CATALYTIC DEHYDROGENATION OF LOW-BOILING HYDROCARBONS IN THE PRESENCE OF OXYGEN

by

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INTRODUCTION

According to A. V. Grosse (10, p.762-767), the tremendous advance in the application of catalysts to industrial uses may develop a need for still another field of chemistry known as "catalytic chemistry". In the petroleum and petrochemical industries, catalytic processes are rapidly replacing almost every other type of hydrocarbon conversion (5, p.98-112). One very important process, especially in war time, has been the dehydrogenation of various low-boiling hydrocarbons. Dehydrogenation is employed to convert the relatively inert paraffins to the more active olefins and diolefins. By such means, an enormous source of raw materials for the production of synthetic elastomers, plastics and useful chemicals is provided. It is hardly necessary to recall the huge quantities of synthetic rubber produced during the recent war to demonstrate the great strides catalytic dehydrogenation has made in less than ten years.

While many of the war time butadiene plants have been closed, there remains a great number of uses for dehydrogenation processes. Of the chemicals which may be synthesized from petroleum products, many begin with a

dehydrogenation step; consequently, more efficient means of dehydrogenation are in demand. One of the more recent modifications to the ordinary catalytic dehydrogenation will be discussed in the following paper. At present, no commercial process employs the principles used here for dehydrogenation; but with further work, there is reason to expect that the application of this type of process may become practical.

OBJECTIVE

One of the objects of this thesis is to demonstrate the applicability of a special catalytic process to the production of ethylene from ethane. This use, however, is auxiliary to the primary objective of the author. It is the chief purpose of the following paper to show the feasibility of what the author believes to be the simplest embodiment of the principle of selective oxidation to dehydrogenation reactions. The term selective oxidation as used hereafter will refer to the selective oxidation of the hydrogen evolved in the course of a dehydrogenation process. Since this represents only a modification of the existing practices, a survey of ordinary dehydrogenation reactions is desirable.

CATALYTIC DEHYDROGENATION OF HYDROCARBONS

The earliest large scale method of producing unsaturated hydrocarbons from paraffins was a pyrolytic process in which the paraffin was subjected to high temperatures in order to remove a molecule of hydrogen. The use of catalytic agents did not become prevalent until quite recently, although one of the earlier discussions was published by Frey and Huppke in 1933 (9, p.54-59). Catalytic dehydrogenation has a number of important advantages over its predecessor. Thermal processes obtain a low selectivity, and in order to produce practical conversions, the reactants must be admitted to the reactor slowly. By using a catalyst, however, the space velocity* of reactants may be as much as 25 times greater for the same conversion, while at the same time higher selectivity is obtained and lower temperatures may be used. For these reasons, most important dehydrogenation reactions involving hydrocarbons are carried out catalytically. Since about 1940, a large number of improvements have been brought out, involving changes in operating conditions, catalyst and reactor design.

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*Space velocity is defined as the volume of reactant gases per volume of catalyst per minute and is inversely proportional to the contact time.

There are many mutually related variables connected with the dehydrogenation of hydrocarbons (9, p.54-59; 11, p.268-272; 27, p.67-69; 28, p.1-14; 32, p.309-315). For convenience these variables will be discussed separately, remembering that each has its effect upon the others.

The temperatures involved in dehydrogenation are normally high, usually ranging from 500-650 degrees Centigrade; for the hydrocarbons from ethane to butane, the temperatures employed almost always lie between 600 and 650 degrees Centigrade. As the temperature is increased, the rate of reaction initially increases according to the first order reaction equation, but becomes more and more retarded due to secondary reactions as the temperature is raised further. In addition, the selectivity, or the per cent of reactants consumed which is converted to the desired product, varies with temperature in a similar manner. Since the reaction itself is endothermic, it is possible to carry it out under either isothermal or adiabatic conditions. In the latter, which is more prevalent, there is continuous diminution of temperature throughout the reactor which must be closely controlled in order to obtain optimum results.

A second important variable is the space velocity, a measure of contact time which in this paper will be defined as the volume of gaseous mixture entering the reactor per

volume of catalyst per minute. As the space velocity is increased (contact time decreased), the extent of conversion naturally decreases; but at the same time, selectivity is increased. At very low space velocities, a large degree of conversion is obtained, but when considerable carbon begins to deposit on the catalyst, its life is greatly shortened. Consequently, an economic balance must be made for each particular example in order to ascertain the optimum rate.

Due to the fact that the reaction produces an increase in volume, it is customary to operate at reduced pressure so as to take advantage of the mass action effect, there being some pressure at which optimum conversion occurs from the standpoint of practicability. It is the usual practice to obtain this lower pressure by using steam as a diluent, and again it is a matter for economics to decide the optimum partial pressure of reactants to be employed.

One of the factors which has been the subject of the most intensive study is the catalyst used. For dehydrogenation, a catalyst must meet certain rigid conditions: it must be selective enough to break the C-H bond (96,000 cal/mol required) and not the C- C bond (82,600 cal/mol required)(30, p.291-294); it should have a long life under reaction conditions and be capable of regeneration if necessary. Among the first catalysts used in

dehydrogenation was a chromic oxide gel (9, p.54-59; 27, p.67-69), which, however, has been found to be unstable with respect to crystalline chromic oxide, reverting rapidly to the latter form above 450 degrees Centigrade (11, p.268-272; 31, p.345-346). The most successful catalysts have not been pure compounds, such as Cr_2O_3, but have been mixtures of several components. Such mixed catalysts may be prepared either by coprecipitation of the constituents from the same solution (17, p.92) or impregnation of a suitable carrier, e.g., Al_2O_3, bauxite, kieselguhr, silica gel, etc., with a solution of the active compounds (2, p.48-52). Mixed catalysts normally contain one component, such as Al_2O_3, in a large excess, with more active elements, such as Cr_2O_3, Ni_2O_3, or a mixture of the two, in minor amounts. Various promoters may be added in quantities of 1% or less of the total catalyst. In general, active compounds such as those of chromium, nickel, titanium, tungsten, copper, berrylium, platinum, iron, etc., may be used as the oxide, hydroxide or in the reduced state, either singly or in various combinations with each other. Promoters may be taken from the difficultly reducible metals of the second, third, fourth, sixth and seventh groups of the periodic table, such as vanadium, columbium, tantalum, molybdenum, cerium, manganese and also silicon and boron. Since there are countless combinations of these various

elements it is only to be expected that there are innumerable catalysts described in the literature (4).

Catalysts are oftentimes subject to poisoning and deactivation, and several means of lessening these effects have been discovered. It has been found possible to lengthen the time between regenerations of the dehydrogenation catalysts (to remove coke deposited in the reaction) by adding small amounts of the oxides of the alkali metals (3; 12). These constituents are catalytic agents for the water gas reaction, and since steam is present in the reactor, considerable carbon is removed in this manner. This principle, first employed in the Standard Oil Development Company's 1707 catalyst, is also used to such a good advantage in the Shell 105 catalyst that in some processes, for example, the dehydrogenation of ethyl benzene, the catalyst is not regenerated but discarded when it is no longer useful (12).

Many catalysts are poisoned by sulphur compounds and organic chlorides, so that means for removing such constituents from the reactants are necessary. However, Shell Oil Company's nickel-tungsten sulphide catalyst is not affected by sulphur compounds.

SELECTIVE OXIDATION

Literature Survey and History

In attempting to increase the yield in a dehydrogenation process, one obvious expediency is to remove the hydrogen liberated in the course of the reaction. If this can be accomplished, it is logical to expect an increased yield of unsaturated products, according to the principle of Le Chatelier. The object of selective oxidation, then, is to effect the removal of hydrogen evolved in the dehydrogenation reaction by oxidizing it selectively to water, without appreciable formation of oxygenated hydrocarbon compounds. Several methods of processing hydrocarbons entailing selective oxidation have been promulgated, but no thorough kinetic investigation of this type of reaction has been published. However, certain studies of the oxidation of hydrocarbons have provided a theoretical basis for the partial mechanism which will be proposed here.

As might be expected from the diverse products formed by oxidizing paraffin hydrocarbons, there are numerous theories concerning the mechanism of the reaction; but in those respects pertinent to the subject of this thesis, there is general agreement in the literature. It will be necessary to make a brief survey of the kinetics of the combustion of both hydrocarbons and hydrogen in order to

apply some necessary postulates to the theory of selective oxidation. Since both of these reactions proceed through a chain mechanism, a definition of terms will prove beneficial (18, p.79-123; 22, p.148-215).

Chain reactions consist essentially of three parts: the chain-initiating reaction; the chain proper; the chain-ending reaction. The chain is propagated by chain carriers, or elements which, while being continuously resupplied by one or more steps of the chain, are necessary to at least one of those steps. Especially important in the oxidation of hydrocarbons is the enormous effect of the chain-branching reactions, by which term is meant a reaction producing several chain carriers instead of one. Semenoff has suggested another type of reaction, the delayed or degenerate chain. Degenerate branching occurs when a stable molecule is formed by a radical chain, the molecule reacting again to start another, but delayed, series of steps (22, p.195).

