PARTIAL OXIDATION OF LIGHT HYDROCARBON GASES AT ATMOSPHERIC PRESSURE

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A THESIS

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INTRODUCTION

For the last thirty years the idea of obtaining useful chemicals from the abundant naturally occurring hydrocarbons by partial oxidation has occupied a high place in the research laboratories of the world. At the present time it is still impossible to effectively stop the oxidation of all of a hydrocarbon at a stable intermediate stage. This is because the partially oxidized carbon atom is more easily oxidized to completion than is the carbon atom, which is bonded only to hydrogen and carbon. The work to date includes reports on the flow rate of the gases, the gas composition, methods of heat removal, temperature at which the gases can be made to react, pressures of the reacting gases, introduction of diluents and gaseous catalysts, and the effect of solid catalysts. Most of the effort has been directed along the lines of catalyst improvement. It is at least conceivable that some material would selectively adsorb hydrocarbon and oxygen and at the same time repel the aldehyde formed, thereby freeing this useful product to the gas stream flowing over the solid surface. Such a catalyst giving a high reaction rate would be ideal. In spite of the apparent failure of research to provide high yields a number of commercial partial oxidation units are in operation today.^{1,2, 3}

The previous research on this subject can be

divided into two large groups: one was carried out in the neighborhood of one atmosphere total pressure; the other at elevated pressures up to several hundred atmospheres. Another classification might be made on the basis of static or dynamic experimental conditions. The bulk of the material published is in reference to new catalysts, and has been done on gases which have not been too carefully purified.

Newitt and Haffner⁴have shown the following effects of increasing the pressure in a static system of methane and oxygen.

- 1. Increase the rate of reaction or lower the temperature required for a certain rate.
- 2. Increase the quantity of methanol and formaldehyde in the product.
- 3. Increase the ratio of alcohol to aldehyde in the product.

Pichler and Reder⁵ found that in the dynamic system at 100 atmospheres, higher temperatures were needed than in the static system, but better yields of useful product were obtained. By lowering the incoming oxygen to 0.6 per cent of the gases, a 60 per cent yield is reported. Newitt and Schmidt⁶ found that higher pressures favored the survival of the higher alcohols. Newitt⁷ attributes to pressure the following influences on reaction:

- Increases collision rate. (Permits use of lower temperature)
- 2. Permits survival of intermediate compounds.
- 3. In chain reactions it deactivates carriers, thus terminating the chain.
- 4. May cause alteration in the electrostatic field, so as to induce an increased polarity.
- 5. Le Chatlier's Principle.

Since the production of formaldehyde is the only case in which no contraction of volume occurs one would expect at least a tendency for low pressures to give the highest ratio of formaldehyde to other products. This is verified by a number of investigators.^{4,7,16,22} Newitt⁷ further shows that with methane the diluents nitrogen, water vapor, and carbon dioxide are detrimental to the survival of both methyl alcohol and formaldehyde at 50 atmospheres pressure. He has also shown that pressure favors the oxidation of the middle carbon atom of propane. This is attributed to a change of polarity of the hydrocarbon molecule, and an alteration of the vibration period of the C-C or the C-H linkages.

Pease⁸ has shown that with propane and oxygen each at 300 mm. pressure and 280°C. the addition of 20 mm. acetaldehyde caused explosion. Without the addition of the acetaldehyde an induction period of 39 minutes was required followed by a 5 minute reaction

time. Aldehyde did not eliminate the induction period except in those cases where explosion occurred. Coating the wall surface with potassium chloride slowed down all reactions. Pidgeon and Egerton⁹ agree with many others that these are chain reactions, that the products of the later stages influence the initial stages, and that the chains are initiated and terminated on the surface, but propagated in the gas stream. Bone and Hill¹⁰ report the explosion of ethane-oxygen mixtures when 1 per cent acetaldehyde is added. Bone and Gardner¹¹ show that induction periods can be shortened with the aid of 1 to 2 per cent alcohol, aldehyde vapors, or nitrogen dioxide. They also prolonged the induction period and slowed down the reaction rate by increasing the surface-volume ratio. Norrish¹² believes that the induction period of methane-oxygen mixtures represents the interval during which an equilibrium quantity of formaldehyde is built up at the surface. Aldehyde is always essential for the occurrence of chain reactions. Harris and Egerton¹³ have shown that coating the walls with potassium chloride, sodium chloride and ferric oxide slow down the reactions and increase the quantity of carbon dioxide formed. This is overcome to some extent in static methods by the constantly changing composition of the gas. Formaldehyde increased the induction period, acetaldehyde and propylene

decreased it, and methyl alcohol had no effect.

Egloff, Nordman and Van Arsdell³ report that heating the reaction mixture slowly gives oxidation at lower temperatures. They also indicate that methyl alcohol, ethyl alcohol, formaldehyde, acetaldehyde, and water vapor shortened the induction period; while iodine, bromine, and lead tetraethyl inhibit the reaction. Boomer and Thomas¹⁴ used small electrolytic copper blocks as a catalyst with dry natural gas containing $3\frac{1}{2}$ per cent ethane. Using dry air as the oxidizing agent, yields of $l\frac{1}{2}$ to 2 per cent of the natural gas introduced were obtained at a pressure of 185 atmospheres. Temperatures of 325 to 350°C. were Pressure and reaction time did not have much used. effect on yields in the pressure range of 147 to 199 atmospheres. Pichler and Reder⁵ noted a sudden pressure increase from 160 atmospheres to 550 atmospheres when methane-air mixtures were heated in a bomb to 350°C.

Newitt and Thornes¹⁵ were able to convert to useful products, 13 to 18 per cent of the propane burned. These results were obtained at 274°C. and 400°C. at reduced pressures. They explain that the cause of the cool flame inflammation is a critical high concentration of higher aldehydes; during the passage of the flame the aldehydes are further oxidized to aldehyde peroxides and finally to formaldehyde.

Another explanation is that the cool flame is formed when peroxides and aldehydes reach a critical high partial pressure. Newitt and Schmidt⁶ were able to obtain somewhat better yields of useful products when propane was burned in cool flame combustion than when burned by slow combustion. The following comparison is also made for the first three members of the hydrocarbon series.

CH4 С₂H₆ С₃H₈ Hydrocarbon Reaction Temperature 380°C. 305°C. 275°C. Total condensible products, as per cent of the carbon of the hydrocarbon burned 7 40 64 Wiezevich and Frolich¹⁶ have found air just as effective as oxygen on natural gas if the pressures are increased to correct for the diluting effect of the nitrogen. These reactions were carried out under a pressure of 135 atmospheres. The flow rate affected reaction only to the extent of ability to heat the gases sufficiently. They obtained 70 cc. of useful product from one cubic meter of gas. Their study included the gases up to and including heptane.

Smith and Milner,¹⁷ using only nitrogen dioxide as the oxidizing agent, have obtained 3.4 per cent of the methane decomposed, (32.5 per cent) in the form of formaldehyde. An analysis was not made for other materials. 2 to 13 seconds contact time, and temperatures in the range of 440 to 680°C. were used.

Bibb,¹⁸ using natural gas containing 16.55 per cent ethane, was able to obtain 19.8 pounds of 40 per cent formaldehyde solution from 1,000 cubic feet of natural gas. A chrome-nickel steel tube was used. The temperature outside the tube is given as 735°C., but gas temperatures were not taken. Matsui and Yasuda¹⁹ found that sodium chloride, potassium fluoride, phosphoric acid, and boric acid, adhering to the sides of a pyrex, quartz, porcelain, or copper tube, decreased the effectiveness of nitrogen dioxide as a catalyst with air. Uranium and beryllium oxides were only slightly better. Bromine was a good catalyst, but hydrogen chloride and sulfur dioxide were poor.

