.

‡ Mineral resources of the United States, 1925—Part II page 601; Separate II: 30, "Coke and By-products in 1925."

§ Estimate from data furnished by G. A. Hopkins, United States Bureau of Mines.

¶ Department of Commerce, Statistical Abstract of the United States, 1926.

** Estimated by Egloff.

†† Estimated by G. A. Burrell.

‡‡ In a private communication to the authors, G. G. Brown estimated the average propane content of unblended refinery gasoline, straight run and cracked, as about 0.5 per cent by weight and the average butane content about 3.0 per cent.

§§ The production of unblended refinery gasoline, straight run and cracked, is estimated by the Bureau of Mines at 12,537,000,000 gallons. Oil Gas J., **26**, No. 41, p. 120 (1928).

TABLE 2

Volumes of gaseous paraffin hydrocarbons available from commercial fuel gases (in cubic feet)

GAS	METHANE	ETHANE	PROPANE	BUTANE
Natural gas	1,487,500,000,000	157,500,000,000	52,500,000,000	17,500,000,000
Coke oven gas	179,100,320,000	76,757,280,000	6,396,440,000	
Gas from refining of crude oil	146,400,000,000	50,400,000 000	28.800,000,000	9,600,000,000
Coal and water gas	27,396.590,000	6,322,290.000	632,229,000	
Cracked gas from pressure distillation of heavy oils	110,000,000,000	36,000,000,000	10,000,000,000	4,000,000,000
Carburetted water gas	14,584,180,000	3,365,580,000	356,558,000	
Oil gas	9,715,600,000	3,643,350,000		
Coal gas	2,297,410,000	74,110,000		
Propane and butane in natural gasoline calculated to gas volumes			1,941,750,000	14,051,000,000
Propane and butane in unblended refinery gasoline, straight run and cracked, calculated to gas volumes			3,301,500,000	12,564,000,000

Summary

	cubic feet
Methane	1,976,994,100,000
Ethane	334,062,610,000
Propane	103,928,477,000
Butane	57,715,000,000
Total	2,472,700,187,000

carbonization of coal, and from carburetted water gas. The volume of methane, ethane, propane and butane available in the United States during the year 1927 was over 2,472,000,000,000 cubic feet.

The present major use of the gaseous paraffin hydrocarbons is for combustion. There are higher uses to which at least a portion of the methane, ethane, propane, and butane present in commercial fuel gases may be put. They may be converted, for example, into useful products such as alcohols, aldehydes, acids and resins by means of oxidation with air, ozone, or chemical reagents.

The volume of the various industrial gases containing methane, ethane, propane, and butane which are available yearly, are shown in table 1.

The volumes of the gaseous paraffin hydrocarbons contained in these gases are shown in table 2.

By oxidation these hydrocarbon gases may be converted into methyl, ethyl, propyl and butyl alcohols, formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde, the acids formic, acetic, propionic, and butyric and resins.

To give an idea of the enormous potentialities of hydrocarbon oxidation, the theoretical yields of methyl, ethyl, propyl and butyl alcohols obtainable from the available gaseous paraffin hydrocarbons have been calculated as follows:

ALCOHOLS	GALLONS
Methyl	21,519,328,930
Ethyl	5,817,493,000
Propyl	2,588,750,000
Butyl	1,754,600,000

To be sure, much study has already been devoted to hydrocarbon oxidation. The reactions are complex and lead to mixtures of products, frequently substances of little value such as oxides of carbon which are obtained in largest amount. But as one analyzes the work which has been done, the impression gained is not that of the completeness, but rather of the fragmentary state of our knowledge. One result of oxidation on a large scale is the production of a mixture of formaldehyde and methyl alcohol from natural gas as a by-product in carbon black manufacture. There is no doubt that many other oxidations can be made useful. The vastness of the field, and the rich rewards awaiting those who can direct these reactions, as yet largely uncontrolled, to the production of useful products, make it an enticing opportunity for research.

The oxidation of the gaseous hydrocarbons has attracted attention at least since the time of Volta (1), who supposed that the aurora borealis might be due to combustion of methane in the air under the influence of lightning. One almost regrets that Davy (2) conclusively disapproved this interesting hypothesis by showing that when diluted with more than seventeen parts of air, methane will not burn.

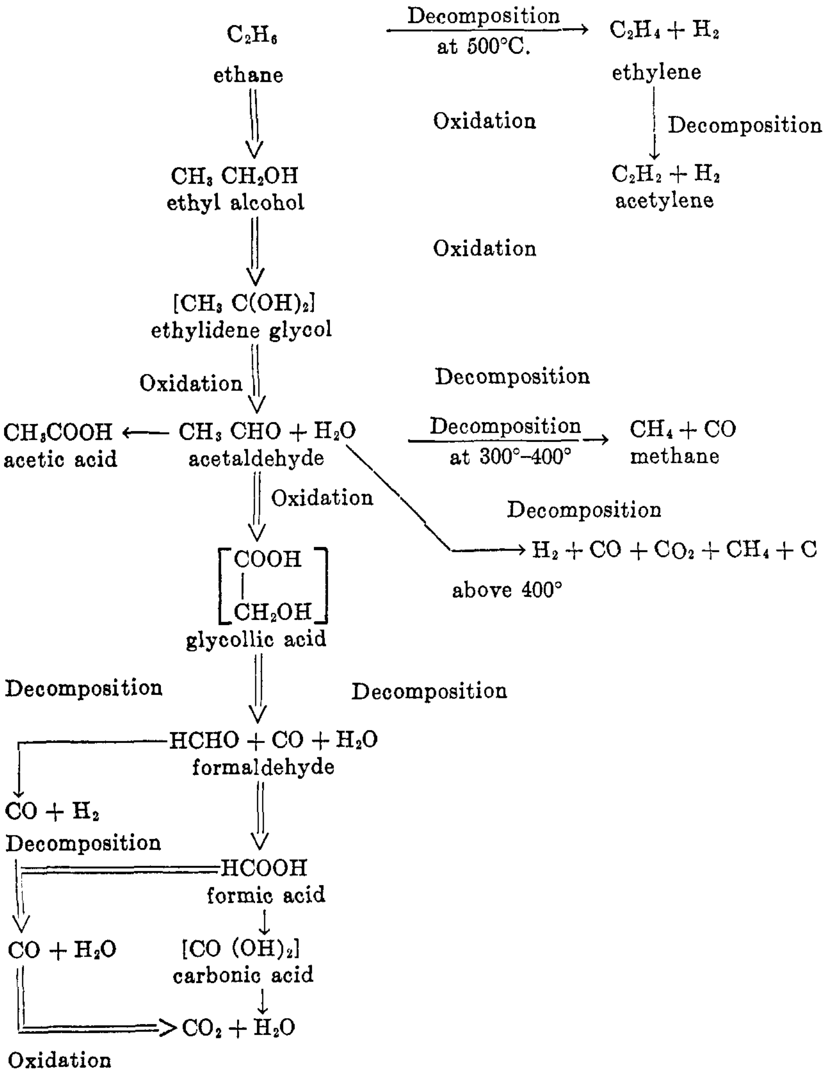
The studies carried on since early times have shown that although the gaseous paraffins do not react with oxygen in anything like the dilutions in which they occur in the atmosphere, they nevertheless undergo diverse oxidation reactions, giving rise to nearly every product theoretically possible. In the literature on their oxidation one finds, in addition to the ultimate products, water and carbon dioxide, the identification of hydrogen, carbon, carbon monoxide, alcohols, aldehydes, acetone, acids, saturated and unsaturated hydrocarbons, resins, (probably aldehyde polymers) and traces of hydrogen peroxide. The difficulty of controlling the reactions to give a single desired product is to be attributed to the greater ease of oxidation of many of the primary oxidation products than of the paraffins used as starting material.

The mechanism of hydrocarbon oxidation which has gained widest acceptance involves the stepwise formation of hydroxyl compounds, each of which may lose water and break down in one or several ways. This theory was put in definite form by Bone (3). As an example of its application the oxidation of ethane is represented graphically in table 3.

One of the most convincing lines of evidence for this oxidation mechanism, according to Bone and Drugman (5), is the formation of water and carbon in rapid hydrocarbon combustion. This is

TABLE 3

Course of the oxidation of ethane



The double lines above indicate the supposed course of the main reactions. Compounds not actually isolated are enclosed in brackets. Table 3 was prepared from the results obtained by Bone (3, 4) and his co-workers.

not consistent with the earlier mechanism proposed by Kersten (6) and revived by Misteli (7) which involved the preferential combustion of carbon. Bone and Drugman (5) write that two explanations seem possible to account for the appearance of water and carbon when a mixture of the composition $C_nH_{2n+2} + \frac{n}{2} O_2$ is exploded, "namely, (1) that, as at lower temperatures, an aldehyde and steam are formed at an early stage, for example:

$$CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2OH \rightarrow CH_3CH_2CH(OH)_2 \rightarrow CH_3CH_2CHO + H_2O$$

the aldehyde would then probably decompose, yielding carbon monoxide and the lower paraffin, and a similar process would be repeated until at length acetaldehyde would break down into carbon, hydrogen, methane, and carbonic acid; or (2) that the primary oxidation product $C_nH_{2n+1}OH$ might decompose into $C_nH_{2n} + H_2O$, the olefin subsequently being burnt in its own peculiar way. In either case, the end result with a mixture $C_nH_{2n+2} + \frac{n}{2} O_2$ would be much the same."

A stumbling block in the way of the unquestioned acceptance of the hydroxylation theory is the failure of Bone, in spite of careful search, to isolate methyl alcohol as a product of the oxidation of methane by oxygen or air, although formaldehyde was found in sufficient amounts to allow its easy identification. Indeed, Wheeler and Blair (8), although favoring the theory of Bone, write "an excess of oxygen inhibits the oxidation of methane little, if any, more than an excess of methane, so that if the law of mass action applies, the equimolecular reaction to formaldehyde would seem to be occurring." In view, therefore, of the lack of absolute proof of Bone's oxidation mechanism, one may fairly ask whether some of the other oxidation theories do not fit many of the experimental facts equally well. The idea of oxidation by dehydrogenation so successfully applied by Wieland (9) to the oxidation of alcohols and to many other oxidation processes may here find application. Or dissociation, as postulated by Nef (10) may be involved. Callendar (11) has brought forward proof that knocking in the cylinder of an internal combustion engine is due to the formation of organic peroxides. Such peroxide formation may be a step in other hydrocarbon oxidation processes.