The first phenomenon which appears in a study of combustion is the induction period, i.e., a period of practically no reaction which is evident for all hydrocarbons. It has been discovered that this lag may be virtually eliminated by the addition of a small amount of an aldehyde, indicating that the formation of the aldehyde may be the first step in the burning of a paraffin (22, p.207;

18, p.79-80; 1, p.297). The oxidation of aldehydes is, in itself, a complex chain reaction; but it is thought that the primary step in such an oxidation is the formation of a peracid, RCO(OOH), as a surface catalyzed reaction (18, p. 82-83). This peracid could conceivably decompose at a surface in two ways, in one forming the radicals RCOO and OH, and in the other RCHO, H_2O and CO_2. Both reactions occur at a surface, but the latter is favored by a large and active surface area. Using this information, the following unbranched chain may be written, beginning after the formation of OH radicals from the peracid (18, p.89):

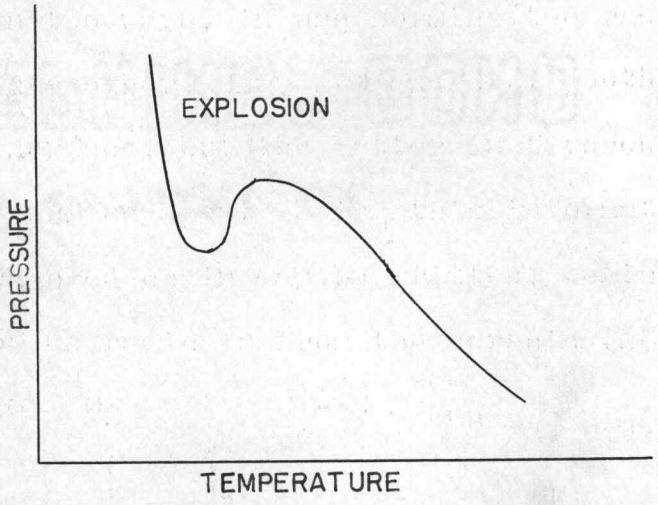
$$RCHO + O_2 \longrightarrow R - C(=O)-OOH \longrightarrow R - C(=O)-O- + OH$$

1. $OH + RCH_3 \longrightarrow H_2O + RCH_2$
2. $RCH_2 + O_2 \longrightarrow RCHO + OH$
3. $RCHO + OH \longrightarrow H_2O + RCO$
4. $RCO + O_2 \longrightarrow \cdots HO_2 + CO$
5. $HO_2 + HCHO \longrightarrow H_2O + CO + OH$
6. $OH + wall \longrightarrow$ destruction?

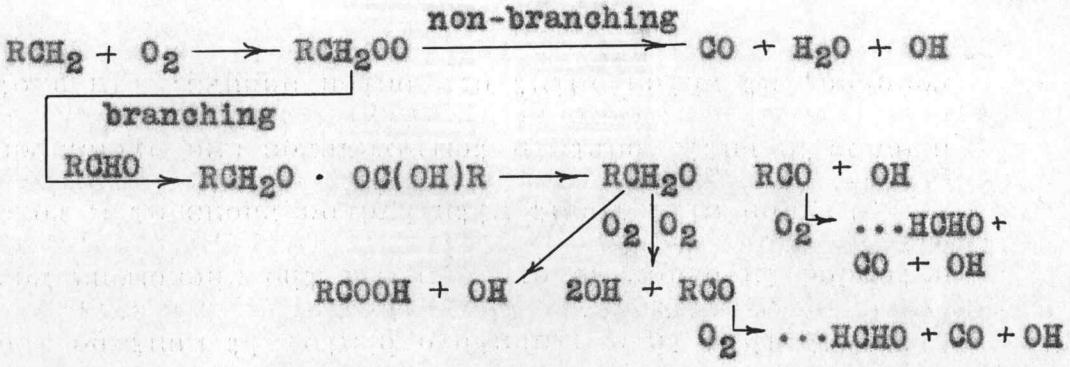
Reaction six is presumed to be the chain-stopping reaction, while reaction two is an example of degenerate branching. Although this is a plausible chain, it must be modified and extended in order to explain all the phenomena reported.

Oxygen will react with hydrocarbons at a relatively slow rate until certain temperatures and pressures are reached, at which point explosion occurs. In plotting

the temperature of explosion against pressure, a continuous curve is obtained which exhibits a "peninsula" lying between upper and lower temperature limits. It is not difficult to offer an explanation for the lower temperature limit, but the upper limit is still rather puzzling.



In order to show cause for a lower limit, it is assumed that at low temperatures the degenerate branching reactions are too slow to contribute enough to the reaction for the explosion to occur. As the temperature is increased at one pressure, a point is reached at which chain-branching becomes important enough to cause an explosion. This transition is illustrated readily by two competing reactions, one a simple chain which would produce a slow reaction, the other leading to branching and explosion. At lower temperatures the former obtains, the latter at higher temperatures. The following scheme depicts this effect (18, p.103):



To find a reason for the upper limit is more difficult, for it could be either a thermal* or chain-branching explosion, since the reaction rate gradually increases as the upper limit is approached. The evidence seems to favor the latter, but it is not conclusive. In the slow reaction region, the reaction rate reaches a maximum at the lower explosion limit, but acquires a negative temperature coefficient before reaching this point (22, p.210-211). The above explanation of the lower limit is consistent with this effect, but it offers nothing to show why the reaction rate should exhibit a second maximum at the upper boundary of the explosion peninsula. As evidence that the latter is due to a chain, and not a thermal, explosion, it has been discovered that upon the addition of helium, keeping the total pressure constant, the reaction is accelerated (18, p.104). If the explosion were thermal, the helium should have had little effect since the dissipation of heat would

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*A thermal explosion is one which occurs when the heat from an exothermic reaction is not dissipated as rapidly as it is released.

have been about the same. For a chain, however, one would predict a velocity increase due to the increased resistance offered to the movement of chain carriers to the wall and destruction. Assuming that the reaction is a chain, Lewis and von Elbe postulated the following, in which equations one, two and three are chain branching and four is the chain stopper (18, p. 105):

1. $HO_2 + RCH_2CHO + O_2 \longrightarrow 2OH + RCH_2CO(OO)$
2. $RCH_2\ CO(OO) \longrightarrow CO + H_2O + RCO$
3. $RCO + O_2 \longrightarrow \cdots HCHO + CO + OH$
4. $HCO + HCHO \longrightarrow CH(OH)CHO \xrightarrow{O_2} 2CO + H_2O + OH$

Such a scheme would explain the upper limit if it becomes important at elevated temperatures.

It is now possible to summarize the main reaction mechanism for the oxidation of hydrocarbons, assuming the aldehyde to have already been formed.

Initiation $RCHO + O_2 \longrightarrow RCO(OOH) \longrightarrow RCOO + OH$

Hydrocarbon oxidation

$OH + RCH_3 \longrightarrow H_2O + RCH_2$

$RCH_2 + O_2 \longrightarrow RCHO + OH$

$RCHO + OH \longrightarrow H_2O + RCO$

$RCO + O_2 \longrightarrow \cdots HO_2 + CO$

$HO_2 + HCHO \longrightarrow H_2O + CO + OH$

$OH + wall \longrightarrow destruction?$

Aldehyde oxidation

$$OH + RCHO \longrightarrow H_2O + RCO \xrightarrow{O_2} \ldots\ldots HCHO + CO + OH$$

$$OH + HCHO \longrightarrow HCO + H_2O$$

$$HCO + O_2 \longrightarrow HO_2 + CO$$

$$HO_2 + HCHO \longrightarrow H_2O + CO + OH$$

Peroxide branching

$$RCH_2OO + RCHO \longrightarrow RCH_2O \cdot OC(OH)R \xrightarrow{O_2} \ldots\ldots 5OH$$

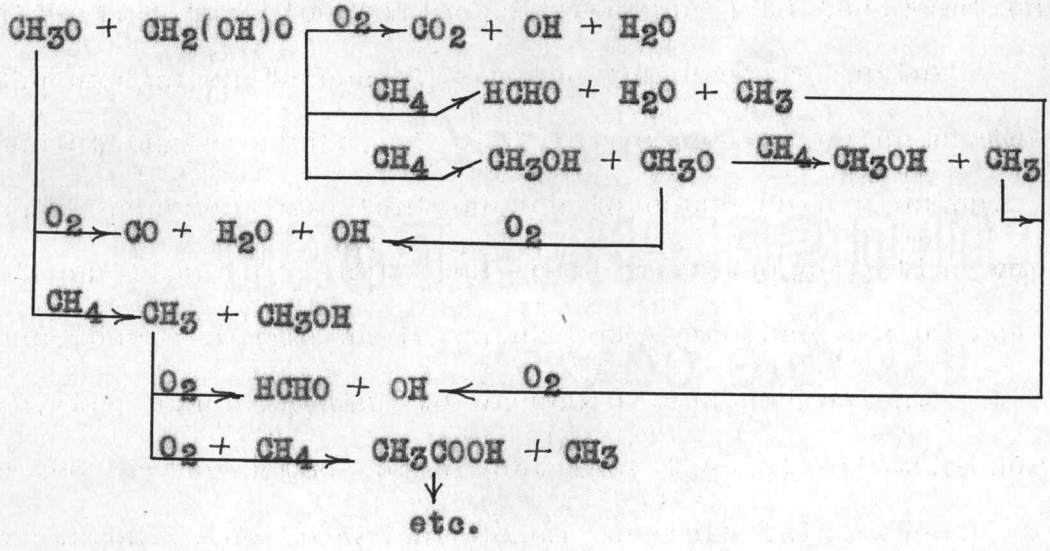
Peracid branching

$$HO_2 + RCHO + O_2 \longrightarrow \ldots\ldots 3OH$$

HCHO condensation

$$HCO + HCHO \longrightarrow CH(OH)CHO \xrightarrow{O_2} 2CO + H_2O + OH$$

Not all of these reactions were discussed here, since they are not necessary to explain experimental findings. It must be remembered also that this is not even schematically complete. As an example of the type of branching which does occur, it may be advantageous to use that proposed for the oxidation of methane at higher pressures (18, p.95).