Lewis²⁰ has shown that powdered glass and pumice increase the rate of peroxide formation while charcoal catalytically destroys peroxides. Bone²¹ believes that the initial step in oxidation occurs by the hydroxylation process. One reason for this is that approximately 30 times more alcohol than aldehyde was formed in the work of Newitt and Haffner⁴. He took this to mean that only the first step in a hydroxylation process had taken place. Higher aldehyde formations are explained by a non-stop run to dihydroxy and aldehyde. Newitt and Bloch²² were unable to find any trace of peroxide. In their copper-lined reaction vessel any oxygen concentration above 11.8 per cent resulted in very difficult temperature control. The

author had this same experience, but found that various catalysts changed the value of this maximum oxygen concentration over a large range. Beal and Reniger²³ indicate that Kaolin or Floridan are suitable catalysts, but that they require frequent revivification either by superheated steam or recalcination. Fuller's earth is also an excellent short-life catalyst which has a longer life when used with superheated steam. Egloff, Nordman and Van Arsdell²⁴ report the following catalysts useful to various degrees.

cupric chloride	uranium oxide
cobaltous oxide	platinum wire
manganese dioxide	silver
vanadium pentoxide	copper
ferric oxide	lead
ceric oxide	selenium dioxide

The extent of their value is not given, except an indication as to which products predominate. This will depend a great deal upon the history of the catalyst and the conditions under which it is used. Lewis²⁵ shows that the temperature of explosion for paraffin hydrocarbon-oxygen mixtures is raised by the metals platinum, copper, and lead, but not affected by tin, zinc, and aluminum. Iron gave the most violent explosion of any of the tests. Octane was used. A tube of small diameter required higher ignition temperatures. James^{26,27,28} in working above the

explosive limit at temperatures of 530 to 700° C., and contact times of $\frac{1}{4}$ to 4 seconds was able to obtain 6 3/4 per cent of the natural gas treated going to formaldehyde. His catalysts were mixed oxides of molybdenum, chromium, tungsten, uranium, cobalt, and vanadium in various combinations.

In any partial oxidation process carried out above 360°C. some cracking always occurs with the fragments formed combining with themselves and/or oxygen to give an oxidized product or polymer. Other portions of the hydrocarbon most probably combines through hydroxylation and peroxide formation. Thomas, Egloff, and Morrell²⁹ have arranged the metals in the various groups of the periodic table according to their catalytic behavior. The catalytic actions of these metals have been divided into three reaction types: dehydrogenation, cracking, and complete decomposition. The results obtained from the catalytic activity of glass, porcelain or quartz was used as the arbitrary zero for evaluating the activities of the metallic catalysts.

Taylor³⁰ believes a catalyst surface to consist of unsaturated atoms, more or less loosely held to the underlying lattice structure with the loose atoms distributed haphazardly over the surface. These surface atoms have free valences which depend upon their relative positions to other metal atoms. These

are called active centers.

One of the great difficulties of evaluating the action of a catalytic substance is attributed to minute quantities of impurities, which may serve as promoters. A promoter is a substance, the addition of which to a catalyst increases its activity. Alone the promoter does not exhibit catalytic activity. C.P. chemicals are no exception. Modern methods of spectroscopic analysis detect the presence of these impurities, but no known method of purification can remove them all. This factor may explain the discrepancy of results obtained by investigators apparently using the same catalyst³,4,13,16

Balandin^{31,32} and Burk³³ agree that catalysis decreases the heat of activation by disrupting the molecules due to a strain action, caused by two or more parts of the molecule striving to reach two different surface atoms. When this strain is great enough, multiple adsorption occurs and the bond between the atoms is broken. A bond might be formed in the opposite case where two molecules occupy the same activated surface atom. The degree of fit between the interatomic distances of the molecules and those of the catalyst lattice determines whether or not positive activation will occur. Some of the major mechanisms of oxidation are as follows:

- Formation of intermediate compounds of higher oxidizing power than the oxidizing substance itself, such as peroxides or ozone. High pressure liquid films may also be formed.
- 2. Activation of the oxygen by exchange of the oxygen from the gas stream for the activated form, or simply liberation of oxygen from the carrier until it reaches a stable state of oxidation.
- 3. The formation of chain reactions.
- 4. Dehydrogenation.
- 5. Autoxidation.

In all the above cases the catalyst is useful in that it lowers the temperature of oxidation and provides for increased selectivity. In many cases products are obtained which it is impossible to gain without the presence of the catalyst.

Ipatieff³⁴ believes that alcohols generated by the reaction are further oxidized to aldehydes in a metal filled tube due to reoxidation of the metal. This can either be brought about by oxygen introduced or by the more active form generated by the decomposition of the water produced. In the latter case the cycle consists of oxidizing the alcohol to aldehyde by the oxygen carrier, decomposition of the water formed in the first step, and finally regeneration of the metal oxide. The equations are as follows: $Metal + H_2 O = MeO + H_2$ $CH_3 CH_2 OH + MeO = CH_3 CHO + H_2 O + Me$

The greatest danger in working with this type of reaction lies in the possibility of obtaining explosive mixtures. The exact values of the explosive range have been determined very carefully. These values are not affected materially by flow rate nor type of surface present. Coward and Jones³⁵ report the following limits of inflammability.

Hydrocarbon	Limits Lower	in air, % Higher	Limits Lower	in oxygen, % Higher
methane	5.3	14	5.4*	59*
ethane	3.2	12.5	4.1*	50*
propane	2.4	9.5	-	

The lower limit means that if the gas mixture contains less than this percentage of hydrocarbon explosion will not occur, likewise when the percentage composition of the hydrocarbon is above the upper limit it is safe regardless of temperature. For instance, the danger range for methane in air is in the interval of composition between 5.3 per cent and 14 per cent methane. Yeau³⁶ reports the following explosive limits in air.

*Values obtained in a closed apparatus.

Hydrocarbons	Limits in Lower	air, % <u>Higher</u>
methane	4.9	15.4
ethane	2.5	15.0
propane	2.2	7.3

Some discrepancy appears, however, this is not serious, because of the safety factor allowed in the work under discussion.

The literature is incomplete on the slow combustion of relatively pure hydrocarbons. As has been cited, natural gas, having a wide range of composition, is the favorite subject. In no case has a comparison been made as to reacting ability of the three lightest saturated hydrocarbons when partially oxidized under identical conditions. The number of variables which control yields are quite numerous. In the present work no attempt has been made to obtain the effects of gas flow rates, tube sizes, concentration of catalyst and various rates of heat removal. In the case of propane, the effect of increasing the reaction temperature from 470 to 650°C. is shown. Since the higher temperature gave the best results for the molybdenum oxide catalyst this was used on the lighter hydrocarbons, because they are more resistant to chemical reaction. Likewise, the effect of oxygen concentration in the propane-oxygen system was investigated, as was the concentration of air in the natural gas-air mixtures. The upper temperature limit of

650°C. was observed because of equipment limitations.

Although copper oxide, vanadium oxide, and molybdenum oxide have been used as catalysts for this process the idea of supporting them in very low concentrations on silica gel is new. The catalysts reported are normally pasted over the carrier to the exclusion of the latter's surface. This not only greatly decreases the surface available, but also fails to make use of the carrier surface, which in this case was found to have some activity of its own.

Most investigators have preferred to work with the cheap and easily obtained hydrocarbons found in the mixture of natural gas. When this was done, large quantities of water vapor were introduced, which may have helped the reaction in some cases and retarded it in others. No reference was found in which powdered metals were used, probably chiefly because of the difficulty in holding the powder in place. It was thought this type of catalyst, with its large surface, was at least of sufficient interest to warrant a trial.





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LINE DIAGRAM OF PARTIAL OXIDATION UNIT

EQUIPMENT

The equipment necessary to determine yields, under various conditions, of the partial oxidation products of hydrocarbons should measure gas flow, provide for a thorough mixing of the gases, control temperature, regulate pressure, and isolate the products for analysis. Part of the temperature control problem involves the rapid removal of heat from high-rate, exothermal reactions. This heat removal can be provided by conduction through the reaction tube wall, or by the use of high flow rates which result in convection of heat to the condenser. Film resistance decreases the value of the first possibility. The necessity of a proper balance among induction period, reaction rate and gas flow rate increases the difficulty of the second. The convection method was used in this investigation and proved satisfactory at low oxygen concentrations for most of the catalysts. However, with a nickel catalyst, or with the higher oxygen concentrations, the flow rates used were too Many attempts to solve this problem, when the slow. reactions are fast and tend to go to completion, are reported in the literature, but the effort has not been successful.