Most of the investigations on gaseous paraffin oxidation have been carried out by the simple heating of the hydrocarbon mixed with oxygen or air. Considerable study has been made also of catalytic oxidation, of oxidation with chemical reagents, of ozone oxidation and of oxidation by such special means as the silent electric discharge, alpha radiation and bacteria.

Flame propagation with the related subjects of ignition temperatures and the limits of inflammability of gaseous mixtures are, strictly speaking, phases of hydrocarbon oxidation, but as these topics will be discussed fully in another paper on the physical and chemical constants of the paraffins, they are given here but this brief mention.

2. THE OXIDATION OF METHANE

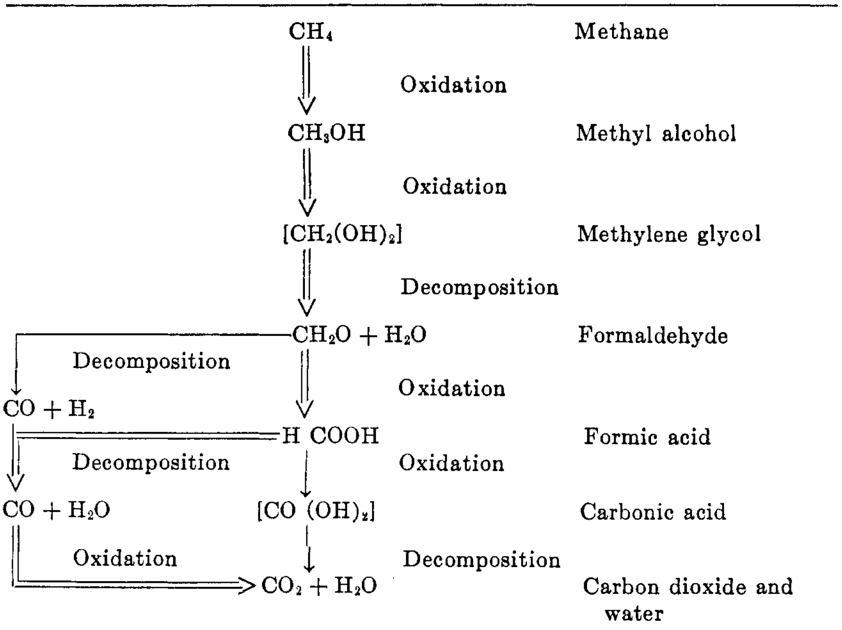
a. General

Carbon monoxide, carbon dioxide and water have usually been the chief products obtained in the many experiments which have been made on the slow oxidation of methane. Bone and his coworkers proved, however, that formaldehyde is formed in the early stages of the oxidation, and in some of their experiments they also detected formic acid. Winter (12) obtained small amounts of free carbon when purified mine gas (methane 80 per cent, nitrogen 20 per cent) was exploded with air or oxgyen. According to him, the free carbon did not arise from the incomplete combustion of methane, but from an equilibrium in which carbon dioxide and hydrogen participated. Hydrogen often appears in the reaction when an amount of oxygen insufficient for complete combustion is used. None of the earlier work showed methyl alcohol to be in the oxidation products of methane, but in 1922 Elworthy (13) stated that under the action of the silent electric discharge, mixtures of methane and oxygen gave a viscous liquid containing methyl alcohol, along with formaldehyde, polymerized aldehydes, resins, and formic acid. The formation of other aldehydes and of resins may be due to the polymerization of formaldehyde, which under favorable conditions is produced in relatively large quantities. Aldehydes, formic acid and traces of alcohols have also been produced by the oxidation of methane with ozone.

This variety of oxidation products is readily accounted for by the hydroxylation theory of Bone. The course of the slow oxidation of methane according to Bone's theory is shown in table 4, which is the outline form constructed by Wheeler and Blair (14).

TABLE 4

Course of the oxidation of methane



Double lines show the usual course of the oxidation. Compounds that have not been isolated are enclosed in brackets.

b. Oxidation by oxygen and air

The numerous investigations which have been made of the oxidation of methane will be taken up in approximately chronological order.

In 1861, as a part of work on the luminosity of gas flames, Kersten (6) made a careful study of the complete and incomplete combustion of methane. He concluded that while at times some free carbon forms, the carbon is normally oxidized to carbon monoxide before the hydrogen is reacted upon.

Schlegel (15) burned mixtures of methane with oxygen and chlorine, writing for the reaction the equation:

$$CH_4 + 2O_2 + 2Cl_2 = CO_2 + 4HCl + O_2$$

The combustion was preferential, the oxygen combining with the hydrogen only when there was a deficiency of chlorine, while no reaction of chlorine and carbon occurred. With insufficient oxygen for complete combustion, carbon monoxide was formed.

By continuously removing the products of the reaction from an apparatus devised to circulate methane and oxygen at 450°–500°, Bone and Wheeler (16) were able to show that neither hydrogen nor carbon was formed at any stage in the oxidation, and that although the final products of the reaction were normally carbon monoxide, carbon dioxide and water, there was a transient formation of formaldehyde. They were able to obtain this substance in amounts up to 22 per cent of the methane reacting, when it was removed from the sphere of action as rapidly as produced by passing the reaction mixture through cold water immediately on leaving the heating zone.

These workers concluded that the oxidation of methane involved the following steps:

1. The simultaneous formation of formaldehyde and water:

$$CH_4 + O_2 \longrightarrow HCHO + H_2O$$

2. The further oxidation of the formaldehyde to carbon monoxide, carbon dioxide and water:

$$\begin{aligned} HCHO + O_2 &\longrightarrow CO_2 + H_2O \\ 2HCHO + O_2 &\longrightarrow 2CO + 2H_2O \end{aligned}$$

A later paper by Bone (17) dealt with the incomplete burning of methane to carbon monoxide and hydrogen.

Using this work as substantiation, Armstrong (18) claimed that the slow oxidation of methane was a series of hydroxylations in which water entered into the reaction and hydrogen peroxide was formed:

$$CH_4 + O_2 + H_2O = CH_3OH + H_2O_2$$
$$CH_3OH + O_2 + H_2O = CH_2(OH)_2 + H_2O_2;\ CH_2(OH)_2 = HCHO + H_2O$$
$$CH_2(OH)_2 + O_2 + H_2O = CH(OH)_3 + H_2O_2;\ CH(OH)_3 = HCOOH + H_2O$$
$$CH(OH)_3 + O_2 + H_2O = C(OH)_4 + H_2O_2;\ C(OH)_4 = CO_2 + 2H_2O$$

This would make carbon monoxide a secondary product, not resulting directly from the oxidation of methane. The validity of Armstrong's mechanism was brought into question, however, by the work of Bone and Andrew (19) on acetylene, which showed that water was not essential to hydrocarbon oxidations.

In the work of Wheeler and Blair (14), carefully purified methane mixed with oxygen was similarly passed through a circulating system in which it was repeatedly heated and the products of reaction promptly removed from the gas mixtures. They state: "A short time of heating and a slow oxidation are the principal factors in obtaining a good yield of formaldehyde. If the oxidation be vigorous it is formed in such a large proportion that it rapidly decomposes. A long time of heating has similar effects." The amount of formaldehyde isolated from the mixture after oxidation varied from 0.25 mgm. per liter of gas passed through the apparatus at 665° and a time of heating of 0.8 second to 2.9 mgm. at 740° with the same heating period or 720° when the gas was heated one second. Far larger amounts of formaldehyde than this were formed, but decomposed in the process to carbon monoxide and hydrogen. The time of heating had least effect on the yield of formaldehyde when methane was present in excess, as the lower the concentration of this product the greater its stability. At high temperature an excess of methane and the presence of steam both tended to increase the yield.

In experiments without circulation of the gas mixture a little formaldehyde was formed up to 820°, but above this temperature its presence could not be established, probably because of its rapid decomposition.

In a second paper Wheeler and Blair (20) reported studies, carried out by means of a circulation apparatus, following the action of oxygen on mixtures of methane and ethylene and their primary oxidation products. Coal gas, which contained these hydrocarbons in about the desired proportions and also considerable amounts of carbon monoxide and hydrogen, was diluted with about one-fifth of its volume of nitrogen to increase its explosive range, and as much oxygen added as was possible without rendering the mixture explosive. The mixture was then heated.

> "As the temperature rises, first one and then another constituent commences to interact, and the rates of interaction rapidly increase until they appear to come into a constant ratio to one another. A comparison of these rates shows how it is that carbon monoxide and water are the chief products of the slow oxidation of methane under conditions in which formaldehyde decomposes, for at these temperatures and times of heating hydrogen is first attacked, next methane, and then carbon monoxide. The rapid increase at high temperatures in the rate of oxidation of carbon monoxide explains the presence of carbon dioxide in the products at such temperatures."
>
> "The rates of oxidation of the hydrocarbons are not affected by the presence of intermediate products, although these dilute the reaction mixture. The yield of formaldehyde was slightly lower in these experiments than that obtained with methane, probably owing to the ethylene present giving a lower yield than methane. Decomposition of formaldehyde may also be induced by simultaneous oxidation of hydrogen, etc."

The yield of formaldehyde varied with the temperature and time of heating much as in the earlier experiments.

Bone and Drugman (3) showed that methane may be oxidized below its ignition point, and that water and formaldehyde are among the first reaction products.

Wieland (9) presented the hypothesis that the formic acid which could be detected in the methane flame was probably formed by the decomposition of the methane into carbon and hydrogen and the immediate reaction of the carbon with water to give carbon monoxide, which was then converted into the acid. When moist methane was passed through a hot tube, it yielded carbon dioxide and hydrogen.

Burgess and Wheeler (21) observed in the study of several mixtures of oxygen and methane that as the proportion of oxygen was increased, more and more of the hydrocarbon was completely burned. With one and one-half times as much oxygen as methane present, half of the methane burned to carbon dioxide and the balance to carbon monoxide, while with the oxygen present in less than this ratio the main reaction was represented by the equation:

$$CH_4 + O_2 = CO + H_2 + H_2O.$$

These investigators held that there was a preferential burning of hydrogen rather than of carbon monoxide in all the mixtures in which the ratio of oxygen to methane was greater than 1.5. They also reported that the propagation of flame in limit mixtures formed carbon monoxide, hydrogen and steam in equal volumes.

Several patented processes cover the preparation of formaldehyde by the incomplete combustion of methane-air mixtures. In the method of Gruszkiewicz (22), a flame is formed by the partial combustion of the gas mixture beneath and partially within a perforated reaction tube closed at the top. The tube is preferably surrounded by a cooling vessel to reduce the temperature of the gaseous oxidation products immediately after their exit from the tube. The stream of hydrocarbon and air coming to the flame is heated to effect a rapid oxidation.