From the numerous radicals appearing in this scheme, it is clear that it could be carried much further.

On the basis of the above general theory, some of the phenomena observed in combustion, such as the pre-ignition of internal combustion engines and "cool" flames (26, p. 2234-2237), may be understood. Of especial interest is the effect of surface on the oxidation reaction. Pease (23, p.1839-1856) has stated that in an empty pyrex tube propane reacted with oxygen at 375 degrees Centigrade, but that upon packing the tube with broken pyrex the reaction did not begin until a temperature of 500 degrees Centigrade had been reached and did not go to completion below 625 degrees Centigrade. In addition, Norrish and Reagh have shown both experimentally and theoretically that the reaction rate decreases with the size of the reaction tube, being almost completely suppressed in a 5mm tube (21, p.429-448). Pease reports further that thermal dissociation begins before oxidation, but that oxidation aids the dissociation in such a manner as to increase unsaturated products without appreciable formation of oxygenated compounds. He suggests that the oxygen reacts directly with propane to form propene and water. Such surface effects are easily understood when it is remembered that many of the radicals and carriers formed would be destroyed at the surface; the chain initiating step is especially sensitive. Any conditions which

increase the ease with which the destruction of chain carriers may occur will suppress the reaction. Wall action is a general phenomenon encountered in chain reactions as either an advantageous or adverse effect; in the oxidation of hydrocarbons, it is detrimental to the reaction.

Another surface effect of interest has been studied by Pease (24, p.2034-2038; 25, p.2296-2299). Since this investigator has used a somewhat different type of mechanism to explain the results he obtained, some mention of this energy chain theory must be made. By coating his reactor with potassium chloride, Pease found that no peroxides were formed, but that the rate of oxidation of the hydrocarbon, propane, was essentially unchanged. The chief liquid products, in addition to gaseous carbon monoxide, were methanol, formaldehyde and water. Here the investigator postulates a chain reaction somewhat similar to an energy chain, that is, a chain in which radicals are formed from activated molecules. Thus, his chain initiating reactions are:

$$2C_3H_8 \longrightarrow C_3H_8^* + C_3H_8$$

$$C_3H_8^* + O_2 \longrightarrow C_2H_5O + CH_3O$$

where the asterik represents an activated molecule. Additional radicals are presumed to originate in a dissociation chain such as:

$$C_3H_8 \longrightarrow CH_3 + C_2H_5$$

$$C_3H_8 + CH_3 \longrightarrow CH_4 + C_3H_7$$

$$C_3H_7 \longrightarrow C_3H_6 + H$$
$$\longrightarrow C_2H_4 + CH_3$$

ending with

$$C_2H_5 + CH_3 \longrightarrow C_3H_8$$

Chain stopping is assumed to be due to the association of two radicals with a third body, M, to form some product.

$$2CH_3O + M \longrightarrow X$$

$$2C_3H_7 + M \longrightarrow Y$$

$$CH_3O + C_3H_7 + M \longrightarrow Z$$

The complete mechanism could then be represented by

1. $2C_3H_8 \xrightarrow{k_1} C_3H_8^* + C_3H_8$
2. $O_2 + C_3H_8 \xrightarrow{k_2} C_2H_5O + CH_3O$
3. $CH_3O + C_3H_8 \xrightarrow{k_3} CH_3OH + C_3H_7$
4. $C_3H_7 + O_2 \xrightarrow{k_4} C_2H_4O + CH_3O$
5. $C_2H_4O + O_2 \xrightarrow{k_5} HCHO + CO + H_2O$
6. $2CH_3O + M \xrightarrow{k_6} X$
7. $2C_3H_7 + M \xrightarrow{k_7} Y$
8. $CH_3O + C_3H_7 + M \xrightarrow{k_8} Z$

At the steady state condition (that is, when the derivative of the concentration of any carrier with respect to time is zero), the following are true:

$$d(CH_3O)/dt = k_1(C_3H_8)^2 + k_4(C_3H_7)(O_2) - k_3(CH_3O)(C_3H_8) - k_6(CH_3O)^2(M) - k_8(CH_3O)(C_3H_7)M = 0$$

$$d(C_3H_7)/dt = k_3(CH_3O)(C_3H_8) - k_4(C_3H_7)(O_2) - k_7(C_3H_7)^2(M) - k_8(CH_3O)(C_3H_7)M = 0$$

Solution for (CH_3O) is cumbersome, but assuming only six to be an effective chain stopper,

$$(CH_3O) = \sqrt{k_1/k_6M}\ (C_3H_8)$$

If only seven is effective,

$$(CH_3O) = 1/k_3 \left\{ k_1(C_3H_8) + k_4 \sqrt{\frac{k_1}{k_7M}}\ (O_2) \right\}$$

If only eight is effective,

$$(CH_3O) \cong \frac{k_1}{4k_3}\ (C_3H_8) \pm \sqrt{\frac{k_1k_4(C_3H_8)(O_2)}{2k_3k_8M}}$$

or

$$(CH_3O)\quad \frac{k_1}{2k_3}\ (C_3H_8)$$

depending upon which approximation is made in the solution.

The rate of disappearance of propane will be principally determined by three, for which

$$-d(C_3H_8)/dt = k_3(C_3H_8)(CH_3O)$$

On substituting the various values for (CH_3O) in this equation, it is always found that the rate will be dependent upon a power of (C_3H_8) between one and two but be relatively independent of the concentration of oxygen. For example, using the first of the above values for (CH_3O)

$$-d(C_3H_8)/dt \cong k_3 \sqrt{\frac{k_1}{k_6M}}\ (C_3H_8)^2$$

The experimental data are in qualitative agreement with these conclusions.

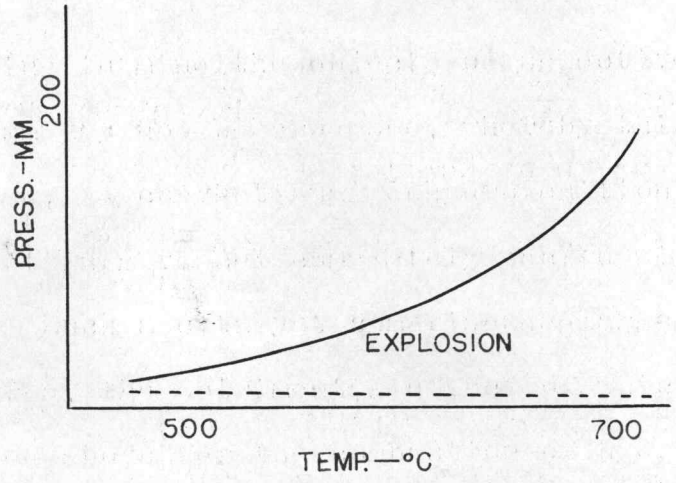
While there are encountered other interesting side reactions and special phenomena in the oxidation of hydrocarbons, those most pertinent to the subject at hand have been discussed, if only briefly. The oxidation of unsaturated compounds is nearly analagous to that of paraffins, and a discussion of such reactions would prove repetitious. Needless to say, the ideas presented are largely speculative and highly controversial, but they do offer an explanation of experimental facts.

Proposed Theory of Selective Oxidation

Keeping in mind the objects of selective oxidation, a mechanism may now be proposed, whereby this process may be effected. A conventional dehydrogenation reaction is carried out in a vessel completely packed with a suitable catalyst. Such a catalyst comprises a large, highly active surface area, the detrimental effect of which has been illustrated above for the combustion of hydrocarbons. It is to be expected, therefore, that if oxygen were admixed with the reactants of a dehydrogenation process while in contact with the catalyst, no appreciable oxidation would occur at dehydrogenation temperatures. In the first place, it is unlikely that oxidation would even commence,

for the chain initiating step would be almost completely suppressed. Since a number of steps in the chain itself are also retarded by the presence of a surface, while the chain stoppers are accelerated, oxidation is still less likely. Thus, it would appear that on a theoretical basis at least part of the object of selective oxidation is feasible, but it must also provide for the removal of hydrogen.

The curve of explosive limits (pressure and temperature) for the combustion of hydrogen exhibits, like that of paraffins, a peninsula; in this case, however, the two boundaries are an upper and lower pressure.



The lower limit is not well defined but is only found at very low pressures; consequently, it is not of general importance here. For the upper limit, on the other hand, a proposed mechanism includes the following important reactions, of which number four is the chain terminating

step (18, p.30-78):

1. $OH + H_2 \longrightarrow H_2O + H$
2. $H + O_2 \longrightarrow OH + O$
3. $O + H_2 \longrightarrow OH + H$
4. $H + O_2 + M \longrightarrow HO_2 + M$

Although the group HO_2 is probably destroyed at a surface, it cannot propagate the chain and the surface does not have an important role in the region of the upper pressure limit. This relatively simple mechanism is subject to criticism, but the experimental data indicate that the reaction is not materially affected by the surface under the conditions prevailing in a dehydrogenation reaction.

The author believes that these facts, the suppressive effect of the catalyst surface on one reaction, and its unimportance in the other, are sufficient to show that selective oxidation can be accomplished with satisfactory results, i.e., with increased olefin production without the attendant oxidation of hydrocarbons. Several processes of selective oxidation, similar to that proposed here, have been patented, and a brief discussion of these inventions with their authors' explanation of their mechanism will follow.