It was decided that rotameters would serve best for the measurement of gas flow rates. The oxygen rotameter (5) had a flow range of 75 to 3,000 cc. per

minute, the air rotameter (5), 75 to 1,300 cc. per minute, and the larger hydrocarbon meter (6) measured rates accurately from 500 to 6,000 cc. per minute. The Fischer Porter Company considers these instruments accurate to within 4 per cent. These flow meters were calibrated, at 70°F. and 739 mm., by the displacement of water. Since the calibrations were made during warm weather it was necessary to place the two gas cylinders, and two surge tanks into a large container, which was held at 70°F. by means of circulating water. This same system was also used to control gas temperature for the earlier runs. during which time room temperature was well over 70°F. It seemed advisable to control gas temperatures at the rotameters rather than rely on alinement charts to correct flow rates for temperature deviation. The accuracy of the latter method is questionable. Use of the manometer (9) and air pump (16) permitted close control of gas pressures behind the manometers to 739 mm. mercury.

One of the first difficulties encountered was the fluctuation of gas pressure from both the hydrocarbon and oxygen cylinders. These pressure variations made it impossible to hold the rotameter floats steady, and thereby made gas flow rate control inadequate. This was remedied by the insertion of the surge tanks (3) and (4). These tanks were identical.

They were made of two pieces of 6 inch pipe 4 feet long, welded shut on each end, drilled and tapped on the sides for quarter inch fittings. The diaphragm valves on the gas cylinders reduced the pressure in the surge tanks to 5 pounds per square inch gauge. Perfectly smooth flow was obtained through the rotameters. Hoke valves were placed at both inlet and outlet of the surge tanks. This allowed removal of the surge tanks from the system for evacuation to an absolute pressure of 7 mm. before the introduction of a different gas. An evacuation to this degree gave contamination of 7/739 or, roughly, 1 per cent. Since gas was passed through the tank rapidly for several minutes before use, the impurity was decreased to an inappreciable amount.

Rather than rely on the gases mixing while flowing through the tubes, a mixing chamber (8) was placed in the line. This consisted of a l inch cylindrical glass tube 8 inches long in which the gases were made to reverse direction. This reversal of direction mixing is quite successful in commercial installations. From the mixing chamber these gases passed through 3 feet of $\frac{1}{4}$ inch copper tube before entering the reaction chamber. Further homogeneity was assured by the mixing in the packed reaction chamber.

Reaction tubes made of two different materials

were used. The first copper tube burned through, so one made of nickel was inserted. The nickel was found to catalyze the reaction to completion; it was discarded. Another copper tube replaced it. Spot thermocouples were placed between the heater and tube wall near the mid point of the copper tube, and near the exit end. These thermocouples were used to detect excessive temperature, which might again cause the tube to melt. The reaction tube size was 1.050 inch outside diameter, 0.112 inch wall, and 28 inches long. 4 inches on each end of the tube was left bare; an electrical heater surrounded the remaining portion. Two thermocouples were placed within the tube. The iron-constantan couple, placed at the mid point of the tube and near its center, controlled the Brown Potentiometer Controller (12). Temperatures of the chromel-alumel couple, placed 6 inches from the gas exit end of the tube and in its center, were read on the Foxboro Potentiometer (14). The two chromelalumel couples outside the tube and the one inside were placed in the circuit of the Foxboro Potentiometer by means of the switch station (13). Thermocouple leads were brought inside the tube through flanged copper fittings which were packed with asbestos and drawn tight to prevent leakage. The wires were protected from the copper tube and fittings with ceramic insulators. Originally, a

reactor tube designed to permit rapid cooling was placed between the heater (10) and condenser (11). Enough radiant energy was lost by this reactor to decrease the gas temperature well below that obtained in the heater. This may have proven satisfactory for conditions under which a sizeable induction period occurred, but for each condition a determination of the extent of reaction in the heater should be made. This reactor was discarded, and high gas velocities were depended upon to dissipate the heat.

The heater caused more delay in the earlier work than any other item. After building one 500 watt unit it was found that a 1,000 watt element was needed. This element was made up of 45.2 feet of Number 16 Chromel A wire. The wire was arbored on a 3/16 inch welding rod, and wrapped over a length of 20 inches. After being set in alundum cement the cylinder was slipped over the copper reaction tube. The copper tube was wrapped with sheet asbestos to prevent a short circuit. Ends of the heater were supported on the copper tube by means of rings of fire clay and alundum cement. Outside the heater was placed successively $\frac{1}{2}$ inch of ground asbestos, 3/4 inch 85 per cent magnesia pipe insulation, and $\frac{1}{2}$ inch of ground asbestos. The ends of the unit were insulated by ground asbestos only. The whole unit was supported by two iron rings around the 85 per cent magnesia covering.

This assembly could be moved about with little danger of short circuit; it was sturdy enough to permit placing in a vertical position when catalyst was added or removed.

The condenser (11) consisted of 18 feet of $\frac{1}{2}$ inch copper tubing turned into a coil of 8 rounds. This copper tube was coiled on a lathe, and fastened into a firm unit of constant downward slope with the aid of 3 pairs of iron strips. The coil turns were held in place and spaced by bolts passing through the pairs of vertical iron strips on either side of the coil. The assembled coil was placed in the cooling tank; ice and water provided the refrigeration medium. At the bottom of the condenser a 100 cc. bottle served as a trap (15). From the trap, which held the condensate formed by chilling, the gases traveled to the absorbers.

Two absorbers (16) of the fritted disc type, and one of the Milligan type, were used. The fritted disc absorbers are the more flexible and served exceedingly well at the higher gas flow rates. The Milligan absorber is more efficient at lower flow rates, but has the disadvantage of creating a large pressure drop. Additional absorbers created such a pressure drop that 20 or more inches mercury vacuum had to be maintained. This would have defeated the purpose of separation by the removal of aldehyde vapors.

Since the data was to be obtained at the one pressure, 739 mm. mercury, it was necessary to compensate for changes in atmospheric pressure as well as back pressure occurring in the line behind the rotameters. An air pump (17) was placed behind the absorbers to provide the vacuum. Control was obtained by placing a T connection between the last absorber and the air pump. A valve was placed on the atmospheric leg of this T to close off or admit air from the room. Opening the valve decreased the vacuum while closing increased it. Exact pressure at which reaction occurred was but slightly different from the pressure indicated by the manometer. It decreased uniformly over the entire length of the 28 inch reactor. There would be some difference in the absolute pressure in the empty tube and the packed For the tube packed with silica gel this tube. variance between ends is approximately 10 millimeters.

Temperature control, for all the data taken at a temperature of 470°C. or below, was made with a Brown Potentiometer Controller. An iron-constantan thermocouple, and thermocouple extension leads furnished by the manufacturer were used. The range of this instrument was 0 to 500°C. For temperatures above 470°C. a Hoskins Resistance Type Temperature Regulator was used, which had a range of 0 to 800°C. The circuits were connected according to recommen-

dations of the manufacturers.³⁷

In working with gases of this nature the possibility of explosion always exists. To decrease the probability of explosion a $\frac{1}{4}$ inch check valve (7) was placed just behind the oxygen rotameter. Although the chances of hydrocarbon backing into the oxygen surge tank was shown by calculation to be small, it did exist at very low flow rates. Both the mixing chamber and the condensate trap were designed to blow off and release pressure in case of explosion. Copper lines were used throughout to eliminate the danger of flying glass. Liberal use was made of Hoke valves to prevent gases from leaking through to some section of the equipment where they were not wanted. Two fuse boxes were placed in the electrical circuit to prevent damage to control instruments by a short circuit.