Lüttgen (23) also cooled the burner tube of a perforated Bunsen burner and interrupted the flame by devices to lower the temperature of the gases. A similar idea inspired the patent of Kunheim (24) in which the gases formed in a methane flame were quickly cooled by directing a jet of gaseous or liquid cooling medium against the flame. Behrens (25) claimed the preparation of formaldehyde by heating methane with a quantity of oxygen insufficient for complete combustion, the reaction being controlled by regulation of the amount of heat supplied. In Walter's (26) method, a mixture of methane, air and water vapor was subjected to high temperature for a short period. The same worker (27) proved in a simple fashion the production of formaldehyde when methane burns by allowing a small methane flame to impinge against snow or cold water, which was then tested for the aldehyde.

In a patent of the I. G.-Farbenindustrie Akt.-Ges. (28), methane, heated to 900° is passed into a flame zone in a quartz tube, where it meets a divided stream of oxygen. Besides unconverted methane, the resultant gaseous mixture contains water vapor, hydrogen, carbon monoxide and acetylene. As an alternative apparatus an iron tube lined with a refractory material and filled with lumps of a porous substance over part of its length may be employed. The yield of acetylene is increased if the products leaving the tube, whose temperature approximates 1000° are heated to 1200° in an electric furnace.

Berl and Fischer (29) investigated the oxidation of methane by air between 500° and 900°, passing various mixtures through heated tubes. A maximum of 1.8 per cent of the methane was converted to formaldehyde.

Tropsch and Roelen (30) passed mixtures of methane and air through quartz tubes heated in an oven. The formaldehyde produced was absorbed in water and determined by titration with standard iodine solution. They studied the effects of varying the methane-oxygen ratio in the gas, the diameter of the tube, the reaction temperature, and the velocity of the gas through the tube. The optimum concentration of methane for the formation of formaldehyde was 16 per cent, which at a temperature of 1000° gave 1.2 per cent of the theoretical yield. The best results were obtained with tubes 4.0 mm. in diameter and with a gas velocity of twenty meters per second, the gas being in the heated tubes about one one-thousandth of a second. The highest concentration of formaldehyde was obtained with equal volumes of methane and oxygen. With increase in the reaction temperatures, the absolute quantity of formaldehyde produced became greater, but the yield per unit of methane decomposed diminished. Based on the total methane entering the system the best yield of formaldehyde was 5.96 per cent at 1000°. Of the methane actually burned, 70 per cent could be converted into formaldehyde at 700°, but the formaldehyde concentration in the products was extremely low.

Brutzkus (31) invented a process for oxidizing methane to formic acid within the cylinder of a power driven compressor. The hydrocarbon and oxygen, in combining proportions, were introduced into the compressor at such a rate that when the piston had completed two-thirds of its stroke the gases were under a pressure of thirty atmospheres and at a temperature of nearly 500°. During the remainder of the stroke, air, independently compressed to forty-five atmospheres, was introduced into the cylinder in a finely divided stream to produce a cooling effect and to increase the oxygen content. At the end of the compression stroke the gases were discharged and the formic acid was absorbed by water. The residual gases were then drawn back into the system to be retreated.

Bone, Davies, Gray, Henstock, and Dawson (32) exploded mixtures of methane and oxygen at constant volume under pressures of ten to fifty atmospheres. They formulated the reaction according to the mechanism of Bone and Drugman (3) as follows:

$$CH_4 + O_2 \rightarrow [H_2C(OH)_2] \rightarrow HCHO + H_2O \rightarrow H_2 + CO + H_2O$$

They also investigated methane-hydrogen, and methane-carbon monoxide mixtures, and showed that the "affinity" (really reaction velocity) of methane for oxygen in explosions was at least twenty to thirty times as great as that of hydrogen.

Winter (12) found that in the explosive combustion of methane-air mixtures containing 5.0 to 9.2 per cent methane the oxidation was essentially complete, while with from 9.2 to 14 per cent methane the products of combustion always contained carbon monoxide. The maximum of the explosion lay at 9.2 per cent methane rather than at the theoretical 9.5 per cent, a slight excess of oxygen being necessary for complete combustion.

Ledbury and Blair (33) have pointed out that for the preparation of formaldehyde from methane on a commercial scale, the use of oxygen rather than air is essential, since the presence of diluents hinders the reaction at temperatures which give good yields. In order to conserve oxygen, as well as methane, they recommend that the oxidation be carried out in a circulating system, gas being withdrawn periodically and fresh methane and oxygen admitted to ensure suitable concentrations of the reactants.

From the results of their laboratory experiments, these investigators have stated the conditions suitable for the production from methane of one ton of formalin per twenty-four hours. A mixture having the initial composition of approximately 80 per cent methane and 20 per cent oxygen would be cirulated, passing through heating and absorbing zones. A temperature of 700° and time of heating of one second are suggested, which should give about 2 mgm. of formaldehyde per liter of gases leaving the reaction zone. It is estimated that 30 per cent of the methane consumed could be recovered as formaldehyde. A volume of methane amounting to 128,000 cubic feet, and 69,000 cubic feet of oxygen would be required per day. The cost of operation is estimated at $180 per ton of formalin exclusive of the cost of methane. It is quite apparent that as far as their process is concerned their statement is true that: "The oxidation of methane on a technical scale for the manufacture of formalin can only be considered as an economic proposition if methane is obtainable in quantity at a low or even nominal cost." It is believed, however, that a far more efficient process than this can be devised, even with the present state of our knowledge of oxidation.

c. *Catalytic oxidation*

Much study has been given to the action of catalysts in promoting the reaction between oxygen and methane. A large proportion of the oxidation processes which have been proposed for commercial application are catalytic. The catalysts that have been employed cover a wide field, ranging from pumice, asbestos, and sand to the noble metals and even to the alpha radiation of radon. As a rule, the catalyzed oxidations are controlled more easily than those not catalyzed.

A recent editorial (34) appearing in Industrial and Engineering Chemistry states that thousands of gallons of methyl alcohol are being produced daily by the catalytic oxidation of natural gas. The details of this process are not disclosed.

A process of oxidizing natural gas is reported briefly in the Refiner (35) as follows:

> "The process is one to catalytically produce methyl alcohol from natural gas, and at the same time conditions of heat and pressure are productive of oil falling in the gasoline range of boiling points. Conversion is effected at proper temperature conditions of pressure and temperature in both steam and natural gas in the presence of a catalytic agent. Field tests which led to the construction of the commercial unit resulted in the yield of 2.5 gallons of methyl alcohol and 2 gallons of oils per thousand cubic feet of gas passed through the system. High pressure equipment of special design is employed."

It was privately stated to the authors during the meeting of the American Chemical Society at St. Louis in April, 1928, that a mixture of methyl alcohol and formaldehyde was being recovered commercially from stack gases produced during the production of carbon black.

Coquillion (36) early found that in the presence of a red hot spiral of platinum or palladium, methane and air yielded formic acid. The palladium was the more powerful catalyst, although after a while it became brittle and lost weight. Because of its importance in the separation of hydrogen and methane in gas analysis, oxidation by palladium has been investigated repeatedly. Hempel (37) reported that methane and oxygen did not burn when passed over palladium at 100°, but that the reaction began at 200°. Winkler (38) stated that methane was not burned when passed over palladium asbestos in a tube heated to incipient redness before introduction of the gas stream while Brunck (39) reported that in this method the thread of catalyst might glow without causing oxidation of methane. On the other hand, Nesmjelow (40) claimed that palladium asbestos oxidized methane at as low a temperature as 150°. Phillips (41) found the lowest temperature for the combustion of methane in the presence of this catalyst to be between 405° and 451°. Denham (42) gave the beginning of oxidation as lying within the range 514° to 546° and proved that the catalytic action of the palladium was not due to superficial oxidation. After a very careful investigation, Richardt (43) concluded that by using palladium wire at 450°, little noticeable oxidation of methane took place, but at 700° there was rapid combustion. Probably the conflict between the results of these different investigators is due to the fact that as a rule no clear distinction was made between the temperature of the vessel containing the catalytic mass and the temperature of the center of the catalyst. Besides this, sometimes palladium wire was used, at times palladium asbestos in a fine capillary tube and in other experiments palladium black in a tube of large diameter. These differences in the experimental methods would naturally lead to discordant results.

Campbell (44) found that methane mixed with air was not oxidized when passed over palladized copper oxide at temperatures below 455°.

A large share of the work on the catalytic oxidation of methane has had as its goal the preparation of formaldehyde. This is particularly true of the numerous processes covered by patents. These have been summarized by Roelen (45).

Glock (46) obtained formaldehyde from methane and air by passing equal volumes of the two gases over granulated copper. He also prepared this aldehyde by reaction of methane with oxygen in the presence of pumice, asbestos or a mixture of these with copper at about 600°. The several passages of the gas mixtures over the catalyst were interrupted by scrubbing and addition of air. No formaldehyde or methyl alcohol was produced when platinum was used as an oxidation catalyst, though this metal was satisfactorily used for removing hydrogen from the mixture by preferential combustion.

The Sauerstoff und Stickstoff-Industrie, Hausman and Company (47) patented a process for making formaldehyde and also methyl alcohol and formic acid by passing methane and air or oxygen over bark or fatty substances at 30 to 50°. However, this scarcely plausible procedure, when tested by Bantlin (48) yielded no trace of formaldehyde. Von Unruh (49) also employed tan bark and similar materials for oxidation of methane to methyl alcohol, formic acid, and formaldehyde, the last being claimed as the chief product.

In 1912, in a publication on the Chemical Technology of Organic Compounds, Wöhler (50) stated that all the experiments on the commercial oxidation of methane to formaldehyde up to that time had been unsuccessful in spite of the need for this product, and the enormous waste of natural gas then occurring. In tests which he described, the oxidation of methane by passing it over nickel or silver gauze at a temperature of 500 to 550° gave only 1 to 2 per cent of formaldehyde. Above this temperature the reaction was of no value. He attributed this failure to the fact that at the temperatures mentioned or above them, the decomposition of methyl alcohol, the primary product of the oxidation, was very rapid, while at lower temperatures its velocity of formation was too low for the process to be of any utility.

A patent of the Verein für chemische Industrie in Mainz (51) claims the formation of a small proportion of formaldehyde when a mixture of about three parts of methane and one hundred parts of moist air is conducted over a metallic surface of copper or silver, for example, at 150° to 200°.

Bone (52) observed that approximately eighty per cent combustion of the hydrogen occurred when a mixture of methane, oxygen, and hydrogen in the molecular proportions 1:1:2 was passed over chamotte at 500°. It is interesting to compare these results with those of Bone, Davies, Gray, Henstock and Dawson (32), on the explosion of methane, hydrogen and oxygen mixtures. In their work, the methane reacted with the oxygen at a very much higher rate than did the hydrogen.