A number of inventions have been published, in each of which the removal of hydrogen from a dehydrogenation stream is effected (16). In some of these patents,

chlorine is made to combine with the hydrogen liberated (6; 7), but in the majority, various means of carrying out selective oxidation are proposed.

One of the first attempts to utilize oxygen for increased yields in a dehydrogenation reaction was made by Hopkins (14). By using lower temperatures, intimate mixing of hydrocarbon and oxygen, and introduction of oxygen at a plurality of points in the course of the reaction, the inventor obtained good yields of unsaturated products in a pyrolytic dehydrogenation reactor. Considerably later H. B. Kipper (15) applied the principle of selective oxidation to the catalytic dehydrogenation of a number of hydrocarbons. Kipper employed an inert gas, such as nitrogen, in addition to oxygen; he maintained the oxygen concentration at below 20% of the reaction mixture and operated at super-atmospheric pressures and low temperatures (100-400 degrees Centigrade).

A further modification has been provided by Schmidt and Stadelman (29). In this embodiment of selective oxidation, carbon dioxide is used in the reaction in at least equimolecular proportions with the oxygen admitted. The inventors disclose that other gases, such as N_2, steam, or CO, may be used as diluents in addition to CO_2 and O_2, but they state that CO_2 "actually favors the reaction by avoiding the formation of explosions and acting as a dehydrating

agent." The use of CO_2 alone or in conjunction with O_2 is discussed by Giulio Natta (19; 20), who also proposes an interesting mechanism for his process. In this instance, CO_2 is considered the most important component, and oxygen is used only in small amounts under closely controlled conditions "in order to avoid the formation of explosive mixtures or anyhow secondary reactions." The CO_2 is believed to aid the reaction by direct combination with the hydrocarbon and hydrogen.

$$C_4H_8 + CO_2 \longrightarrow C_4H_6 + CO + H_2O$$

$$CO_2 + H_2 \longrightarrow CO + H_2O$$

While the above mechanism is not proved, Natta states that the CO_2 certainly does produce a much more pronounced effect than a like amount of steam.

The process of Frey is quite similar to that used in this thesis, differing chiefly in the fact that oxygen is admitted at a plurality of catalyst free spaces in the course of the reaction (8). In his patent Frey makes the following statements: "The addition of oxygen in the conventional manner to hydrocarbons in the presence of catalysts at such elevated temperatures as would be necessary for dehydrogenation causes destruction of the hydrocarbon molecular skeleton with formation of carbon monoxide and other reaction products. . . . Furthermore, undiluted oxygen or air will burn out completely on initial contact

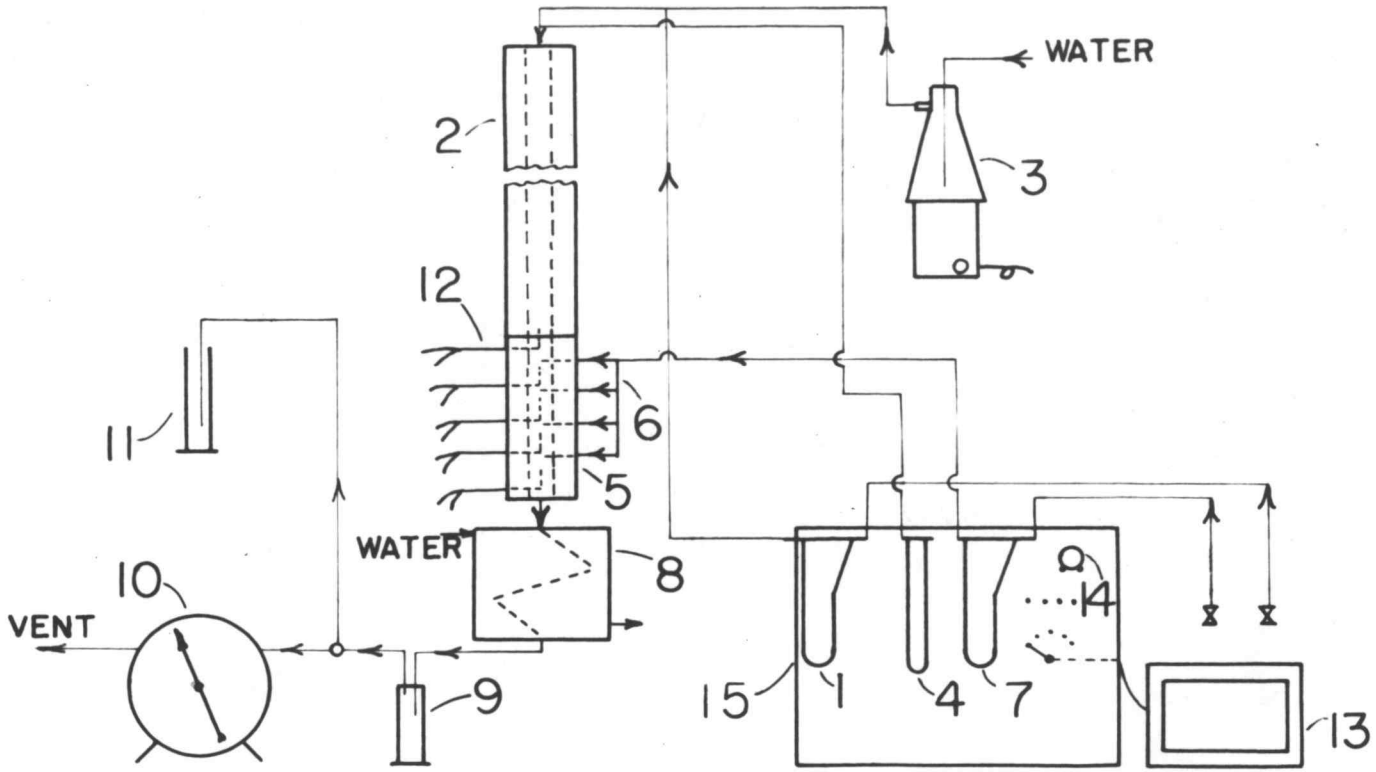
with the catalyst, thereby becoming unavailable for aiding in the dehydrogenation reaction in lower areas of the catalyst bed." (8, p.1) In order to prevent this, Frey raises the kindling temperature by intimately mixing the reactants with oxygen in specially constructed catalyst free spaces. By such means the inventor has obtained substantial increases in the yield from a dehydrogenation process.

It is this author's opinion that most of the above processes are considerably more complex than is necessary. While such devices as the catalyst free mixing vessels of Frey may benefit the reaction, it is believed, both for theoretical reasons and from experimental findings, that they are almost superfluous. In most of the inventions cited, means for preventing explosions or oxidation of the reactants are chiefly based on the explosive limits and kindling temperatures for the ordinary combustion of hydrocarbons. As has been demonstrated above, such ordinary conditions do not prevail within a catalytic dehydrogenation reactor. For this reason selective oxidation may be accomplished in the relatively simple process which is the subject of this thesis, and several expediencies resorted to in previous work may be entirely omitted without ill effect.

EXPERIMENTAL PROCEDURE

Both a description of the apparatus used in these experiments and the manner of operating can best be presented by reference to the accompanying diagram on page 26, Figure 6. Technical ethane of approximately 92% purity was passed through a flowmeter (1) into the top of a vertical preheater (2) consisting of a four foot length of one inch standard iron pipe packed with small porcelain raschig rings. The internal surfaces of both the preheater and reactor were coated with a thin layer of sodium silicate in order to prevent coking at the walls since metallic iron is a very active dehydrogenation catalyst. Heat was supplied by two twenty-foot coils of 21 gauge nichrome wire separately controlled by rheostats. Steam from a boiler (3) was mixed with the hydrocarbon at the top of the preheater. The pressure was also measured at this point with a mercury manometer (4). After leaving the preheater, the mixture was at the proper temperature and passed directly into the reactor (5). The latter vessel was sixteen inches long and of the same material and construction as the preheater; the two were joined with a sleeve coupling. Four iron-constantan thermocouples (12) were spaced evenly in the reactor, and four ports (6) for the admission of oxygen metered in a flowmeter (7) were provided. The reactor was heated by a third nichrome element. With the