PROCEDURE

Most of the runs were of one hour duration. In the earlier work, some were shortened to 30 minutes in order to determine whether or not the catalyst was losing its activity. Since this was not the case, the time was increased successively to four hours. It was decided that one hour gave enough product for accurate determination and would permit a broader scope of investigation. One difficulty encountered was passing the proper mixture of gases through the reactor without risking some deactivation of catalyst before the run was begun. The procedure followed was to have the heater on with the temperature coming up, then start the hydrocarbon into the system, followed as quickly as possible by the oxygen. When the reaction temperature desired was 470°C., this was done at 425°C., while for a run of 650°C. the gases were introduced at 600°C. A maximum time of 10 minutes was then required to obtain the desired temperature. When this higher temperature was reached the condenser and absorber were placed into the stream and the pressure regulated. In all cases where natural gas was used the oxygen flow was momentarily stopped until the vacuum from the air pump had been roughly set. This was necessary because of the low pressure at the natural gas source. On those runs made at 470°C. or below, temperature control $\pm 5^{\circ}$ C. was possible, while at the higher

temperatures the deviations amounted to $\pm 10^{\circ}$ C. Since the thermocouples were not shielded from infra red radiation, the actual reaction temperature deviations were probably somewhat higher than those indicated by the potentiometers. There were a few runs in which the temperature control indicated above was impossible because of the highly exothermic nature of the reaction. This was true when nickel or copper oxide on silica gel was used as a catalyst and practically zero product was obtained; also when molybdenum oxide catalyst was used in mixtures containing a high oxygen content. In some of these cases just enough heat was given off to hold the temperature fairly constant above the controller temperature, while in others a very rapid temperature increase was observed. In the latter cases it was necessary to stop oxygen flow and allow the unit to cool.

The following order was followed in stopping the run:

- 1. Turn off valve controlling oxygen flow.
- 2. Disconnect absorbers from condenser and each other.
- 3. Stop air pump.
- 4. Turn off hydrocarbon control valves.

5. Introduce nitrogen.

After a 10 to 15 minute purge with nitrogen, oxygen

was introduced to burn off carbon deposits. Since all of this work was done above the explosive range, constant checks were made to be certain that air did not leak into the system, particularly in front of the reaction chamber. Precautions were also taken to keep rotameters vertical, prevent surges in the gas flow system and always to introduce hydrocarbon into a nitrogen filled reaction chamber. Surges in gas flow from the storage tank to the surge tank occurred with both methane and ethane unless heat was supplied to the diaphragm valve. The cooling effect of these gases was sufficient to cause the diaphragm to stick. Heat was supplied by a stream of air flowing from a small compressor.

At the end of each run the condenser was washed with 4 or 5 25 cc. portions of distilled water. In cases where condensate was obtained it was weighed separately and combined with the washings of the condenser, unless it occurred in sufficient quantity to be analyzed alone. The solution from each absorber was analyzed separately in order to be certain that excessive quantities of product were not lost.

In all cases where metal tubes and turnings were used activation was made in the same manner by alternate oxidations and reductions. Three such cycles consisting of 10 minute oxidation by oxygen, 15 minute purge with nitrogen, and 10 minute reduction

by hydrogen were carried out before the initial run. Following this first use of the particular catalyst a long oxidation of one hour or more burned off the carbon deposit. This was followed by two cycles as described above. Inspection of the catalyst showed the desired thoroughly roughened surface. This was simply an attempt to obtain the type of surface which Balandin^{31,32} believes to be active. Prolonged use embrittled slender turnings to such a degree that they crumbled; therefore even if a catalyst of this type proved useful it would probably need to be made up of larger pieces.

The silica gel used was made by Davison Chemical Company of Baltimore, Maryland as a commercial catalyst support. It was 8-14 mesh. When used alone this gel was quickly transferred from its container to the catalyst tube in order to prevent it taking on excessive water. Any water taken on, however, was driven off in the tube at 450 to 600°C. into a stream of Neither the gel nor any of the catalytic nitrogen. substances supported on it were reduced by hydrogen. Ordinary drying of silica gel (100-110°C.) reduces its moisture content to 5 to 8 per cent. Higher temperatures were used to remove the chemically held water almost to zero. According to Ruff and Mautner, 38 one gram of silica gel contains about 450 square meters of surface, and the pore volume is 40 to 50 per

cent of the total volume. The 120 grams of catalyst placed in the tube filled it completely. Glass wool was used at the entrance and exit ends of the tube to prevent carryover. Carryover of catalyst in this equipment was highly improbable because of the construction, nor were solids observed in the condensate. The condensate resulting from high temperature runs using molybdenum oxides on the gel did give a straw color solution, which was believed to be due to polymer. It was not a solid unless of colloidal dimensions.

In order to compare the catalytic activity of copper turnings to copper oxide supported on silica gel, 40 grams of copper nitrate was deposited on 129 grams of the dry gel. A solution of the copper nitrate was made and added to the desiccant. This substance, after being heated to 800°F. for 2 hours. appeared black, indicating that the nitrate had broken down to the oxide. 120 grams of this material was charged to the reaction tube. The catalyst caused the reactions to go all the way to carbon dioxide and water as was indicated by the quantity of heat evolved. Temperature control was impossible even though the rate of oxygen flow was reduced from 560 cc. per minute to 140 cc. per minute. Some useful product was detected as shown in the following section under runs 54 and 55.

The vanadium oxide catalyst was prepared by adding 170 grams of silica gel to a solution obtained from 2 grams of ammonium metavanadate (NH_4VO_3) dissolved in 150 grams of water. The catalyst was heated to 1,200°F. in a muffle furnace for several hours. This higher temperature was used, rather than the 750°F. recommended by Jaeger and Bertsch, 39 to increase the rate of decomposition. Since the catalyst was subsequently to be used at temperatures up to 1,200°F., any detrimental effects of high temperature would be exhibited throughout its use. In the preparation a stream of oxygen was not passed over the salt to form only vanadium pentoxide. This higher oxide would surely be reduced to the various states of oxidation after only short use. The catalyst after use did appear to be a mixture of the black oxide V_2O_3 , the blue oxide V_2O_4 , and reddish-yellow V_05.

The molybdenum oxide catalyst was prepared in the same way as the vanadium catalyst, only the starting material was now molybdic acid. A thin slurry was made of this insoluble material and the desiccant added while rapidly stirring the mixture. Water did not appear in the bottom of the beaker in which the mixing was carried out, nor was there any evidence of powdered chemicals which had not been adsorbed. New molybdenum oxide catalysts, which were made up in as

nearly the same way as possible, were charged just before runs number 66, 83, and 93. The only evidence of a loss of activity on the part of the catalyst was the failure to obtain checks on one high yield, which was obtained in the first of a series of runs under identical conditions. This may have been caused by carbon deposit even though long periods of oxidation were used. After use the molybdenum appeared to be in both the form of the colorless trioxide MoO_3 , and the blue oxide MoO_2 .

One notable difference between the low temperature reactions and those carried out at higher temperature was the larger quantity of carbon deposited in the second case. Since all of the high temperature runs except numbers 106 and 107 were made with silica gel in the tube, the temperature condition may not have been entirely to blame. Silica gel may have caused pyrolysis. This condition was especially noticeable in those runs using propane. Oxidation for burning off the carbon was carried out for 2 to 3 hours at 550°C. in these cases. Because of the limitations of the copper tube, higher temperature oxidations could not be carried out, and some carbon always appeared on the discharged catalyst. A great deal of cracking occurred, especially with propane, and light oils were observed on the glass around the watergas interface of the absorbers. These same polymers

may have caused the straw color in the condensate as mentioned previously.

The substances used as catalysts contained the following impurities as reported by the supplier.