Wheeler and Blair (14) extended their experiments on the direct oxidation of methane to include the use of catalysts. In the oxidation of this hydrocarbon in the presence of metals and their oxides, even with a very short time of heating, they could detect no formaldehyde. "This is not surprising. The formaldehyde produced in our circulation experiments is in a concentration much greater than that given by the equation:

$$HCHO \longrightarrow H_2 + CO$$

The rapid cooling enables it to be isolated before equilibrium is attained or further oxidation can occur. But with catalysts the true equilibrium is attained almost instantly at the temperatures necessary to oxidize methane. The composition of the final gas, however, leads us to believe that catalysts do not change the course of the oxidation of methane, and that with very high rates of gas passage . . . . some formaldehyde might be detected in the exit gases. . . . . The action of surfaces was similar to that of catalysts, but much less pronounced. Formaldehyde was frequently detected when they were used."

These investigators (20) also studied the effect of catalysts on the oxidation of methane and ethylene mixed with their primary oxidation products. They found that using pumice, at low temperatures, the oxidation and decomposition of the intermediate products were accelerated more than the oxidation of the hydrocarbons themselves, while at high temperatures the rate of oxidation of the latter increased, so that hydrogen and carbon monoxide accumulated. Similar results were obtained using ferric oxide as catalyst. By using mercury the oxidation of ethylene, carbon monoxide and hydrogen was accelerated, but not that of methane.

A process patented by H. Otto Traun's Forschungs-Laboratorium (53) consisted in oxidizing methane or natural gas in the presence of ammonia in tubes of copper, silver, nickel-steel, iron or its alloys at a high temperature to give hexamethylene tetramine. In an example, six volumes of methane and twelve volumes of oxygen or a corresponding quantity of air were mixed with four volumes of ammonia and passed through a reaction space within a copper or silver tube, which had been pressed flat; for a distance of about 8 cm., from a normal diameter of 15 mm. to a separation of the walls of from 1 to 2 mm. throughout the constricted portion. When the reaction was carried out at reduced pressures, the flat portion of the tube was heated to 500° to 700°, but when the gases were allowed to interact at ordinary pressure it was found advisable not to have temperatures higher than 300° to 500°. The yield of hexamethylene tetramine was said to be approximately 70 per cent of the methane decomposed. Schönfelder (54) however, was unable to carry out this process successfully, and Wheeler and Blair (14) stated that while ammonia has some stablizing effect on the formic acid produced in methane oxidation, it does not stabilize formaldehyde.

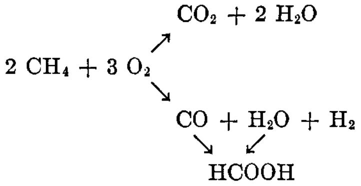
According to a patent of the Thermal Industrial and Chemical Research Company (55) the partial oxidation of methane may be accomplished by passing a mixture of sixty to eighty volumes of methane and forty to twenty volumes of air (or its equivalent of oxygen) in the form of fine bubbles through molten metal heated to 350° to 400°. The unchanged gases and the vapors of formaldehyde which escape from the reaction vessel are then treated to collect the formaldehyde.

Elworthy (13) found that passing natural gas (containing eighty per cent methane) and oxygen over such catalysts as magnetite and other oxides of iron, oxides of copper, silver, thorium, cobalt, vanadium, and uranium, borosilicate glass, and platinum gave traces of formaldehyde. The only partial oxidation which he found to give promise of commercial value, however, was the action of the silent electric discharge on mixtures of natural gas and oxygen. This produced a viscous liquid containing methyl alcohol, formaldehyde, formic acid, polymerized aldehydes, and resins. These results may well be compared with those described later in this paper on the action of ozone on methane.

A patent of Selden (56) covered the use of vanadium peroxide as a catalyst for the oxidation of methane to formaldehyde, while Wöhl (57) claimed the use of vanadic acid, molybdic acid and a number of other substances at temperatures below red heat. Müller (58) patented the preparation of formaldehyde from methane by the use at 150° of cerous cobalt nitrate as the oxidation catalyst.

The Bakelite Gesellschaft and R. Hessen (59) stated that methyl alcohol and formaldehyde might be manufactured by heating methane with excess oxygen, air, or ozonized air at red heat (600° to 1000°) under pressure in the presence of porous non-metallic inorganic contact material such as pumice, brick, earthenware fragments, highly porous slag, asbestos, quartz sand, or slag wool. Immediately after the reaction had taken place, the pressure was reduced and the methyl alcohol and formaldehyde condensed by a stream of air or gas flowing in a direction opposite to that of the hot gases. When working either at ordinary or elevated temperature, it was found advantageous to add to the catalyst, either in layers or mixed with it, substances which take up water, and give it up again at high temperatures, such as the oxides and hydroxides of the alkalies or alkaline earths, magnesium or calcium chlorides, or anhydrous copper sulfate.

Nielsen (60) conducted methane over a catalyst consisting of metallic oxides at temperatures above 200°. He formulated the reactions occurring as follows:



$$\begin{tikzcd} & CO_2 + 2\,H_2O \\ 2\,CH_4 + 3\,O_2 \arrow[ur] \arrow[dr] & \\ & CO + H_2O + H_2 \arrow[d] \\ & HCOOH \end{tikzcd}$$

The reaction temperatures ranged between 200° and 500°. After a short period, apparently corresponding to the consumption of a certain fraction of the oxygen present in the oxide, the reaction always stopped and the methane came over unchanged.

Nielsen and Laing (61) prepared formic acid from a gas mixture containing methane by passing it at a temperature of 250° to 800° over a metallic oxide catalyst consisting of activated copper suboxide. This was prepared by roasting in air the copper obtained by precipitating copper sulfate with zinc.

Mittasch, Willfroth and Balz (61a) claimed that the oxidation of methane is effected by passing the gas mixed with various amounts of oxygen at about 575° "over a contact mass prepared by impregnating burnt clay with a solution of boric acid, or phosphoric acid, and heating subsequently, or by mixing boric acid, or phosphoric acid, or salts of them, with diatomaceous earth and heating to red heat."

Medvedev (62) investigated the oxidation of methane by atmospheric oxygen using the phosphates and borates of tin as catalysts. The effectiveness of the borates depended upon the presence of hydrogen chloride in the reaction mixture, and their catalytic power decreased as the hydrogen chloride initially present was gradually dissipated. Medvedev showed also that in the absence of hydrogen chloride only about 2 per cent of the methane was decomposed, whereas the addition of 4 per cent of hydrogen chloride caused the decomposition of 27 per cent of the hydrocarbon. In the presence of low concentrations of hydrogen chloride, formaldehyde was the main product, while higher concentration gave chiefly carbon monoxide. The best catalyst for the production of formaldehyde proved to be a mixture of phosphates of aluminum, tin and iron. Using this material and a gas mixture having the composition, methane 58.2 per cent, oxygen 26.1 per cent, nitrogen 8.7 per cent, hydrogen 6.96 per cent and hydrogen chloride 0.13 per cent at a temperature of 600°, methane amounting to 6.7 per cent of the total volume was decomposed, half of it being converted into formaldehyde, perhaps by the intermediate liberation of chlorine and chlorination of the methane. When a large excess of hydrogen chloride was used, about 90 per cent of the methane was converted into carbon monoxide, conditions then being favorable to maximum decomposition of formaldehyde. In order to obtain the largest yields of formaldehyde it was found advisable to carry out the oxidation in a series of communicating tubes rather than in a single tube.

In an earlier investigation on the oxidation of methane to formaldehyde, Medvedev (63) used gold, platinum, manganic oxide, nickelous oxide, aluminum oxide, cupric oxide, silver oxide, lead monoxide, and cerium dioxide catalysts on an asbestos base. Carbon dioxide alone was obtained with low rates of flow (3 liters per hour) and at low temperatures (250° to 350°). At moderate temperatures, manganic oxide was the most, and cupric oxide the least active catalyst. At temperatures, above 500° and with a rate of flow of 1 liter per minute, cupric oxide produced traces of formaldehyde and a little carbon monoxide, while the other catalysts did not. A large yield of formaldehyde was produced in the presence of glass surfaces at 600°, which was attributed to the fact that the low chemical activity of such surfaces made them unable to form peroxides. In the case of metals and their oxides, the formation of peroxides was thought to be the reason for the oxidation going farther than the formaldehyde stage. Catalysts consisting of the borates and phosphates of lead, alone or in mixtures gave the highest yields of formaldehyde at 500° to 700°. The activity of these catalysts seemed due to the presence of volatile impurities, such as lead chloride, since a long series of experiments showed that even a small concentration of hydrogen chloride (0.13 per cent) in the gases was very beneficial in raising the yield of formaldehyde. Medvedev obtained higher yields of formaldehyde than most investigators. At 600°, from a mixture containing 13.8 per cent of methane and 17.98 per cent of oxygen with a velocity of flow of 0.23 liter per minute, the yield of formaldehydes was equivalent to 5.02 per cent of the methane passed through the apparatus.

James (63a) obtained aldehydes and acids by the oxidation of natural gas containing methane and also ethane, propane and butane in the presence of catalysts, the best of which was molybdic oxide, "but . . . . other oxides and compounds of the high melting point electro-negative low atomic volume metals, such as molybdenum, vanadium, manganese, tungsten, uranium, chromium, titanium, zirconium and thorium may be used." Silver oxide could be used also as a catalyst. The oxidation reaction could be carried out at a lower temperature if the air was first passed through an ozonizer. The oxides could be mixed with each other or compounds of one metal with another could be used. With natural gas or methane molybdic oxide was most active at 550°, while the reaction was less either below or above this temperature.

The gas mixture was passed through a layer of the catalyst supported on wire gauze in an externally heated reaction vessel. At 550° the ratio of gas to air should not be over 1:3.5, and preferably 1:1. A rate of flow of 2 liters per minute was the best for the 1:1 mixture. This rate gave about one second for a molecule of the gas to pass the catalyst layer.

Formaldehyde, formic acid and water were obtained as products of the oxidation of methane. Under the best conditions the formaldehyde isolated, amounted to 6.75 per cent based on the weight of methane treated.

Schönfelder (54) found that when methane was passed with steam and air over copper or silver heated to 500°, 55 to 58 per cent of the hydrocarbon was oxidized to formaldehyde, and 10 to 20 per cent to carbon monoxide, carbon dioxide, and water, while 25 to 40 per cent remained unchanged. By the use of other metallic catalysts, activated carbon, or the silent electric discharge, a considerable amount of formaldehyde could be obtained from methane and air, but the quantities produced were too small to make the process a commercial possibility.