FIGURE 6



FLOW DIAGRAM

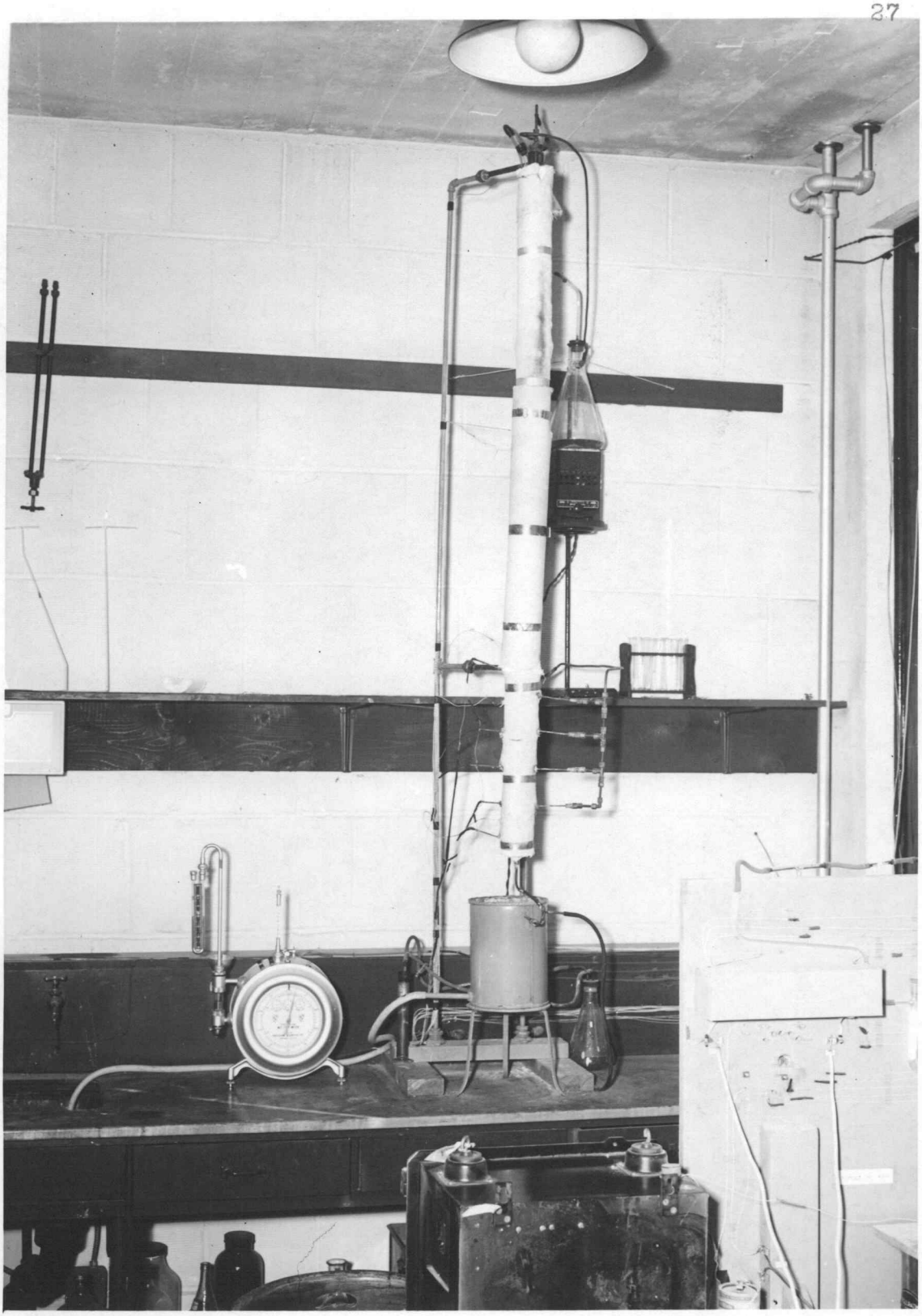


PLATE 1- EXPERIMENTAL APPARATUS

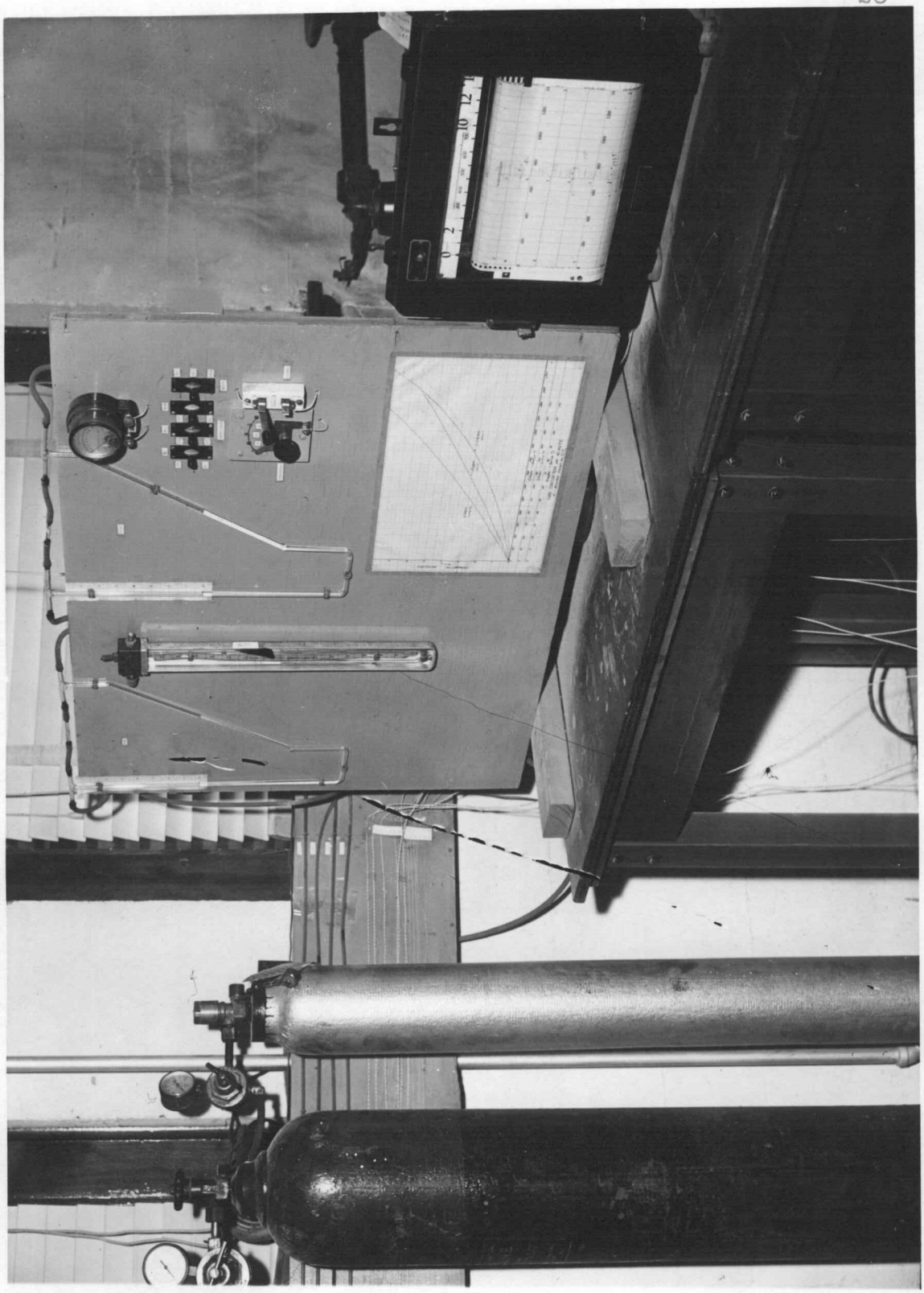


PLATE 2- CONTROL PANEL

reactor completely filled with catalyst, the reaction took place and the products were rapidly cooled in a condenser (8). After the liquid products were collected in a trap (9), the remaining gas passed to a three-way stopcock, from which it could be sent to the wet test meter (10), or the ammoniacal cuprous chloride bubbler (11), or the sample bottle. Almost all control was accomplished at the control panel (15), and temperatures from the five thermocouples were recorded with a Tagliabue recording potentiometer (13). Gas flows were regulated with gas regulating valves attached to the cylinders, and the volume of steam was controlled with a variable electric heater. Close temperature control could be obtained by observing the currents flowing in the three heating coils with an ammeter (14).

Although the apparatus as described was easy to operate, a number of faults did appear. Some difficulty was experienced in the effect of the liquid condensate on the pressure of the system. By designing the condenser and traps so that no slugs of liquid could form in the lines, this defect could be made negligible. Due to pressure fluctuations, regulation of the steam volume was difficult and time consuming. The apparatus was, however, satisfactory for the research program contemplated, with the only real problem being the aforementioned difficulty in control of the steam flow.

Without excessively expensive equipment and lengthy laboratory procedures, analysis of the products from a high temperature hydrocarbon conversion process cannot be made complete. A large number of compounds may result from the various cracking, polymerization, and dehydrogenation reactions which occur simultaneously in a process such as that being considered. For this reason certain assumptions must be made which are thought to be not too greatly in error. It was necessary to assume that no unsaturated compounds other than ethylene were formed. Since the most likely of these other unsaturates was acetylene, a continuous qualitative test for this substance was made by bubbling the product gas through an ammoniacal cuprous chloride solution. At no time was a precipitate of the red copper acetylide recovered. In addition to the possibility of several multiple bond hydrocarbons, there is reason to believe that some propane or even higher molecular weight paraffins might have been formed. It was assumed that these saturates were negligible in comparison to the ethane and methane which would be present.

A further type of compound very necessary to detect if produced in appreciable quantities was the oxygenated hydrocarbon. In the present reaction, the chief such components would be acetaldehyde and formaldehyde, which would appear in the liquid condensate trap. For detection

purposes, the fuschin-aldehyde test was employed; for quantitative analysis, the bisulfite addition compound was formed from a known normality bisulfite solution, the excess bisulfite then being titrated with 0.1 normal iodine solution.