Molybdic Acid	,	Cupric Nitrat	e
C.P. Bakers Anal	yzed	C.P. Bakers Anal	yzed
Component	2	Component	2
Cl	0.001	Insol. Matter	0.005
S04	0.01	Cl	0.001
P0 ₄	0.0005	S04	0.002
Insol. in NH_4OH	0.01	Alkalies as SO_4	0.02
H. Metals (as Pb)	0.001	Fe	0.0015
NH3	0.0005	Ammonium Sulfide	
NO 3	0.003	Fe (as Ni)	0.005

C.P. ammonium metavanadate obtained from Fisher Scientific Company was used. No analysis was given by the supplier.

The sintered bronze catalyst tube used in runs 106 and 107 was obtained from the Moraine Products Division of General Motors Corporation. The tube was filled with bronze shot of mesh size minus 40, plus 60. The analysis was 7.93 per cent tin and 92.07 per cent copper.

The propane obtained from Phillips Petroleum Company was of their Pure Grade, and was listed as 99 Mol per cent minimum purity. The methane and ethane of 99 and 95 per cent purity respectively were obtained from the Matheson Company at East Rutherford, New Jersey. Consumers Power Company's analysis showed the natural gas to be of the following composition.

Natural Gas

Component	Z
Methane	82.3
Ethane	7.2
Propane and higher	0
Nitrogen	10.5

Walker⁴⁰ suggests the following method for the estimation of formaldehyde in the presence of alkali sensitive products, and impurities such as cresol, phenol, and resinous materials. The method is that of Brochet and Cambier⁴¹ The basis of reaction is the liberation of hydrochloric acid when hydroxylamine hydrochloride reacts with formaldehyde to form formaldoxime as represented by:

 CH_2O (aq.) + NH_2OH . $HCl = CH_2$: $NOH + H_2O + HCl$ The procedure consisted of treating a 50 gram sample (20 grams when sample was condensate) with 10 milliliters of 10 per cent hydroxylamine hydrochloride solution. At the same time another 10 milliliters of hydroxylamine hydrochloride was pipetted out to serve as a blank. After 15 to 20 minutes the two were titrated with standardized tenth normal potassium hydroxide using bromophenol blue as an indicator. The end point is marked by a color change from yellow

to light purple. The difference between the milliliters of standardized base required for the sample and for the blank indicates to what extent hydrogen chloride has been liberated in the above reaction. This method is specific for formaldehyde determination, but part of the ketones formed might show up here. Ketone has not been detected by investigators at atmospheric pressure, and only to the extent of 3 to 5 per cent of the total product at elevated pressures.^{6,16}

Walker⁴² recommends titration with carbonate free sodium hydroxide for the determination of formic acid. Bromothymol Blue is used as an indicator. This indicator changes from yellow to blue at a pH of 6 to 7.5 so that acetic acid as well as formic would be neutralized. The results were reported as formic acid. 20 milliliter portions of sample were titrated with a standardized tenth normal alkaline solution. The alkali was made carbonate free by using barium chloride after which atmospheric air was excluded.

The determination of aldehydes above formaldehyde was made according to Cumming, Hopper and Wheeler.⁴³ Use was made of the addition reaction between aldehydes and sodium bisulphite. Since the quantity of formaldehyde was determined independently, the higher aldehydes could be obtained by difference. When higher aldehydes are absent this is a good method for the determination

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of formaldehyde. The method consists of contacting 20 milliliters of aldehyde solution with an excess of sodium bisulphite, containing 12 grams of the salt per liter. The difference between the iodine titre of the sample, and that of the blank indicates the quantity of sodium bisulphite that has formed the addition product with aldehyde. The bisulphite solution should not be too strong because in more concentrated solutions the hydrogen iodide liberated reduces the sulfuric acid formed to give the reverse reaction. Tenth normal iodine and sodium thiosulphate solutions were used.

Detailed procedure for the determination of alcohol is available in Walker⁴⁴ The original work was done by Blank and Finkenbeiner⁴⁵ The method consists of complete oxidation of alcohol, aldehyde and acid to carbon dioxide and water. This is brought about by an excess of chromic acid. The quantity of chromic acid used in the oxidation can be determined with the aid of a blank. The only time calculations are possible is in those cases where exact quantities of compounds are known. For example one quantity of chromic acid is required to oxidize a molecule of acetaldehyde, but a different amount is needed for a molecule of propanal.

DATA AND RESULTS

Table I is the result of 107 partial oxidation tests made under various conditions. Over 1,600 analyses were made. The average yield of formaldehyde as obtained by two different methods of analysis is given. The first 31 runs are not listed, because only traces of the desired product were obtained. The nickel tube used in the first 21 runs catalyzed the oxidation reaction to completion. The next 9 runs were necessary to locate the approximate conditions under which detectable yields could be obtained. Table II shows the effects of catalyst and experimental conditions on the ratio of grams of formaldehyde to grams of formic acid surviving. Table III compares the yields of the various catalysts toward propaneoxygen mixtures treated in identical ways.

		Table I						Table I		
Run No.	Duration of Run, min.	Hydrocarbon Flow Rate, _cc./min.	Oxygen Flow Rate, cc./min.	Reaction Temperature,	Formaldehyde Surviving, mg.	Formic Acid Surviving, mg.	Total Quantity of Useful Products Surviving, <u>mg</u> .	Per Cent of Formaldehyde	Oxygen S Formic <u>Acid</u>	urviving as: Total Useful Products
				Propane -	Oxygen -	Copper Turn	lings			
32	60	2290	560	470	56	6	62	0.07	0.01	0.08
35	90	3000	715	470	40	11	51	0.03	0.02	0.05
36	90	3000	715	470	47	16	63	0.03	0.03	0.06
37	180	2290	560	470	56	15	71	0.04	0.02	0.06
38	90	2 290	560	470	44	28	72	0.03	0.05	0.08
39	90	2290	560	470	34	14	48	0.03	0.02	0.05
40	30	2290	560	470	21	18	39	0.07	0.03	0.10
41	60	2290	560	470	58	24	82	0.07	0.04	0.11
				Propane -	Oxygen -	Empty Coppe	er Tube			
42	60	2290	560	470	51	10	61	0.06	0.02	0.08
43	60	2290	560	470	49	20	69	0.06	0.03	0.09
4 4	60	2290	560	470	48	18	66	0.06	0.03	0.09
45	60	2290	560	470	17	16	33	0.01	0.03	0.04
46	60	2290	560	470	18	5	23	0.02	0.01	0.03
				Propane -	Oxygen -	Silica Gel				
47	60	2290	560	470	212	25	237	0.26	0.04	0.30
48	60	2290	560	470	136	3	139	0.17	0.00	0.17
49	60	2290	560	470	187	6	193	0.24	0.01	0.25
50 ^a	60	2290	560	47 0	228	5	233	0.28	0.01	0.29
51 ^a	60	2290	560	47 0	316	5	321	0.39	0.01	0.40

a--Gases bubbled through water took on about 10 grams per one hour run.