Layng and Soukup (64) investigated the catalytic partial oxidation of various mixtures of natural gas, methane and ethane with oxygen by passing the mixtures through capillary tubes heated to 100° to 700°C. The solid catalysts used were mounted in the heated portion of the system while gaseous catalysts were mixed with the influent gas mixture before admitting it into the reaction chamber. After passage through the chamber the effluent gases were rapidly cooled, the intermediate products were removed by condensation and scrubbing, and the gases were then passed into a reservoir where they were accurately measured and analyzed. The initial and final gas compositions were determined by analysis in a modified Orsat apparatus.

In the analysis of intermediate products from methane oxidation, formic acid was determined by permanganate titration of residual liquors after removal of formaldehyde and methanol by distillation. Formaldehyde was determined separately in an aliquot part of the distillate obtained by neutralizing the combined condensate and wash water and removing formaldehyde and methanol by distillation. The aldehyde was determined either by the iodometric or hydroxylamine hydrochloride titration method. Methanol was estimated from the amount of standard permanganate solution required for the oxidation of both methanol and formaldehyde in another similar portion of the distillate.

Catalysts of copper and silver, their oxides, activated charcoal, platinum oxide and barium peroxide were unsatisfactory for the production of alcoholic and aldehydic intermediates on the basis of the hydrocarbon consumed and products obtained.

Oxides of nitrogen may also be used as oxygen carriers in the conversion of methane into formaldehyde. In the patent of Bibb, (65), air charged with one to two per cent by weight of nitric acid fumes, and mixed with one-fifth of its volume of methane, is preheated to about 200° and then subjected to a temperature of from 250° to 560°, preferably in a chamber containing broken pieces of fire clay. Rapid reaction ensues, practically all the methane being converted in eight seconds into formaldehyde and other oxidation products including methyl alcohol and formic acid in minute amounts. After the removal of the products by scrubbing, the residual gases, still containing oxides of nitrogen, may be recirculated. In place of methane, natural gas may be used in the process.

Reis and Waldbauer (66) found abundant formation of formaldehyde in the flame produced by burning a mixture of methane with nitric oxide or nitrogen peroxide.

When Layng and Soukup (64) added small amounts of nitrogen dioxide to mixtures of methane and oxygen, and ethane and oxygen and passed the mixtures through heated capillary tubes, the oxidations were promoted materially by the nitrogen dioxide. Yields of oxygenated derivatives were obtained varying from fifteen to thirty per cent by volume of the amount of hydrocarbon used.

They made experiments also on a large scale with nitrogen dioxide as catalyst in order to obtain data on the character of oxygenated derivatives formed in these oxidation reactions carried out in a semi-continuous apparatus. "In a typical series of experiments, using pure methane as the hydrocarbon source, four passages of the gas through the system (adding oxygen before each pass in order to maintain a constant oxygen: hydrocarbon ratio) resulted in a yield of oxygenated derivatives amounting to 25 mgm. methanol, 205 mgm. formaldehyde, and 76 mgm. formic acid per liter (standard conditions) of methane decomposed."

Methyl nitrite in concentrations of one to two per cent exerted a promoting action less vigorous than that of nitrogen peroxide but more pronounced than that of the other catalysts investigated by Layng and Soukup under approximately similar operating conditions. The promoting action of five per cent of hydrogen chloride was less than that obtained by Medvedev (63). This difference can probably be explained by the additional contact catalysts employed by Medvedev.

Voss (67) reviewed the patents of Glock (46), Hausman (47), Bibb (65), and Plauson (68), which deal with the direct oxidation of methane to methyl alcohol. The first three of these have been discussed earlier in this paper. Plauson used carbon dioxide as an oxygen carrier of mild action. By heating methane and carbon dioxide in the presence of such catalysts as copper, silver, and nickel, or alloys of these metals with one another or with aluminum, tin or zinc, a mixture of methyl alcohol and formaldehyde was formed. The course of the reaction depended much upon the velocity of flow of the gas mixture; a slow rate of flow favored the formation of methyl alcohol while rapid passage of the gas encouraged the formation of formaldehyde.

By the incomplete combustion of methane, Patart (69) obtained mixtures of carbon monoxide and hydrogen for use in the catalytic production of methyl alcohol and other oxygenated hydrocarbon derivatives. In this method methane was mixed with about half its volume of oxygen and injected into a mass of coke maintained at approximately 1000°. In a later patent (70), he claimed the operation of the process in such a way as to produce the gases in the ratio of two moles of hydrogen to one of carbon monoxide. This mixture was then submitted to the action of pressure and a catalyst in order to form the methyl alcohol and related products.

Yant and Hawk (71) oxidized mixtures containing approximately four per cent of methane in air to carbon dioxide and water, working through the temperature range of 150° to 350° and employing as catalysts a large number of metals and oxides, including uranium oxide, thorium oxide, cerium oxide, platinum black, nickel, platinum and nickel, copper and cobalt, cobaltic oxide, nickel oxide, and a mixture of cobaltic oxide and nickelic oxide with manganese dioxide, ferric oxide and chromic oxide. Cobaltic oxide was the most efficient catalyst while manganese dioxide and nickelic oxide were next in order of effectiveness.

Reyerson and Swearingen (72) tested the catalytic activity of metallized silica gels on the oxidation of methane. Metallic films of platinum, palladium, copper and silver were deposited over the entire surface of the gel by reduction of the respective metallic salts. Mixtures of methane and oxygen containing from 20 to 31 per cent of oxygen and also a mixture containing 73 per cent of that gas were streamed at rates varying from 15 to 200 cc. per minute through an apparent volume of 5 cc. of catalyst at temperatures between 200° and 400°. After reaction, the gases were analyzed for carbon dioxide and oxygen, as preliminary experiments had shown that carbon dioxide was the only oxidation product formed in a sufficient amount to be detected.

In the case of the copper catalyst, apparently it was necessary for some of the copper to be oxidized before it could catalyse the oxidation. The silver catalyst consumed oxygen, probably forming silver oxide, but exerted no catalytic action on the methane. With the platinized and palladized gels there was a limited range of oxygen percentage within which marked catalysis occurred; both below and above this range the oxidation diminished. The platinized catalyst began to be active at 240° while the palladium had no effect below 330°. The platinized gel was the most active of all the catalysts.

A phase of oxidation in which catalysts are of particular importance is the preferential oxidation of gas mixtures. The large amount of work which has been done on the oxidation of hydrogen in the presence of methane by the use of palladium had already been outlined. Bancroft has summarized in two papers what is known regarding preferential oxidation of other mixtures containing methane. One of these (73) considers the influence of cupric oxide, chamotte and borosilicate glass on the combustion of mixtures of hydrogen and methane. Much of the same information is presented in the second paper (74), in which he tabulates the known data on the preferential oxidation of such gas mixtures as follows:

1. In the presence of platinum, hydrogen and ethane burn more readily than methane.
2. In the presence of copper oxide at 250°, all the hydrogen in a methane-hydrogen mixture can be burned without any of the methane being decomposed.
3. In the presence of chamotte at 500°, hydrogen burns much more readily than methane.
4. In borosilicate tubes at 300° to 400° (the work of Bone) methane combines with oxygen with an enormously greater velocity than does hydrogen, while ethane burns much more readily than methane.

5. When mixtures of methane, oxygen and hydrogen or carbon monoxide are exploded by an electric spark, the methane burns much more rapidly than the hydrogen or carbon monoxide.
6. By suitable selection of catalytic agent, it should be possible to get all stages from the complete burning of methane to the complete burning of hydrogen.
7. It seems that methane burns more readily than hydrogen at high temperatures, and in the absence of solid catalytic agents.

What little is known of the influence of radioactive material on methane oxidation is contained in two papers by Lind and Bardwell. In the first brief account of their work (75), they stated that under the influence of the alpha radiation from radon the oxidation of methane proceeded completely to carbon dioxide and water. In the later paper (76) they reported that the oxidation took place in one step, and from the numerical relation between the number of gaseous ions produced and the methane molecules oxidized, they postulated the formation of triplet ion clusters, as shown in the following reaction:

$$(O_2 \cdot CH_4O_2) + (O_2^- \cdot CH_4O_2) \rightarrow 2\ CO_2 + 4H_2O$$

The quantities of oxidation products appearing showed that the gas ions produced 75 per cent of the oxidation theoretically possible. These workers (77) also studied the influence of antiknock reagents and showed that in the presence of alpha radiation from radon, selenium diethyl accelerated the oxidation of methane.

d. Oxidation by ozone

A number of workers have studied the oxidation of methane by ozone. The first experimenters in this field, Houzeau and Renard (78) reported negative results at ordinary temperatures. Maquenne (79) also stated that pure methane did not react with ozone, but he found that when it was mixed with oxygen and subjected to the silent discharge, it yielded formaldehyde and formic acid. Mailfert (80), however, succeeded in oxidizing methane with ozone producing carbon dioxide, formic acid and acetic acid. Otto (81) reported that in the cold, ozone converted methane into formaldehyde, traces of methyl alcohol and formic acid, while formaldehyde and formic acid were produced when the mixture was heated to 100°. Drugman's (82) results were very similar. He found the reaction to be very slight at 15°, but noticeable at 100°. He did not report methyl alcohol in the reaction products.

Ozone apparently does not react at all readily with methane when the hydrocarbon is in great dilution, as Urbain found (83), in searching for the cause of the disappearance of methane from the atmosphere, that in a dilution of one to one hundred, it was very difficult to separate methane from air by ozonization. After circulating the gas mixture through an ozonizer for five hours, he found that but one-third of the methane had been acted upon.

There have already been mentioned the rather incidental use of ozonized air in a patent of the Bakelite Gesellschaft (59) for the production of methyl alcohol and formaldehyde, and the experimentation with the silent electric discharge by Elworthy (13) and by Schönfelder (54).

The most extensive investigations that have been made on this method of methane oxidation are those of Wheeler and Blair (84). They passed a mixture containing three per cent of the hydrocarbon in oxygen through an ozonizer and then led it into hard glass tubes heated to various temperatures in an electric furnace. The gaseous products were washed with water and neutral potassium iodide and then collected in a gas holder over a fifty per cent mixture of glycerol in water. Formaldehyde was the first product isolated from this reaction.

These workers' results are summarized in table 5.