In summary, with the equipment used in this project, it was possible to determine acetylene qualitatively and the following quantitatively: carbon dioxide, ethylene (unsaturates), oxygen, hydrogen, carbon monoxide, ethane, methane, and aldehydes. It was assumed, therefore, that only these substances were present in the products. Standard absorbents were used for some of the gases, potassium hydroxide for carbon dioxide, fuming sulfuric acid for the unsaturates, and alkaline pyrogallol for oxygen. Hydrogen and carbon monoxide (the latter never present in appreciable amounts) were determined with a copper oxide tube maintained at 300 degrees Centigrade. For most of the runs the ethane and methane remaining after the removal of all other constituents were determined by oxidation with oxygen in a catalyst tube maintained at 500 degrees Centigrade. This last method gave reproducible results and was believed to be accurate. After most of the data had been collected, however, an attempt was made to analyze the ethane feed gas, purchased as of 95% purity. Although reproducible results were again found for a large number of analyses,

the value for the per cent ethane was far too low. The Portland Gas and Coke Company then provided an analysis of the same gas, carried out by their regular methods, which indicated the ethane content of the gas to be 92%. Determination of the heating value of the gas in a Junker's calorimeter verified this result. While no explanation can be made for this discrepancy, undoubtedly a part of all the analyses is erroneous. The analysis is good except for the relative amounts of ethane and methane in the products; however, the total of these two quantities is correct and a qualitative indication of the trend of selectivity might be obtained from the data as taken. Furthermore, as will be explained below, it is possible to calculate the percentage of ethane and methane by making use of certain assumptions together with the other analytical data obtained.

From the data secured, i.e., analysis of reactants, volume of gas entering the reaction, volume of products leaving, and per cent ethylene in the products, it is a simple matter to calculate the per cent of the entering ethane which was converted to ethylene. Hereafter, this quantity will be referred to as the "conversion", one of the two important pieces of formation which were the objectives of this research. The second quantity desired was the selectivity, which must be calculated and defined

for this particular case due to the analytical difficulties just mentioned.

It can be seen from any of the data given that there is a disappearance of oxygen which would be caused chiefly by its combination with hydrogen. Upon taking into account the hydrogen lost in this manner, the total free hydrogen content of the exit gas (including that combined with oxygen) is invariably greater than that which would be equivalent to the ethylene formed. There are several manners in which this excess hydrogen could be produced: (1) by the water-gas reaction; (2) by the formation of acetylene, which was negligible; (3) and finally by the cracking of ethane. This last method is probably the most important and is assumed for purposes of calculation to take place in the following manner:

$$C_2H_6 \longrightarrow CH_4 + C + H_2$$

If all other side reactions are neglected, the hydrogen in excess of that equivalent to the ethylene formed will then be equal to the methane in the products. By adding this quantity to that known to be in the original gas, the amount of methane in the exit gas is obtained. From this figure, it is then possible to arrive at the quantity of ethane remaining in the products. Thus, a calculated "complete" analysis is derived from which the selectivity may be determined in the conventional manner. There may

be some considerable inaccuracy in this method, but it is thought that correct qualitative results are found and that the values of selectivity are in approximately the right region quantitatively. It must be remembered, then, that the selectivity results given here are subject to serious question, but that the conversions are accurate within experimental error.

Although the experimentally determined per cents of ethane and methane in the products are undoubtedly incorrect, they should indicate the proper trend of selectivity since they are subject to the same errors. Using these values to calculate selectivity, the same qualitative results are obtained as in the above described method, but as would be expected, the selectivities thus determined are lower than those which are based on the calculated analysis. These facts are further indications that the above manner of obtaining selectivity is approximately correct.

The ethane used in all of these experiments had the following composition:

Component	Volume Per Cent
C_2H_6	92.0
CH_4	2.3
illuminants (C_2H_4)	2.7
O_2	2.3
N_2	0.7

All calculations were based on this analysis, which was provided by the Portland Gas and Coke Company. Since some oxygen was in the original gas, it is necessary to define the term "per cent oxygen added" as used in this paper. This figure does not include the oxygen in the ethane but represents only the amount of oxygen added to the reactants.

The catalyst used in this work was the Shell 105 dehydrogenation catalyst which was mentioned previously. This material was provided in 3/16" pellets and was of the following approximate constitution (13):

Fe_2O_3 - 70%
Cr_2O_3 - 30%
$CuSO_4$ - 1%
KNO_3 - 0.5%

Very excellent results have been obtained by the use of this catalyst, particularly in the dehydrogenation of butylene and ethyl benzene. Its activity is reported to remain substantially constant after approximately eight hours on stream.

DISCUSSION OF RESULTS

The effect of oxygen on the yield of the desired product, ethylene, and upon the selectivity of the reaction is shown specifically by the results given in Figure 1 and Table 2. On this graph, and also all subsequent figures, those points marked by a circle and labeled "A" refer to

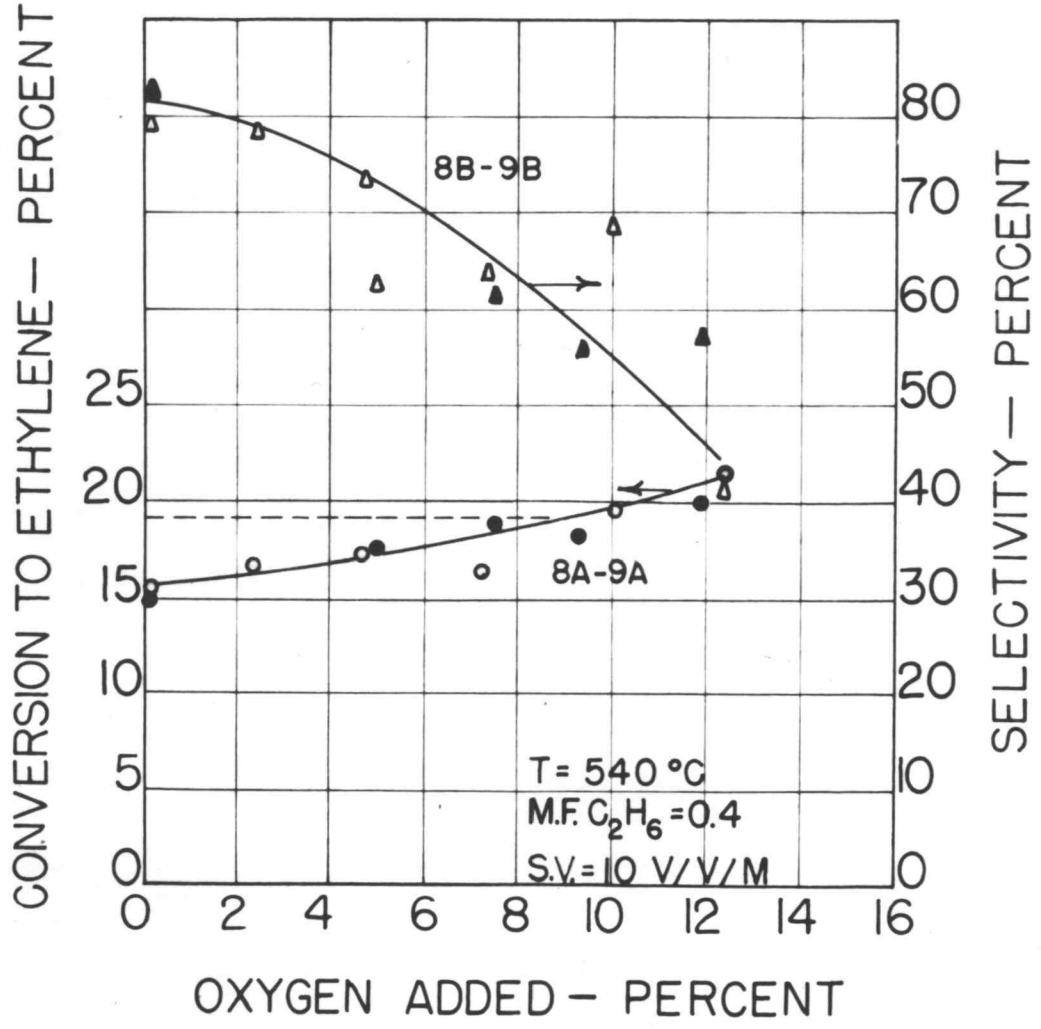


FIGURE 1

EFFECT OF OXYGEN

the conversion, those denoted by a small triangle and labeled "B" to selectivity; the dashed line drawn to the conversion curves indicates the expected equilibrium conversion at the particular average temperature and partial pressure of ethane in the reactants, neglecting any effect which the removal of hydrogen might have on the reaction. The data readily show that selective oxidation had occurred with the desired results. By increasing the amount of oxygen added, it is possible to attain a degree of reaction exceeding the theoretical maximum in ordinary dehydrogenation processes which take place in the absence of oxygen. In addition, very little oxidation of the hydrocarbon takes place, the quantity of CO_2 always being small (6% of the products was the maximum value found in any run) and the maximum degree of aldehyde formation amounting to only 0.03% of the ethane charged. Furthermore, as can be shown by the disappearance of oxygen, some of the hydrogen was definitely burned. In every respect, then, the objects of the process as stated above appear capable of realization. At different space velocities and temperatures, even more striking results were obtained, as will be shown by some of the other information collected.

Contrary to the author's expectations, the calculated selectivity diminished as the amount of oxygen was increased. In view of the complex nature of the reactions

occurring within the apparatus, it is difficult to show precisely how this might take place. However, it is possible that the oxygen reacts with ethane and ethylene in such a manner as to form methane, carbon and water. This is analagous to the effect of a very active component in a catalyst; if the amount of this constituent is made too large, excessive dehydrogenation activity produces more carbon and hydrogen than usual. Excessive oxygen may well have a similar effect.