52^a

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Formic Acid	Total Useful Products
0 01	0.08
0.02	0.05
0.03	0.06
0.02	0.06
0.05	0.08
0.02	0.05
0.03	0.10
0.04	0.11
0.02	0.08
0.03	0.09
0.03	0.09
0.03	0.04
0.01	0.03
0.04	0.30
0.00	0.17
0.01	0.25
0.01	0.29
0.01	0.40
0.01	0.31
0.03	0.34

0.30

0.31

Run No.	Duration of	n Hydrocarbon Flow	ration Hydrocarbon of Flow	rbon Oxygen Flow	Reaction Temperature.	Reaction Formaldehyde Formic	Total Quantity of	Per Cent of Oxygen Surviving as:		
	Run, 	Rate, cc./min.	Rate, cc./min.	°c	mg	Surviving,	Surviving,	Formaldehyde	Formic Acid	Total Useful Products
				Propane -	Oxygen -	Copper Oxid	e on Silica Gel			
54	60	2290	560	470	134	170	304	0.16	0.27	0.43
55 ^b	40	2290	560	(470)	51	77	128	0.14	0.12	0.26
56	60	3000	75	375	22	9	31	0.13	0.02	0.15
57	60	3000	240	300	7	15	22	0.00	0.03	0.03
				Propane -	Oxygen -	Vanadium Ox	ides on Silica Gel			
58	60	2290	560	470	329	26	355	0.40	0.04	0.44
59	60	2290	560	47 0	285	28	313	0.36	0.05	0.41
60	60	2290	560	470	308	16	324	0.38	0.03	0.41
61	60	2290	560	470	303	16	319	0.37	0.03	0.40
62	60	2290	560	470	3 06	31	337	0.37	0.05	0.42
63 ⁰	60	2290	5 6 0	470	306	25	331	0.34	0.03	0.37
64 [°]	60	2290	560	4 7 0	259	23	282	0.30	0.04	0.34
65 [°]	60	2290	560	470	259	18	277	0,32	0.03	0.35
				Propane -	Oxygen -	Molybdenum	Oxides on Silica Gel			
66	60	2290	560	470	967	43	1010	1.19	0.07	1.26
67	60	2290	560	470	1182	48	1230	1.44	0.08	1.52
68	60	2290	560	470	952	49	1001	1.18	0.08	1.26
69	60	2 290	560	470	951	43	994	1.18	0.07	1.25

Table I --- continued

b--Temperature control impossible due to highly exothermic nature of reaction.

c--Gases bubbled through water took on about 10 grams per one hour run.

Run	Duration	Hydrocarbon Flow	0xygen	Reaction	Formaldehyde	Formic	Total Quantity of	Per Cent of	Oxy gen S	urviving as:
<u></u>	Run, min.	Rate, cc./min	Rate, cc./min.	0C	mg.	Surviving,	Surviving,	Formaldehyde	Formic <u>Acid</u>	Total Useful Products
				Ethane -	Oxygen -	Molybdenum	Oxides on Silica Gel			
70	60	2290	560	470	535	19	554	0.67	0.03	0.70
71	60	2290	560	470	466	12	478	0.57	0.02	0.59
72	60	2290	560	570	1301	39	1340	1.60	0.06	1.66
73	60	2290	560	570	1280	30	1310	1.58	0.05	1.63
74	60	2290	560	650	1813	43	1856	2.25	0.07	2.32
75	60	2290	560	650	2098	39	2137	2.59	0.06	2.65
76	60	2290	560	650	2121	46	2167	2.65	0.08	2.73
				Methane -	Oxygen -	Molybdenum	Oxides on Silica Gel			
77	60	2290	560	650	605	13	618	0.75	0.02	0.77
78	60	2290	560	650	751	19	770	0.94	0.03	0.97
79	60	2290	560	650	597	17	614	0.65	0.03	0.68
				Propane -	Oxygen -	Molybdenum	Oxides on Silica Gel			
80	60	2290	560	650	2058	62	2120	2.53	0.10	2.63
81	60	2290	560	650	1285	42	1327	1.58	0.07	1.65
82	60	2290	560	650	1159	48	1207	1.43	0.08	1.51
83	60	2290	560	47 0	1319	50	1369	1.64	0.02	1.66
84	60	2290	560	650	1879	46	1925	2.30	0.08	2.38
85	60	2290	560	470	955	39	994	1.18	0.06	1.24

Table I --- continued

Run No.	Duration of	Hydrocarbon Flow	Oxygen Flow	Reaction Temperature.	Formaldehyde Surviving.	Formic Acid	Total Quantity of Useful Products	Per Cent of	Oxygen S	urviving as:
	Run, min.	Rate, cc./min.	Rate, cc./min.	°c	mg	Surviving,	Surviving, mg.	Formaldehyde	Formic Acid	Total Useful Products
			I	Natural Gas -	Oxygen -	Molybdenum	Oxides on Silica Gel			
86	60	2290	560	650	640	25	665	0.80	0.04	0.84
8 7	60	2290	560	650	646	25	671	0.80	0.04	0.84
88	60	2290	280	650	660	25	685	1.63	0.09	1.72
89	60	2290	280	650	675	22	697	1.65	0.07	1.72
90	60	2290	140	650	588	10	598	2.89	0.07	2.96
91	60	2290	140	650	474	14	488	2.34	0.10	2.44
92	60	2290	140	650	, 517	16	533	2.57	0.11	2.68
93	60	2290	140	650	470	22	492	2.32	0.15	2.47
94	60	2290	75	650	227	8	235	2.09	0.10	2.19
95	60	2290	75	650	218	9	227	2.00	0.11	2.11
96 ^d	60	2290	840	650	603	10	613	0.49	0.01	0.50
				Natural Gas	- Air -	Molybdenum	Oxides on Silica Gel			
97	60	2290	500	650	311	6	317	2.06	0.05	2.11
98	60	2290	500	650	218	6	224	1.43	0.05	1.48
99	60	2290	800	650	259	6	265	1.07	0.03	1.10
100	60	2290	800	650	351	7	358	1.41	0.04	1.45
101	30	2290	1000	650	181	5	186	1.23	0.02	1.25
102	60	2290	1000	650	448	15	463	1.48	0.06	1.54
103	60	2290	1000	650	446	9	455	1.47	0.04	1.51
104	60	2290	800	650	368	6	374	1.54	0.03	1.57
105	60	2290	500	650	293	5	298	1.99	0.04	2.03

Table I --- continued

d--Temperature control impossible due to highly exothermic nature of reaction. Highest temperature well over 800°C.

Table I --- continued

Run No	Duration	Hydrocarbon Flow	0xygen Flow	Reaction Temperature	Formaldehyde Surviving	Formic	Total Quantity of	Per Cent of	Oxygen S	urviving as:
	Run, min.	Rate, cc./min.	Rate, cc./min.	°C	mg	Surviving,	Surviving, mg.	Formaldehyde	Formic <u>Acid</u>	Total Useful Products
				Natural Gas	- <u>Air</u> -	Sintered Br	onze Tube			
106	60	2290	500	650	69	5	74	0.48	0.04	0.52
107	60	2290	500	650	73	6	79	0.48	0.05	0.53

Table II

Ratio of Formaldehyde to Formic Acid

A		В		
Effect of Catalyst		Effect of Hydrocarbon		
Propane-Oxygen-470 ⁰ C.		0xygen-Molybdenum 0xides-650°C.		
<u>Catalyst</u>	<u>Ratio</u>	Hydrocarbon	Ratio	
Empty tube	3	Natural Gas	24	
Copper oxide on	1	Methane	38	
Venedium exides on	Ŧ	Ethane	45	
Silica Gel	13	Propane	28	
Molybdenum oxides on Silica Gel	21			
Silica Gel alone	43			
C	D		Е	

Effect of Temperature Effect of Oxygen Flow Rate Effect of Temperature

Ethane-Oxygen- Molybdenum Oxides		Natural Gas-Oxygen- Molybdenum Oxides-650 ⁰ C.		Propane-Oxygen- Molybdenum Oxides	
Temperature	<u>Ratio</u>	Flow Rate	Ratio	Temperature	<u>Ratio</u>
470 ⁰ C.	31	840	26	470 ⁰ C.	21
570	36	560	24	650	28
650	45	280	27		
		140	35		
		75	26		

Table III

Average Percentage Yields for Various Catalysts 2,290 cc./min. Propane-560 cc./min. Oxygen-470°C.

Catalyst	Yield, %
Empty tube	0.07
Copper turnings	0.07
Silica Gel	0.29
Copper Oxides on Silica Gel	0.35
Vanadium Oxides on Silica Gel	0.39
Molybdenum Oxides on Silica Gel	1.17







FIG. 5

Table I was compiled in accordance with the following sample calculations on Run No. 75. The function of the various solutions mentioned was discussed in the section pertaining to procedure. The data needed is as follows.