At all temperatures the greater portion of the methane was oxidized to carbon dioxide. No carbon monoxide was detected in any experiment. It is assumed that the ozone oxidized the formaldehyde first formed to formic acid which in turn was oxidized rapidly to carbon dioxide and water. Mixtures containing over 60 per cent of methane in oxygen gave similar results, but because the concentration of ozone was lower, less interaction occurred.

In other experiments oxygen alone was passed through the ozonizer and methane then mixed with it, in the ratio of five volumes of oxygen to one of methane before the methane entered the reaction tube. The reaction was slightly greater than in the first experiments because of the greater concentration of methane. In the presence of catalysts, such as nickel oxide-pumice, aluminum oxide-pumice, ferric oxide-pumice, and platinized asbestos-pumice, the ozone decomposed so rapidly even below 100° that very little oxidation of the methane occurred. Methyl alcohol was not detected among the products in any of these experiments.

Ledbury and Blair (33) believe that an industrial process for the production of formaldehyde by the ozonization of methane has little prospect of success, because of the low yields of formaldehyde, as compared with the amount of ozone consumed. Furthermore, in a large scale circulating system such as would be required, the danger of explosion would be great.

TABLE 5

Ozone oxidation of methane

	EXPERIMENT 1	EXPERIMENT 2	EXPERIMENT 3	EXPERIMENT 4	EXPERIMENT 5
Temperature of reaction tube	10°	100°	200°	300°	400°
Milligrams of formaldehyde produced per liter of mixture used	0.3	0.8	1.5	2.2	0.5
Formic acid	Trace	Trace	Trace	Trace	Trace
Carbon dioxide formed, cc. per liter of mixture used		5	7	6	5
Methane converted into formaldehyde, per cent		9	14	20	9
Ozone reacting, per cent	5	53	76	68	52
Ozone directly decomposed per cent	Nil	15	15	32	48

e. Oxidation of methane by chemical reagents

Though the action of a wide variety of chemical oxidants on methane is reported in the literature, the field has not been worked intensively.

Investigators differ as to the behavior of methane with concentrated sulfuric acid. Aime (85), long ago, stated that concentrated sulfuric acid attacked the hydrocarbon with the formation of water, sulfur dioxide, and carbon. Buckton and Hofmann (86), however, reported no change even at 100°.

On passing mine gas through neutral palladium chloride, Böttger (87) obtained a black precipitate. Phillips (88) later showed, however, that methane alone did not reduce palladium chloride, either when cold or at 100°.

Mueller (89) found that methane reduced ferric oxide to the magnetic oxide at the temperature of a Bunsen flame. At higher temperatures ferrous oxide was formed. Methane reduced the red oxide of manganese, cobalt oxide, copper oxide, and bismuth oxide, the last named slowly; lead peroxide was decomposed explosively, while the oxides of zinc and tin remained unchanged. Darvydowa (90) found that methane did not react with silver oxide up to 150°. A process was patented by Blackmore (91) in which methane was heated with various metallic oxides to form methyl alcohol or formaldehyde. He claimed a yield of 125 pounds of methyl alcohol from 1500 cubic feet of methane at temperature of 127° while at 157° the same amount of methane produced 118 pounds of formaldehyde. The oxides used were ferrous-ferric oxide, cupric oxide, and manganese and barium dioxides.

Ludwig (92) reported that chromic acid had no action on methane. The acid was used in both high and low concentrations, but no change occurred during a week's contact.

Cooke (93) reported the reaction of methane with nitric oxide under the influence of an electric spark, when the volume of the hydrocarbon was "not less than one twentieth nor more than one-eighth of that of the nitric oxide used." The carbon of the methane was entirely oxidized to carbon dioxide. Bailey (94) employed oxides of nitrogen in an oxidation process, in which natural gas or some other gaseous mixture with a high methane content was mixed with two volumes of nitric oxide and sufficient air or oxygen to convert the nitric oxide into nitrogen peroxide. The mixture was then passed through a red hot porcelain tube. Formaldehyde was formed, and its further oxidation was prevented by one of the following expedients: either (1) the gases were quickly cooled by passing them through water containing calcium carbonate in suspension, the calcium carbonate at once decomposing any nitric or nitrous acid that might have formed; or (2) the hot gases were passed over a dehydrating agent such as lime, whereby the water formed during the reaction was absorbed and the formation of acid prevented in this way. Had these acids been permitted to form, they would have oxidized the formaldehyde to carbon dioxide and water. It will be recalled that Bibb (65) and also Reis and Waldbauer (95) employed oxides of nitrogen in small proportion in oxidation processes essentialy catalytic. Berl and Fischer (29) found that the combustion of methane in nitrogen peroxide produced formaldehyde.

Lang (96) stated that between 700° and 800° methane began to reduce carbon dioxide with the liberation of carbon, while the formation of carbon monoxide from these two gases was brisk at 950° to 1054°. The reaction of methane with water vapor at high temperature yielded carbon monoxide and hydrogen in the presence of an excess of water, while under other conditions much carbon was formed.

According to a patent by H. Otto Traun's Forschungs-Laboratorium (97), the oxidation of methane to formaldehyde and methyl alcohol was effected by momentarily heating the hydrocarbon with carbon dioxide. Heat decomposed the carbon dioxide and gave nascent oxygen which, under suitable conditions, produced much methyl alcohol and formaldehyde, but only a little formic acid. The process could be carried out by passing the mixture of gases through a constricted tube which was heated at the constriction. Slow passage of the gas favored the formation of methyl alcohol while rapid passage favored the production of formaldehyde. The tube in which the gas was heated was made of copper, silver, nickel or alloys of these metals or alloys with aluminum, tin, or zinc, and acted catalytically in promoting the reaction. The tubes could also be made of iron or steel, in which cases small quantities of copper, silver, aluminum, nickel or their alloys were useful in the form of turnings or wire within the iron or steel tubes.

Dreyfus (98) found that acetic acid, acetone, or mixtures of these were made by passing methane together with carbon monoxide or carbon dioxide under pressure and at temperatures below 500°, over a catalytic material such as copper, iron, nickel, cobalt, palladium black, platinum black, nickel carbonate or other metallic carbonate which decomposed at temperatures below 500°. The rate of passage of the mixed gases over the catalyst depended upon the temperature and pressure. Pressures of 12 to 50 atmospheres and temperatures of 120° to 300° could be used, under which conditions the speed of the gas mixture was from 1 to 20 liters per minute.

Phillips (88) reported a lengthy series of experiments with methane and a number of oxidizing agents. Potassium permanganate in 2 per cent solution, either neutral or acidified with sulfuric acid was not affected by this hydrocarbon nor was potassium ferricyanide changed. However, when methane was conducted into strong sulfuric acid containing solid potassium permanganate, immediate oxidation occurred. Osmic acid was unaffected in the cold, while potassium ruthenate was slowly reduced to metallic ruthenium. Hydrogen peroxide mixed with lime water remained clear when in contact with this gas while calcium hypobromite precipitated no carbonate. Dehn (99) later reported that sodium hypobromite also was without effect on methane even after standing with it for several months.

At elevated temperatures methane reduced ferric oxide with the formation of carbon monoxide and carbon dioxide. Iodic acid (in crystal form) was not reduced on heating nearly to its dissociation temperature nor was iodic pentoxide attacked at any temperature up to its point of decomposition. Nickel chloride, though it had no apparent effect on methane, was changed in its crystal form by exposure to this gas at low temperature. At higher temperature a peculiar crystalline mass was formed, which at low red heat decomposed with reduction of the metallic salt and separation of carbon.

V. Meyer and Saam (100) found that methane was very slowly oxidized on shaking with a five per cent solution of potassium permanganate. The oxidation was more rapid than in the case of ethane.

An English patent was granted to Lance (101) for a method of preparing methyl alcohol from methane by the use of hydrogen peroxide, with or without ferrous sulfate or monopersulfuric acid, or by the use of monopersulfuric acid alone. A similar process was claimed by Lance and Elworthy (102) in a French patent, which also included the production of formaldehyde.

Hoffman and Schneider (103) found that a small amount of methane was absorbed by chlorate solutions in contact with certain metals in finely divided form. On using platinum there was measurable absorption while with rhodium and palladium there was some evidence, but no conclusive proof of reaction. All of the other noble metals were tried without any absorption occurring. These authors were able to separate hydrogen from mixtures with methane by absorption methods.

Berl and Fischer (29) found that oxidation of methane with sulfur dioxide produced no formaldehyde, while by the action of sulfur trioxide under optimum conditions 0.5 per cent of formaldehyde was formed.

f. Oxidation by bacteria

Several investigators have published papers on the bacterial oxidation of methane. Although this phenomenon is apparently common, only a few of the organisms bringing it about have as yet been identified.

Kaserer (104) found that methane was oxidized by the microorganisms of the soil, and that they also consumed hydrogen. He noticed that nitrification was hindered by the presence of hydrogen or methane, as these gases were utilized by the bacteria in preference to nitrogen.

Söhngen (105) and also Urbain (83) observed that mixtures of methane and oxygen were slowly oxidized in the presence of green plants, probably because of bacteria introduced with the plants. Later Söhngen (106) described a bacterium (Bacillus methanicus) which oxidized methane when that hydrocarbon was mixed with two volumes of air.

Giglioli and Masoni (107) also studied the biological removal of methane from gas mixtures. They found the optimum temperature for this process to be 30°. In studying the distribution of the organisms which in the presence of oxygen consumed methane, they found that the deeper layers of the ground contained more of them than the surface layers, and that they were abundant in the slime of rivers and in dungheaps.

Harrison and Aiyer (108) showed that the organized film overlying the surface of swamp rice and paddy soils was capable of oxidizing methane to carbon dioxide and water. Aiyer (109) later identified the organisms responsible for the oxidation as B. fluorescens liquefaciens. In culture, this bacterium was able to oxidize considerable portions of methane only as long as it was propagated on purely mineral media. In the presence of much organic matter, its power to oxidize methane was markedly reduced.

3. THE OXIDATION OF ETHANE

a. General

By reason of the larger number of products theoretically possible, the oxidation of ethane is an even more complex process than that of methane. The products obtained and their proportions vary widely with the different methods and the conditions of oxidation.

Slow oxidation of ethane in sealed borosilicate glass bulbs at a pressure of 1.75 to 2.33 atmospheres produces a gaseous mixture consisting of carbon monoxide, carbon dioxide, methane, free carbon, and water vapor, while the circulation of mixtures of ethane and oxygen at reduced pressure with continuous removal of the products yields carbon monoxide, carbon dioxide, hydrogen, ethylene, formaldehyde, acetaldehyde and water, with some indications of the formation of formic acid.