Considerably more phenomenal results are shown in Figure 2, which illustrates the effect of space velocity. The three sets of curves are at different conditions as follows:

4 - 540 degrees Centigrade, 5% O_2, no steam

6 - 540 degrees Centigrade, 5% O_2, 0.38 mol fraction C_2H_6 in reactants

10 - 590 degrees Centigrade, 7% O_2, 0.38 mol fraction C_2H_6

In all three examples, the conversion falls from a point greatly above equilibrium at low space velocities to very small figures at high rates of flow. Approximately twice the equilibrium value was obtained in run 10, but at space velocities much lower than the smallest given, a large quantity of carbon and hydrogen were formed with very little conversion to ethylene. The effect of oxygen is

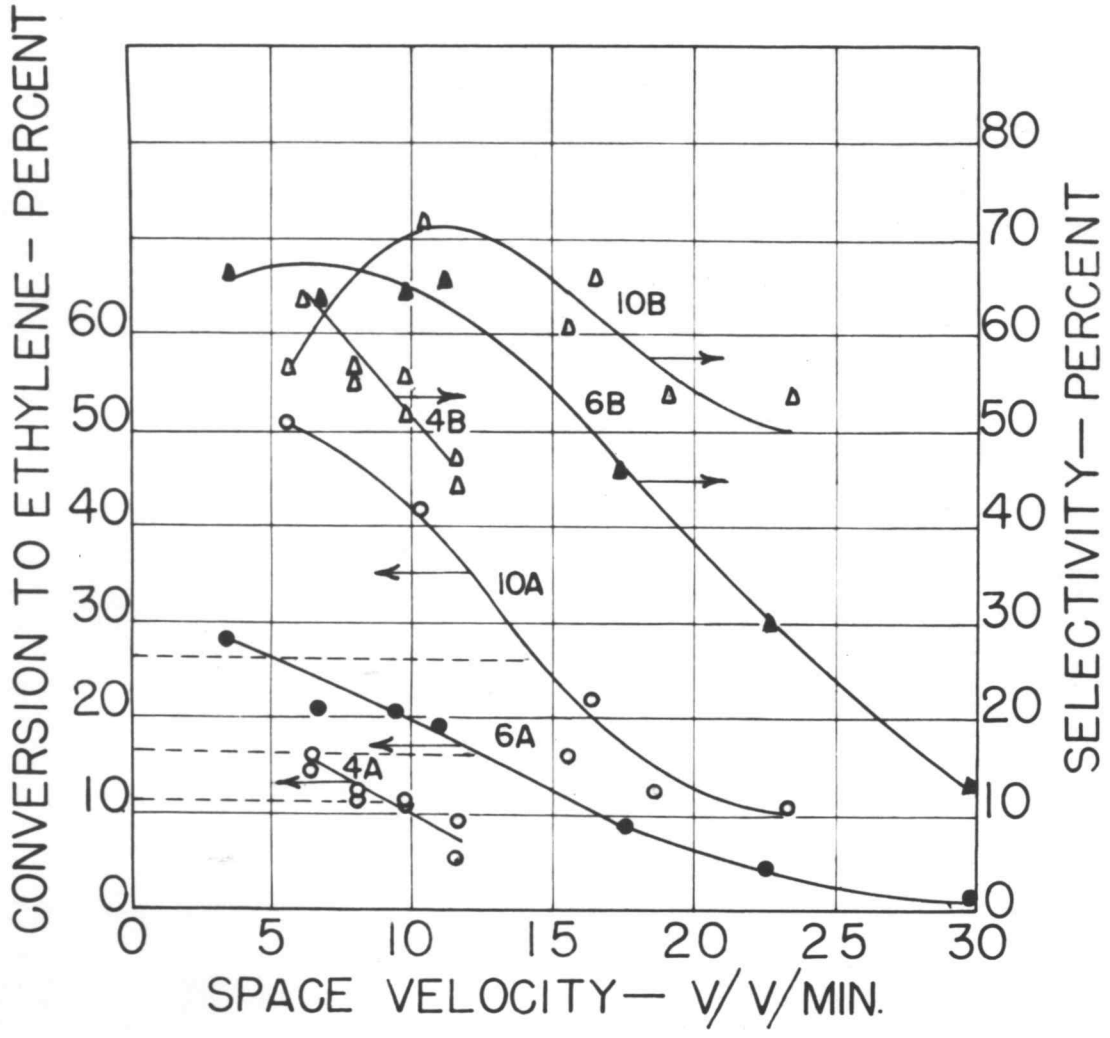


FIGURE 2
EFFECT OF SPACE VELOCITY

brought out clearly by these same curves if it is recalled that the conversion without oxygen would never surpass the equilibrium value shown. Very little information is available regarding other attempts at catalytically dehydrogenating ethane. As a comparison, however, from 50 to 80 per cent of the equilibrium conversion is the maximum which has been attained in previous work. Since these earlier experiments were carried out at relatively low temperatures (500 degrees Centigrade) and without the addition of steam, the actual conversions amounted to only 2.3 to 4.0 per cent (27, p.67-69).

It is difficult to reconcile the selectivity curves of Figure 2 with those familiar in ordinary dehydrogenation. Assuming that the method of calculating this data was qualitatively correct, it is possible to give an explanation for the shape of the curves. Although sufficient data were not obtained to provide a good kinetic study of the reaction, the data of run 10 are plotted according to the first order reaction equation (Fig. 5). Since a straight line does not result, it is evident that the reaction is not first order throughout, but it appears to be so at high space velocities. (The curve is drawn back to infinite space velocity, at which point no conversion occurs.) As the space velocity decreases, more ethylene is formed than would be indicated by the extrapolated first-

order line. It is not possible to say why this change of order should take place, but there are several variations which might occur in the reaction. If the dehydrogenation reaction by selective oxidation proceeds through a mechanism entirely different from that of the conventional process, it could well be that the effect of selective oxidation is subject to an induction period such as that reported for the combustion of hydrocarbons. Thus, at high space velocities, the induction lag could account for almost all of the time the reactants were in contact with the catalyst, and the mechanism would be that ordinarily expected without oxygen; that is, the reaction would proceed by a first order mechanism whose rate constant would be determined by the straight part of the curve in Figure 5. However, as the space velocity is decreased, the proposed induction period represents a smaller fraction of the total contact time and, at its end, another and more rapid mechanism might supersede the former. The amount of conversion, then, would be greatly increased, even above the equilibrium value for the first reaction (see Fig. 2). Assuming that the side reactions show no such change in mechanism, the effect of space velocity on these secondary reactions could be much less than on the primary dehydrogenation step. Some support is given to this view by the fact that the amount of methane formed in runs 6 and 10 was

practically constant. If the foregoing is true, it might be expected that, as the space velocity is decreased, the conversion to ethylene would at first increase more rapidly than would the formation of undesirable products. From the definition of the term, this would indicate that the selectivity might increase with decreased rate of flow. Since curves 6B and 10B pass through a maximum, it would seem that the induction period loses its effect at lower velocities and that the selectivity behaves in the normal manner thereafter.

Without more complete information as to the kinetics of selective oxidation, it is impossible to speculate further. The above is given only as one possible explanation of the selectivity results obtained, assuming them to be correct.

In Figure 3, the effect of pressure on the reaction is illustrated. Run 5 was made at an average temperature of 540 degrees Centigrade and a space velocity of approximately 17. Varying amounts of steam and ethane were chosen so as to result in as nearly the same space velocity as possible for all different partial pressures of ethane. The results are entirely normal, and the graph is self-explanatory.

Figure 4 demonstrates the role of temperature in selective oxidation. In this experiment the space