Run No. 75

Weight of Sol'n. grams	Vol. of KOH Used <u>ml.</u>	Size of Sample <u>ml.</u>	Vol. of I2 Sol'n. Used 	Size of Sample <u>ml.</u>	Vol. of NaOH S Used <u>ml.</u>	Size of Sample <u>ml.</u>
486	0.91	50	7.53	20	0.08	20
229	0.55	50	4.52	20	0.08	20
146	0.35	50	3.37	20	0.00	20
154	6.45	20	33.14	5	0.90	20
y of KC	DH Sol	Lution			1.105	N
by of Id	odine	Solutio	on		0.111	N
y of Na	aOH Sc	olution			0.091	7 N
	Weight of Sol'n. <u>grams</u> 486 229 146 154 154 259 of KC 29 of KC	Weight Vol. of of Sol'n. KOH Used grams ml. 486 0.91 229 0.55 146 0.35 146 0.35 154 6.45 Sy of KOH Sol Sy of Iodine	Weight Vol. Size of of of Sol'n. KOH Sample Used grams <u>ml. ml.</u> 486 0.91 50 229 0.55 50 146 0.35 50 154 6.45 20 y of KOH Solution by of Iodine Solution by of NaOH Solution	Weight Vol. Size Vol. of of of of Iz Sol'n. KOH Sample Sol'n. Used grams ml. ml. ml. ml. 486 0.91 50 7.53 229 0.55 50 4.52 146 0.35 50 3.37 154 6.45 20 33.14 cy of KOH Solution Solution Solution cy of NaOH Solution Solution Solution	Weight Vol. Size Vol. Size of Size of Size of Size of Sample Sample	Weight Vol. Size Vol. Size Vol. of of <tho< th=""> of <tho< th=""> of<!--</td--></tho<></tho<>

The volume of potassium hydroxide and iodine solution required for the blank determinations have been subtracted from the total titre.

The basic equations used for the determination of formaldehyde are:

$$CH_2O$$
 (aq.) + NH_2OH . $HCl = CH_2NOH + H_2O + HCl$ (A)

 $KOH + HC1 = KC1 + H_2O$ (B)

It is evident that the mols of hydrogen chloride liberated are equal to the mols of formaldehyde reacting. The mols of potassium hydroxide required are equal to the mols of formaldehyde plus the mols

of the base used in the blank titration of hydroxylamine-hydrochloride. Equivalent weight of formaldehyde = 30.0 Number of equivalent weights of formaldehyde = number of equivalent weights of potassium hydroxide used on the sample minus number of equivalent weights of potassium hydroxide used on blank. Grams of formaldehyde = (Sample titre - Blank titre) x N of KOH x 30.0 1.000 (C)or per cent formaldehyde = (Sample titre-Blank titre) x N of KOH x 30.0 x 100 (D) Weight of Sample (grams) x 1,000 Applying formula (C) above to the data given for Absorber 1: $= 0.91 \times 1.105 \times 0.030$ Formaldehyde present = 0.03016 grams = 30.16 mg. Total mg. of formaldehyde in Absorber 1 $(\frac{486}{50} \times 30.16)$ = 293 mg.Values obtained for the remaining solutions are as follows: =83 mg. Absorber 2 =34 mg. Absorber 3 =1646 mg. Wash plus Condensate The total quantity of formaldehyde is 2.056 grams. The higher aldehydes will now be calculated

according to the equations which follow.

 $CH_3CHO + NaHSO_3 = CH_3CH(OH)SO_3Na$ (E)

 $HCHO + NaHSO_3 = H_2C(OH)SO_3Na$ (F)

$$2NaHSO_3 + I_2 + H_2O = Na_2SO_4 + 2HI$$
 (G)

The rate of addition for the aldehyde-sodium bisulfite reaction decreases with the length and branching of alkyl groups. From equations (E), (F), and (G) it is seen that one molecule of either formaldehyde or acetaldehyde reacts with one molecule of sodium bisulfite. Since one mol of iodine reacts with two mols of sodium bisulfite, the equivalent weight of the aldehydes is one-half the molecular weight.

 $= \frac{1 \times 0.100 \times 44}{2}$ 1 ml. of 0.100 N iodine solution = 2.2 mg. acetaldehyde = 1.5 mg. formor aldehyde Correction for the deviation of iodine solution from 0.100 N is applied as follows: 1 ml. of 0.111 N iodine solution = 1.66 mg. form- (0.111×1.5) (0.100)aldehyde = 2.44 mg. acetaldehyde Ml. of iodine required for the formaldehyde in =176 ml. (293)(1.66)Absorber 1 Total ml. of iodine used $(\frac{486}{20} \times 7.53) = 183$ ml.

Ml. of iodine required for acetaldehyde (183 - 176)= 7 ml. Mg. of acetaldehyde (7 x 2.44) = 17 mg. In a similar manner the quantity of acetaldehyde in the other solutions was found to be as follows: Absorber 2 = 4 mg. Absorber 3 = 10 mg. Wash plus Condensate = 71 mg. Total acetaldehyde was 102 mg. Per cent of total aldehyde found to be acetaldehyde

$$\frac{(102 \times 100)}{(2056 - 102)} = 4.7 \%$$

This value is approximately the limit of experimental accuracy. Results obtained in the other runs indicate that the two methods of analysis always gave close checks. No acetaldehyde was formed.

The neutralization reaction NaOH + HCOOH = NaOOCH + H_2O is the basis for acid calculation. One mol of base reacts with one mol of acid. Molecular weight of formic acid = 46 One ml. of 0.100 N NaOH neutralizes

 $(1 \times 0.100 \times 46) = 4.6 \text{ mg.}$

One ml. of 0.0917 N NaOH neutralizes

$$\frac{(0.0917 \times 4.6)}{(0.100)} = 4.22 \text{ mg.}$$

Mg. formic acid in Absorber 1

$$(\frac{486}{20} \times 0.08 \times 4.22) = 8$$
 mg.

Formic acid content of the other solutions were found to be as follows:

Absorber 2	= 4	mg.
Absorber 3	= 0	mg.
Wash plus Condensate	= 29	mg.

The total acid obtained was 41 mg.

Calculation of the percentage of oxygen surviving as formaldehyde and formic acid in Run No. 75. follows. Mols oxygen introduced per hour

$$\left(\frac{560 \times 60 \times 492 \times 739}{22.4 \times 530 \times 760} \right) = 1.35$$
 mols

Mols of formaldehyde produced (2.098) = 0.070 mols Mols of oxygen contained in the formaldehyde produced (0.070) = 0.035 mols

produced $\left(\frac{0.070}{2}\right)$ = 0.035 mols Percentage of the oxygen introduced surviving as formaldehyde $\left(\frac{0.035}{1.35} \times 100\right)$ = 2.59 % Mols of formic acid produced $\left(\frac{0.041}{46}\right)$ = 0.00089 mols Mols of oxygen contained in the formic acid

produced = 0.00089 mols Percentage of the oxygen introduced surviving as formic acid (0.00089×100) = 0.07 %

Most of the tests were made at flow rates of 2,290 cc./min. of hydrocarbon and 560 cc./min. of oxygen. The contact time of the gas and silica gel supported catalyst and empty tube is calculated as

follows:

Volume of gas (S.T.P.) passing per second

$$\frac{(2290 + 560 \times 492 \times 739)}{60 \times 530 \times 760} = 429 \text{ cc./sec.}$$

Volume of empty tube

$$\left[\frac{(0.824)^2 \times 3.1416 \times 28 \times (2.54)^3}{4} = 240 \quad \text{cc.}\right]$$

Pore space in the filled tube

 $(240 \times .425) = 102$ cc.