The explosion of mixtures of ethane and oxygen produces considerable amounts of unsaturated hydrocarbons, whose proportion increases as the initial pressure of the mixture is diminished. The products which have been identified are carbon monoxide, hydrogen, methane, ethylene, acetylene, and water vapor.

The presence of ethyl alcohol has not been established in the products of oxidation by any of these means mentioned above, but it is produced when the oxidation is effected by means of ozone. Acetaldehyde, acetic acid, and traces of hydrogen peroxide are also formed by this method.

The reactions producing this variety of products, as formulated by Bone on the basis of his hydroxylation theory, are summarized in table 3.

b. Oxidation by oxygen and air

The incomplete combustion of ethane was investigated first by E. von Meyer (110). He found that a large excess of oxygen was required to produce ignition when ethane was mixed with hydrogen and oxygen. The oxidation of ethane by oxygen was also studied by Berthelot and Vieille (111), who compared the pressures produced in a number of gas reactions. They found that when one mole of ethane interacted with seven moles of oxygen, a pressure of 16.18 atmospheres was developed by the explosion, about the same pressure as that developed by the rapid combustion of other saturated and unsaturated hydrocarbons.

According to Schlegel (112) the combustion of ethane in the presence of oxygen and chlorine takes place in accordance with the following equation:

$$C_2H_6 + 3Cl_2 + 2\ O_2 \rightarrow 2\ CO_2 + 6HCl$$

Thus there is preferential reaction of the hydrogen with chlorine.

Bone and Stockings (113) observed that under similar conditions, ethane burns much more rapidly than methane. In borosilicate glass bulbs both hydrocarbons were oxidized considerably below 400°. There was apparently no preferential combustion of either hydrogen or carbon when ethane reacted in these bulbs at 250 to 400° under pressures of 1.75 to 2.33 atmospheres with a quantity of oxygen insufficient to burn it to carbon monoxide and water. Carbon monoxide, carbon dioxide, oxygen, methane, and ethane were among the end products.

When the oxidation of similar mixtures of ethane and oxygen was carried out under reduced pressure by continuously circulating the gases through a tube kept at 400° to 500°, the gaseous products included carbon monoxide, carbon dioxide, hydrogen, ethylene, oxygen, and ethane. Both formaldehyde and acetaldehyde were detected in the water through which the gases passed immediately after leaving the heated tube. There was also some evidence of the intermediate formation of formic acid.

Bone and Wheeler (16), following their work on methane with studies on ethane oxidation, obtained additional experimental evidence for the hydroxylation theory.

Bone and Drugman (5) found that equimolecular mixtures of ethane and oxygen, when exploded in a closed borosilicate glass bulb, formed carbon monoxide, hydrogen, methane, acetylene and ethylene. The quantites of unsaturated hydrocarbons, as well as of water, in the final products showed a tendency to increase as the initial pressure diminished. It is worthy of note that these workers detected aldehydes in the products of the burning of oxygen in ethane and also in the interconal gases of an ethane flame.

In other experiments, it was found that acetaldehyde decomposed at about 400° into methane and carbon monoxide while at higher temperatures it formed hydrogen, methane, carbon monoxide and free carbon. The presence of all of these substances together with steam in the products of the explosion of mixtures of ethane and oxygen was pointed out as being in conformity with the assumptions of the hydroxylation theory.

The relative rates of oxidation observed at low temperatures with mixtures containing varying proportions of oxygen were interpreted as showing that the monohydroxy—and not a dihydroxy—derivative was formed initially. It seemed to these authors that it was the oxygenated molecule which decomposed in a flame and not the original hydrocarbon.

Bone, Drugman and Andrew (4) found that the lower the pressures at which a glass globe was filled with ethane, mixed with an amount of oxygen insufficient for its combustion to carbon monoxide and water, the greater was the quantity of water, aldehydes and unsaturated hydrocarbons produced when the mixture was fired. In accordance with Bone's ideas, these results would indicate that water, unsaturated hydrocarbons and aldehydes were produced during the initial stages of combustion while carbon was a later product.

The results obtained by the detonation of mixtures of ethane and oxygen in a coil of lead tubing 20 feet long indicated that no preferential combustion of carbon or hydrogen occurred in the explosions. After the explosion of an equimolecular mixture of ethane and oxygen, the products included acetylene, ethylene, methane, and hydrogen, besides water, carbon monoxide, carbon dioxide, and free carbon. The rinsings of the explosion chamber gave a strong aldehyde reaction with Schiff's reagent. These workers considered the mechanism of combustion to be essentially the same in both detonation and inflammation.

In later work, Bone (114) exploded other mixtures of ethane and oxygen, and always found in the products of the reaction substances of aldehyde nature which were recognized by the use of Schiff's reagent.

Bone, Davies, Gray, Henstock and Dawson (115) studied the explosion of ethane with an equal volume of oxygen and represented the reaction as taking place in the following steps:

$$\begin{tikzcd}
 & & & \text{(1) } CH_4 + CO + H_2O \\
CH_3CH_3 \arrow[r] & CH_3CH_2OH \arrow[r] & CH_3CH(OH)_2 \arrow[ur] \arrow[dr] & \\
 & & & \text{(2) } C + 2H_2 + CO + H_2O
\end{tikzcd}$$

Andrew (116) extended his study of the water gas equilibrium to the mixtures, $2C_2H_6 + 3O_2$ and $2C_2H_6 + 5O_2$, which on ignition in a spherical vessel or in a coil gave carbon dioxide, carbon monoxide, hydrogen, water vapor, methane, acetylene, and ethylene. The yields of carbon and of aldehydes showed wide variation, depending on the type of vessel used.

Marks (116a) found that formaldehyde could be produced with greater ease by the partial oxidation of ethane than was the case with methane. He passed a mixture containing one volume of ethane and two volumes of air at a rate of 27 liters per hour through a silica tube 0.5 inch in diameter heated to 700 to 710° over a length of 2 feet. The exit gases were divided into two streams so that ten volumes of exit gas were recirculated with each volume of fresh mixture. The liquid condensed in the cooled receiver consisted of an aqueous solution of formaldehyde. Formaldehyde was formed in the amount of 8.5 pounds per thousand cubic feet of ethane treated; 1.4 pounds of acetaldehyde being produced simultaneously. The formaldehyde produced amounted to 7.4 per cent of the ethane treated. Some of the ethane decomposed and gave 33.4 per cent of ethylene during the reaction.

Propane and butane or higher paraffins may be used with similar results. The ease with which the paraffin hydrocarbons oxidize increases with their molecular weight.

Catalysts such as heavy metals and their compounds were found to be useless in the oxidation reactions of the paraffin hydrocarbons tried by Marks.

c. Catalytic oxidation

Phillips (117) studied the conditions for the oxidation of ethane (3.1 per cent in a mixture with air) in the presence of palladium asbestos. He found that the "lowest initial oxidation temperature," was high, being 450° for ethane while for hydrogen it was 20°. He did not state the nature of the oxidation products.

Richardt (43) studied the combustion of ethane mixed with other gases in the presence of palladium wire. He found that mixtures of methane and ethane were difficult to separate by the use of platinum or palladium, but that if hydrogen was present, it might be removed from the mixture by fractional combustion.

Acetaldehyde, acetic acid, and ethyl alcohol are given by Glock (118) as the products of his patented process for the oxidation of ethane with air using pumice, asbestos, or copper as catalytic agents.

The I. G. Farbenindustrie Akt-Ges. (28) obtained ethane by adsorption with active charcoal or silica from the gas produced by low temperature carbonization of bituminous material, and subjected it to imcomplete combustion. The hydrocarbon was passed, with oxygen, through a porcelain tube filled with fragments of pumice and heated to 900°. They claimed that the products contained over 25 per cent of ethylene.

Bancroft (73), discussed the preferential catalytic combustion of ethane and concluded, on the basis of Bone's data, that ethane as well as methane burns more rapidly than either hydrogen or carbon monoxide in borosilicate bulbs at 300° to 400°.

Under the action of alpha radiation from radon, ethane was completely oxidized in one step in the experiments of Lind and Bardwell (75, 76). In the initial stages the reaction between ethane and oxygen was nearly twice as fast as in the case of methane, but the velocity decreased sharply when the reaction was about 70 per cent complete. The assumed groupings of ethane and oxygen molecules about the gaseous ions were as shown in the following equation:

$$(O_2 \cdot O_2 \cdot C_2H_6 \cdot O_2 \cdot O_2)^+ + (O_2^- \cdot C_2H_6 \cdot O_2 \cdot O_2) = 4CO_2 + 6H_2O$$

As in the case of methane, the yield of oxidation products was 75 per cent of the maximum theoretically possible on the basis of the total number of ions present.

d. Oxidation by ozone

The work of Bone and Drugman (119) on ozone oxidation of ethane is of great importance from a theoretical standpoint, and it possesses some industrial interest as well. They obtained ethyl alcohol by the interaction of ethane and ozone at 100°. In their experiments ethane and ozonized air (ozone 2.33 per cent) were led separately into the top of a wide vertical glass tube, about 18 inches long, packed with glass beads and heated by a steam jacket. The proportion of the gases was so regulated that the ethane was always present in large excess. Under these conditions the ozone disappeared entirely as the mixture descended the tube. The gases were then drawn through a series of cooled glass worms containing water for the absorption of soluble products. Each experiment extended over three or four days, during which time about 4 liters of ethane and 13 to 15 liters of ozonized air passed through the apparatus. Examination of the liquid from the condenser showed that ethyl alcohol, acetaldehyde, acetic acid, and traces of formaldehyde were present. An examination of the gaseous products showed that they did not contain acetylene, ethylene or free hydrogen.

In further work the interaction of ethane with oxygen containing 10 per cent of ozone was studied by Drugman (82). The oxidation was slow at 15°, although much faster than in the case of methane. The products obtained were ethyl alcohol, acetaldehyde, and acetic acid, besides traces of hydrogen peroxide. At 100°, using a large excess of ethane, the reaction was more rapid and much less acid was formed. Acetaldehyde was the main product of the reaction, though traces of hydrogen peroxide were also formed and ethyl alcohol was produced in larger quantities than at the lower temperature. Drugman made the statement: "It is clear, then, that ethyl alchol is the first stage in the oxidation process, and that acetaldehyde and acetic acid are secondary products of the reaction."

e. Oxidation by chemical reagents

The information available on the chemical oxidation of ethane is extremely fragmentary.

Phillips (117) found that potassium ruthenate was slowly reduced to the metal by ethane and by other hydrocarbons, that potassium permanganate produced some carbon dioxide when treated with ethane, and that iodine pentoxide was not attacked up to its dissociation temperature.