Contact time (102) = 0.24 Sec. (429)

Contact time for empty tube (240) = 0.56 Sec. (429)

Contact surface (120 x 450) = 54,000 Sq. Meters

DISCUSSION

Table III shows that catalysts have a great effect upon the success of the partial oxidation process. A comparison of the results obtained by use of the empty copper tube and one containing copper turnings shows that surface area of the electrolytic copper catalyst has little effect on yields. It is difficult to carry this comparison to copper oxide powder supported on silica gel because the gel itself gives yields approximately four times as great as the electrolytic copper catalyst. Copper oxide, when supported on silica gel, does increase yields about 0.06 per cent above that of the silica gel alone. The increase resulting from the copper oxide addition is near the total yield for the empty tube or the copper oxide turnings. The difference between the history of the metallic copper and the powdered copper oxide might easily cause a great difference in their activities. By far the best catalyst for the conditions under which Table III was compiled is the molybdenum oxides. They are seen to be roughly 1,700 per cent better than the empty tube and 300 per cent better than vanadium oxide, the second in activity. Gas flow rates and space velocities used were in the range reported best for high yields.^{14,18,22} Other conditions might very well have changed the results.

The earlier tests using nickel as a catalyst were made with an ethane flow rate of 1,300 cc./minute. By changing the flow rate of oxygen an attempt was made to obtain a reaction that would not go to completion. The exothermic nature of the complete oxidation reaction caused temperatures to rise very rapidly. At times temperature increases of 20 to 30°C. per minute were observed. Only traces of aldehydes were found, regardless of whether the reaction produced enough heat to keep the temperature up or whether the heater was used to supply additional heat. For each oxygen flow rate there was a specific temperature above which large quantities of heat were evolved. For oxygen flow rates of 450 to 600 cc./minute (26 to 32 per cent of the total gas) the specific temperature was 326°C. Above and below this oxygen concentration this specific temperature was not investigated. It is apparent that the oxygen concentration on the catalyst surface is not affected appreciably over the concentration range studied.

In those runs (70-76) dealing with the effect of temperature on conversion of ethane, there was some relationship between the weight of condensate and the quantity of useful product obtained. Higher yields were obtained when larger quantities of condensate were collected. This comparison does not hold rigidly. In the natural gas-oxygen runs where oxygen

flow rates were changed, the high oxygen concentrations gave the most condensate, but not the most product. Larger quantities of water would be expected at higher oxygen concentrations. The condensate weights were not consistant enough to be functions of yields.

Temperatures near the exit end of the copper reaction tube did not correlate with yields. The temperatures for the better yields were in the range of 475 to 560°C. Some cooling occurred in that part of the tube not surrounded by the heater. The thermocouple from which end temperatures were read was located in this section of the tube.

The effect of adding water vapor to the incoming gases is twofold. First, there is a tendency to decrease the equilibrium quantity of formaldehyde by adding the same material that is produced by the reaction; second, there is the possibility of forming hydrocarbons and oxygenated compounds by reversing the water gas reaction. The latter is desirable. At the high temperatures of the reacting gases the hydrocarbon and water would not react to form alcohol, a fact shown by the positive free energy of the reaction.⁴⁷

There are a number of different bases that may be used in calculating yield. The yield could be based on (1) the percentage of the hydrocarbon burned resulting in oxygenated product, (2) the percentage of the hydrocarbon input resulting in useful product,

(3) the percentage of the oxygen input resulting in useful product, or (4) it could be based on some theoretical equation. The first method requires complete exit gas analyses; this would greatly decrease the scope of investigation possible per unit time. The second would be valuable below the explosive range where the hydrocarbon is the limiting reactant, and the third could be used for data above the explosive range where hydrocarbon is in excess. The fourth basis would probably be different with different operators since each may believe that reaction had occurred in a different manner. The results in this paper have been reported by the third method. A comparison to a theoretical equation shows that 100 per cent yields for the reactions, when based on oxygen input, are impossible because water vapor and oxides of carbon always are present as products of reaction. Based on the equation

 $C_3H_8 + 5/2 O_2 = 2HCHO + 2H_2O + CO$ 2/5 of the oxygen introduced appears as desired product and a theoretical formaldehyde yield of 8.98 per cent is obtained for Run No. 75. This compares to 2.59 per cent obtained in Table I. The fact that carbon dioxide is always reported by investigators who analyzed effluent gases shows the above equation to be a conservative one for calculating yields.

Figures 2 and 3, page 44, compare the gram and

per cent yields obtained when using air and oxygen as the oxidizing agents under the same conditions. Both figures represent the rate of flow of the oxygen component of the air. A flow rate of 500 cc./minute of air is plotted as a flow rate of 105 cc./minute of oxygen. The curves show that the diluent nitrogen, at higher oxygen flow rates, causes a decrease in yield of oxygenated product, but at the lower oxygen flow rates the diluent begins to have less effect. The effect of total flow rate may be involved in that the contact time is shortened with air so that the reaction is stopped before equilibrium is reached. At higher oxygen flow rates the high oxygen concentration would have a tendency to give a more complete oxidation, thus helping to decompose formaldehyde formed. Opposing the effect of high concentrations of oxygen at the high flow rates is the shortening of contact time. Which of these factors affects percentage yield to the greatest extent could well be made the subject of further research. Slowing down both natural gas and air flow rates in the same proportion should increase the per cent yield due to the longer contact time. Likewise, increasing the flow rates of natural gas and oxygen in the same proportion might increase the yield at higher rates, or no effect might be observed due to the predominance of the oxygen concentration effect on the catalyst or

in the gas stream.

When air is used as the oxidizing agent a maximum percentage yield must occur between zero and 110 cc./minute of oxygen gas flow per minute. Compared with the oxygen curve in the same Figure (3), the maximum is displaced to the left toward lower flow rates. Over the short flow range where both curves are shown they are parallel, indicating that the nitrogen present in air depresses yields to the same extent regardless of flow rate. A comparison of the two Figures shows that the highest yield in grams occurs at a flow rate of 280 cc./minute of oxygen, but the highest percentage yield came at a flow rate of 140 cc./minute of oxygen. The increment of grams product per cc./minute of oxygen decreased above the oxygen flow rate of 140 cc./minute.

Figure 4 indicates that, under the experimental conditions used, higher temperatures than 650°C. might give more product for the ethane-oxygen system. The per cent yield is practically a straight line function of the temperature. Eventually a maximum would surely be reached on this curve, which would represent the temperature above which more product was being decomposed than the extra made by stepping up the reaction rate. Extrapolation of this curve shows zero product at 400°C. Runs 22 to 25 gave only traces of formaldehyde over the temperature range of

350 to 400°C.

Figure 5 shows the effect of hydrocarbon chain length on yields. It is seen that the 650°C. curve has a negative slope in going from 2 to 3 carbon atoms, while the 470°C. curve has a positive slope. Since propane is shown to be more easily oxidized it appears that 650°C. is above the temperature required for maximum yield of this gas. Other conditions were identical for the three gases.

Table II shows the effect of various conditions on the ratio of formaldehyde to formic acid surviving. In parts B, C, D, and E the highest ratios correspond to the highest percentage yields, even though all are not in order of the yields. In part A, silica gel used alone is most obviously out of line, but first and second are in the proper order. The differences in the ratios means that a good catalyst for formaldehyde formation is not necessarily good for producing formic acid.

Determination of the quantities of alcohol produced was accomplished by oxidizing all oxygenated compounds to carbon dioxide and water. Chromic acid was used as the strong oxidizing agent. The indirect iodimetric method was used to find the quantity of chromic acid that had reacted with oxygenated material. No alcohol was found in runs 30 to 37, and only very small quantities in tests where better yields of

formaldehyde were found. Actually inappreciable ^{*} quantities of both alcohol and acid were detected in the oxygenated product.

SUMMARY

Data is presented on the yields of formaldehyde and formic acid, the partial oxidation products of pure hydrocarbons and natural gas. The data reported was taken at 739 mm. total pressure and at several controlled temperatures. The catalysts used were:

Electrolytic copper

Silica gel

Copper oxide supported on silica gel Vanadium oxide supported on silica gel Molybdenum oxide supported on silica gel Sintered bronze tube

The effect of varying oxygen flow rates is shown for natural gas. Comparison is made of pure oxygen and air as oxidizing agents for natural gas when using the molybdenum oxide silica supported catalyst.

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