Meyer and Saam (100) reported that the oxidation of ethane by 5 per cent potassium permanganate was less rapid than that of methane.

4. THE OXIDATION OF PROPANE

Incomplete as is our knowledge of the oxidation of methane and ethane, it is yet far superior to that regarding the oxidation of the higher gaseous hydrocarbons, propane, butane, isobutane, and 2,2-dimethyl propane. The literature offers but a few scattering references on these members of the series.

The combustion of propane in the presence of chlorine, was found by Schlegel (112) to lead to the formation of carbon dioxide and hydrogen chloride:

$$C_3H_8 + 3\ O_2 + 4\ Cl_2 \rightarrow 3\ CO_2 + 8\ HCl$$

In this case, as with ethane and methane, the chlorine reacted preferentially with the hydrogen and the carbon with the oxygen.

Bone and Drugman (5) investigated the combustion of propane with oxygen by exploding two volumes of the hydrocarbon with three of oxygen in a closed tube. They found as products of the reaction: aldehydes, carbon monoxide, carbon dioxide, methane, unsaturated hydrocarbons (including acetylene), and hydrogen.

Phillips (117) found, by studying the slow oxidation of propane in the presence of palladium asbestos and air, that the ignition point of a mixture containing 3.1 per cent propane was between 339° and 383°. He reported also that palladium chloride and potassium ruthenate were reduced by propane as they were by methane. Acidified permanganate produced some carbon dioxide from propane. Iron oxide was reduced by the hydrocarbon at elevated temperatures.

Lind and Bardwell (76) found that the oxidation of propane did not ordinarily go to completion under the influence of the alpha radiation from radon. Liquid products other than water indicated incomplete oxidation. The oxidation of propane could be brought to completion, however, by prolonged exposure to alpha radiation.

5. THE OXIDATION OF BUTANE

The substances which have been identified as products of the combustion of butane in oxygen include aldehydes, carbon monoxide, carbon dioxide, water, methane, ethylene, acetylene, hydrogen and carbon. Schlegel (112) found that the oxidation of butane in an excess of a mixture of chlorine and oxygen took place according to the equation:

$$C_4H_{10} + 4\ O_2 + 5\ Cl_2 \rightarrow 4\ CO_2 + 10\ HCl$$

Bone and Drugman (5) exploded mixtures of butane with oxygen and reported the formation of aldehydes, methane, unsaturated hydrocarbons including acetylene, carbon monoxide, water, hydrogen and carbon.

On exploding a mixture of 34 per cent butane and 60 per cent oxygen, Bone, Drugman and Andrew (4) obtained as gaseous products: carbon monoxide, carbon dioxide, methane, ethylene, acetylene and hydrogen. They considered the hydroxylation theory to account satisfactorily for these products.

In 1849 Frankland (120) reported that butane, mixed with 50 per cent of oxygen and conducted over spongy platinum, remained unchanged at ordinary temperature, but upon gentle heating, the platinum became incandescent and with the oxidation of the butane, water and carbon were formed.

Lind and Bardwell (76) observed, as in the case of propane, that the oxidation of butane under the influence of alpha radiation from radon was not complete; the appearance of liquid products other than water indicated but partial oxidation.

Reference has been made to the application of the catalytic oxidation process of James (63a) and of Marks (116a) to propane, butane, and even higher paraffin hydrocarbons.

6. THE OXIDATION OF ISOBUTANE

Experiments of Meyer and Saam (100) showed that when isobutane was agitated with a 5 per cent solution of potassium permanganate for an hour, the amount of oxidation was scarcely perceptible.

The oxidation of isobutane in the presence of palladium asbestos was reported by Phillips (117). A mixture of 3.1 per cent of isobutane with air burned at 200° to 250°. Similarly a 3.1 per cent mixture of isobutane and air was oxidized at 214° to 250° on being passed over ruthenium asbestos. The products of the combustion included water and carbon dioxide; olefines could not be detected.

7. THE OXIDATION OF 2,2-DIMETHYL PROPANE

No reports of work on the oxidation of 2,2-dimethyl propane have apeared in the literature.

8. SUMMARY OF THE SUBSTANCES PRODUCED BY THE OXIDATION OF METHANE, ETHANE, PROPANE, BUTANE AND ISOBUTANE

A recapitulation of all of the substances which have been found as products of the oxidation of the gaseous paraffins is given in table 6. The blanks in this table, to a considerable extent, indicate gaps in our knowlege rather than the proven nonformation of the listed substances.

9. SUGGESTED PROBLEMS FOR FURTHER RESEARCH

There can be no doubt that the oxidation of the gaseous paraffin hydrocarbons is a subject of rich promise about which far too little is known. The mechanisms of the many sided reactions, are, to say the least, highly uncertain. The experimental data are in many cases conflicting, indicating that all the conditions affecting the experiments have not been taken into account or accurately described by the various investigators. Apparently there are equilibria involved, inviting studies in kinetics. The oxidation of the gaseous hydrocarbons in the presence of hydrogen so as to show preferential oxidation has been studied just enough to indicate its interest and complexities. The investigation of the action of chemical oxidants has but begun, while little attempt has been made to accelerate or retard the chemical oxidation of the gaseous paraffins by catalytic means. There is particular need for more study of the oxidation reactions of propane, the butanes and 2,2-dimethyl propane.

TABLE 6

Substances identified as oxidation products of methane, ethane, propane, butane and isobutane

	METHANE	ETHANE	PROPANE	BUTANE	ISOBUTANE
Methyl alcohol	Yes				
Ethyl alcohol		Yes			
Formaldehyde	Yes	Yes			
Acetaldehyde		Yes			
"Aldehydes"			Yes	Yes	
Formic acid	Yes	Yes			
Acetic acid		Yes			
Methane		Yes	Yes	Yes	
Ethylene		Yes		Yes	
Acetylene		Yes	Yes	Yes	
"Unsaturated" hydrocarbons			Yes	Yes	No olefins
Carbon monoxide	Yes	Yes	Yes	Yes	
Carbon dioxide	Yes	Yes	Yes	Yes	Yes
Carbon	Yes	Yes	Yes	Yes	
Hydrogen	Yes	Yes	Yes	Yes	
Water	Yes	Yes	Yes	Yes	Yes
Hydrogen peroxide		Trace			

The following problems are suggested as offering opportunities for investigation:

A. Mechanism and course of the reactions

1. Investigation of the dissociation of the gaseous paraffins during oxidation.
2. Work on the mechanism of formation of unsaturated hydrocarbons in oxidation reactions.
3. Determination of the order in which alcohols, aldehydes, hydrogen, carbon monoxide, carbon dioxide, and free carbon are formed in the oxidation reactions.
4. Comparison of the steps and mechanisms of the following types of oxidations.

    a. Slow oxidation with air or oxygen.
    b. Explosive combustion.
    c. Oxidation by means of ozone.
    d. Catalytic oxidation.
    e. Oxidation by use of chemical oxidizing agents.

5. Study of the oxidation of the gaseous paraffins by mixtures of chlorine or other halogens with oxygen, air and ozone respectively.
6. Comparison of the oxidation of n-butane and of isobutane.

B. Equilibria and kinetics

1. Investigation of the reversibility or irreversibility of the steps in the oxidation reactions.
2. Study of the equilibria produced by the reversible reactions and the shifting of these equilibria by variations in temperature, pressure and time.
3. Observation of the effects of temperature and pressure on the velocities of single oxidation reactions.

C. Catalytic oxidation and preferential combustion

1. Study of the rates of oxidation of single hydrocarbons in mixtures with other gases and of hydrocarbons themselves in admixture as influenced by temperature, pressure and catalysts.
2. Effect of the presence of knock suppressing and also of knock inducing substances on the rates of oxidation of the gaseous paraffins.
3. Influence of traces of water on the rate and course of the oxidation reactions. Is the presence of water essential to the oxidation of these hydrocarbons?

4. The retardation by catalysis of some or all of the reactions occurring in a given oxidation process.

5. Simultaneous dehydrogenation, condensation, and oxidation by employment of zinc chloride, carbon, metals, or metallic oxides as catalysts. Also use of metals such as copper, cobalt, nickel, iron, platinum, and palladium in finely divided condition together with oxides such as the lower oxides of manganese, tin, uranium, molybdenum and vanadium, in anhydrous form, which Sabatier and his associates found effective in the dehydrogenation of alcohols.

6. Determination of the function of hydrogen chloride in promoting the oxidation of methane in the presence of the borates of tin.

7. Investigation of the results of producing oxidation by passing a hydrocarbon mixed with air or oxygen through a bath of molten metal.

8. Endeavor to catalyse a specific reaction without accelerating others going on simultaneously.

D. Chemical oxidation

1. Extension of the work which has been done on the chemical oxidation of methane to its higher homologues, and the testing of other oxidizing agents, such as chromyl chloride and the oxides of chlorine.

2. Determination of the effect of catalyst promoters and demoters.

3. Obtaining data on the effects of temperature, pressure and time on chemical oxidation, in the gas phase using oxides of nitrogen or other gaseous oxidants.

4. Use of air or oxygen with higher concentrations of nitrogen, hydrogen or carbon dioxide at high pressures.

5. Oxidation under controlled temperatures, low or high, with or without electrical discharge.

6. Oxidation of the gaseous paraffin hydrocarbons while in liquid state.

7. Experimental work on the oxidation of these hydrocarbons under the influence of radiant energy, especially infra-red and ultra-violet, and perhaps x-ray radiation.

8. Determination of the influence of alpha radiation on the oxidation of isobutane and 2,2-dimethyl propane.

E. Bacterial oxidation

1. The isolation and classification of the effective organisms.

2. Study of the influence of oxygen and other gases on the methane consuming bacteria.

3. Investigation of the oxidizing action of bacteria on ethane, propane, the butanes and 2,2-dimethyl propane.

F. Problems of possible commercial value

1. Evaluation of the many patents for the preparation of formaldehyde and of the process for oxidation of methane in the presence of ammonia to form hexamethylene tetramine.
2. Preparation of alcohols by properly controlled catalytic oxidation of the gaseous paraffins or perhaps of olefins resulting from the thermal decomposition of the paraffins.
3. Investigation of the action on the gaseous paraffins of ozone formed at low temperatures by the action of the silent electric discharge on mixtures of these hydrocarbons with oxygen or on such mixtures diluted with nitrogen or with some other inert gas.
4. Oxidation in the gas phase in the presence of oxides of carbon, nitrogen, sulfur and halogens.
5. Use of vanadium pentoxide, vanadic acid, molybdic acid, and a number of other substances not yet thoroughly investigated as oxidation catalysts.

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