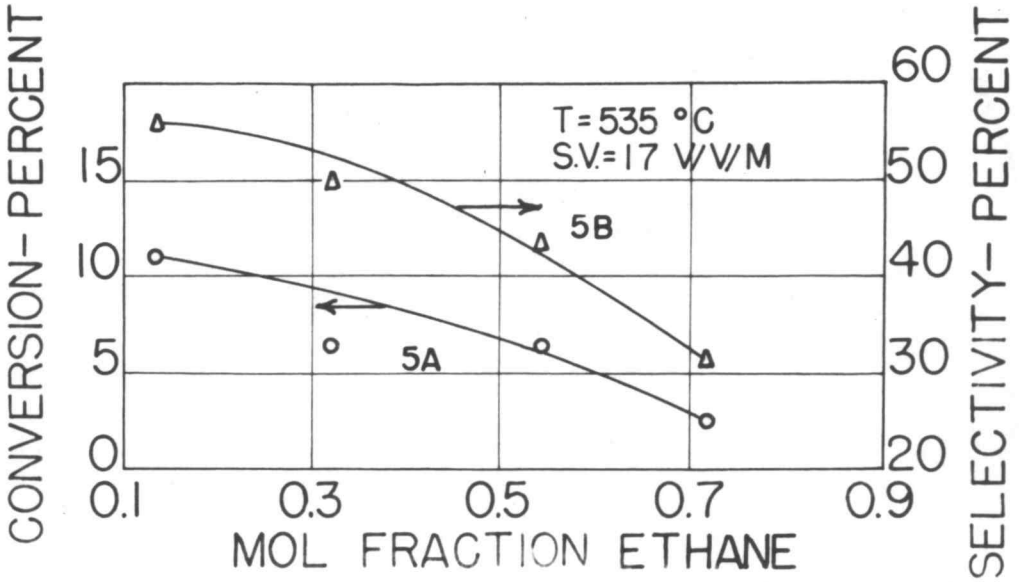


FIGURE 3
EFFECT OF PRESSURE

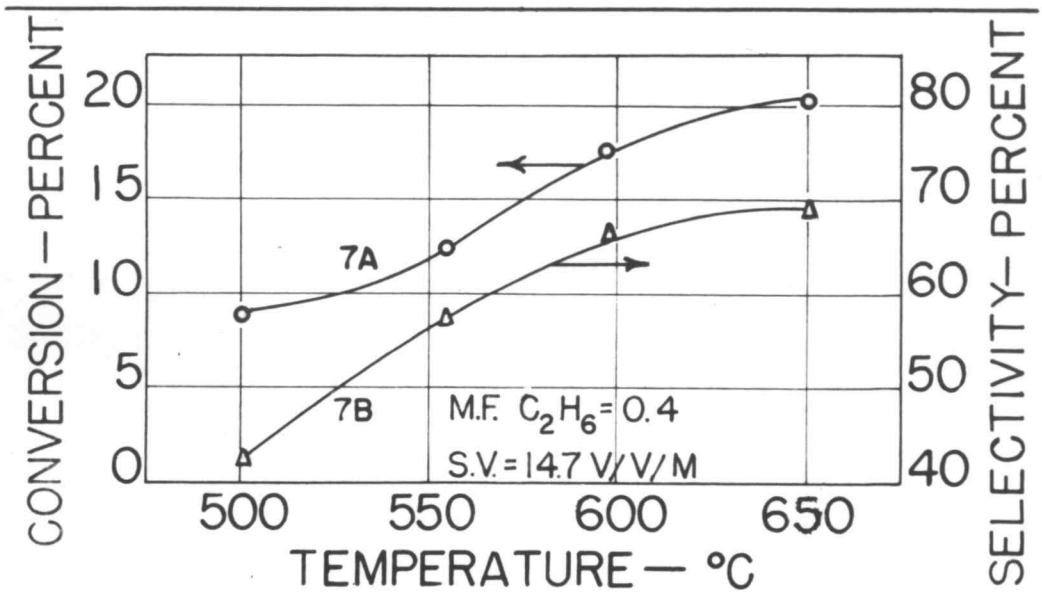


FIGURE 4
EFFECT OF TEMPERATURE

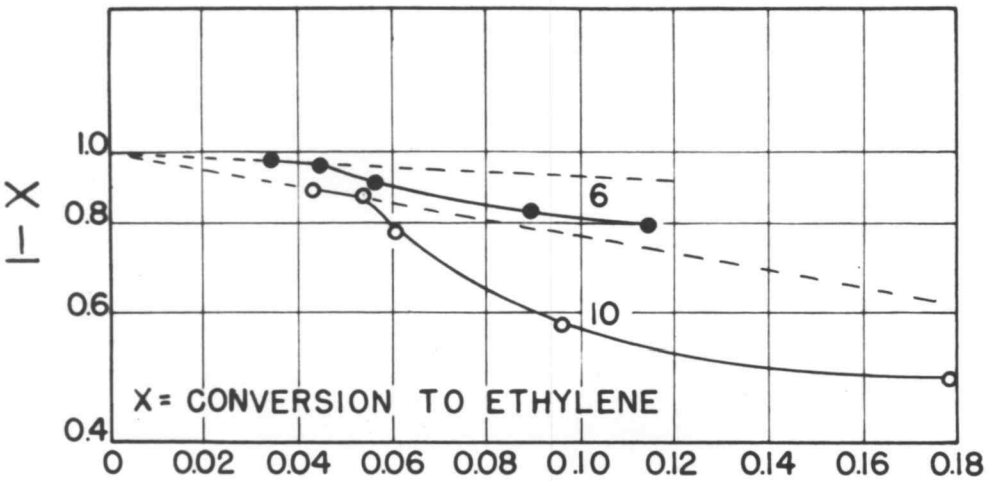


FIGURE 5

FIRST ORDER PLOT

velocity, oxygen content, and mol fraction of ethane were maintained at 16, 4.8% added and 0.45, respectively. An increase in conversion results with increased temperature, but above about 600 degrees Centigrade this effect becomes less pronounced. This negative curvature is undoubtedly due to the increased number and extent of the side reactions which become possible at more elevated temperatures. A maximum would occur at some undetermined temperature since some side reactions, such as the formation of acetylene, would eventually become predominant. At the temperatures used no acetylene was formed in detectable quantities.

Further information may be derived from a comparison of some of the curves given; for instance, the three space velocity curves show clearly the effect of differing conditions upon the process. However, such comparisons of one run against another are not always possible. The catalyst activity was an uncontrollable variable, although the catalyst used is reported to have a constant activity for a considerable length of time. This was not found to be the case since the catalyst became almost completely deactivated at one time (probably a result of the very low space velocities which were occasionally used). Not enough time was available to make a sufficiently large number of runs to eliminate this effect of catalyst

activity; consequently, the quantitative comparison of the results of two different runs may be in error.

A further effect of this deactivation is that on the points of a single run. In run 6 (Fig. 2), the samples were taken at consecutively larger space velocities with the exception of that for the space velocity, 6.7, which was the last to be collected. Deactivation of the catalyst had occurred in this run as is shown by the low position of this point. At constant catalyst activity, then, this curve would lie slightly above that found experimentally. This effect upon the position of the diagrams is not large in any case and almost negligible in some runs; e.g., runs 8 and 9 show excellent reproducibility (Fig. 1), so that the data from both fit one set of curves.

CONCLUSIONS

Although a number of conclusions may be drawn from the data presented, the practicability of a process for selective oxidation should be judged from a larger amount of data than was collected here. At this point, nevertheless, there is reason to state that a process for dehydrogenation by selective oxidation is physically capable of realization. Increased yields of unsaturated products may be obtained, in some cases larger than the maximum theoretically possible by conventional means. At the same time, the oxidation process is highly selective in

that there is little oxidation of any hydrocarbons; but due to other side reactions, the overall selectivity is diminished as the amount of oxygen added is increased.

By the proper choice of temperature, space velocity and oxygen concentration, it is possible to attain a high conversion and at the same time maintain a high degree of selectivity. The results of Figure 2 indicate that at temperatures of 600 degrees Centigrade to 650 degrees Centigrade, a space velocity of about 10 v/v/minute, from 7-10% oxygen added, and from 2-5 mols of steam per mol of ethane, a conversion perhaps 50% in excess of the equilibrium value can be expected at a selectivity of 70% or greater. Such results are considered to show that the process is capable of accomplishing more satisfactory dehydrogenation than any process in commercial use today.

There are two principal drawbacks to the use of this process. The first is the aforementioned decrease in selectivity with increased oxygen added; secondly, there is a decrease in selectivity at the higher space velocities. Since the use of high rates of flow is an advantage, this is not desirable. At present there does not seem to be any way of eliminating these effects and they must be considered a part of the penalty to be paid for the improved conversion. An economic study of the process should be made before attempting to select the optimum conditions

of operation. Without such a survey it is impossible to judge the process in comparison to ordinary dehydrogenation from a practical standpoint, but its experimental performance indicates that such a comparison would be favorable to selective oxidation.

Just as this process departs from the mechanism of ordinary dehydrogenation, the author believes that it requires a catalyst specially designed for its purposes. For instance, the catalyst should have an oxidation effect in addition to that of dehydrogenation. This property would probably not be sufficient to cause an appreciable formation of oxygenated compounds but would aid in the removal of hydrogen. The proper constitution of a selective oxidation catalyst would have to be the object of extensive investigation.

While the experimental work of this thesis was limited to the use of ethane, there is no reason to believe that comparable results may not be obtained for the dehydrogenation of other hydrocarbons. For instance, the same principles could undoubtedly be applied with profit to such processes as the production of butadiene from butylene or styrene from ethylbenzene. Many other uses of controlled and selective oxidation appear to be theoretically possible, once the technique of operation has been worked out to a sufficient degree.

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APPENDIX

TABLE 1

Thermodynamic Data

C_2H_6 C_2H_4 H_2

Temperature °Kelvin	F° cal/mol	Keq
800	7,700	0.0079
900	4,600	0.077
1000	1,300	0.520
1100	1,800	2.28
1200	5,000	8.14

TABLE 2

Effect of Oxygen---Basis: one minute

Run 10

Oxygen added, %	7.1	11.2	6.7	0.0
Vol. ethane, cc	1000	1000	2040	2040
Vol. steam, cc	1060	1100	2590	2400
Space velocity, v/v/M	10.4	10.8	23.3	21.8
Mol Fr. ethane	0.47	0.45	0.43	0.46
Volume Prod., cc	1393	1470	2085	1980
Temperatures, °C				
1	600	605	618	610
2	470	465	477	483
3	592	592	577	595
4	--#	--#	--#	--#
5	575	572	615	619
Ave. temp., °C	590	590	600	610
Anal. of prod. % by vol.				
CO_2	0.4	10.	0.9	0.0
C_2H_4	29.3	31.0	12.1	8.5
O_2	2.1	4.0	4.2	1.3
H_2	30.0	35.4	9.7	8.8
C_2H_6*	26.3	13.7	63.8	74.7
CH_4*	11.9	14.9	9.2	6.7
Conversion, %	41.7	46.6	10.5	6.0
Selectivity, %	71.5	63.6	53.5	52.5

*Calculated
#Coked and not reading accurately

TABLE 3

Effect of Oxygen---Basis: one minute

Run 8

Oxygen added, %	12.3	10.0	7.3	4.7	2.4	0.0
Vol. ethane, cc	713	713	713	713	713	713
Vol. steam, cc	1150	1150	1150	1150	1150	1150
Space velocity v/v/H	9.5	9.5	9.5	9.5	9.5	9.5
Vol. prod., cc	1070	1130	1050	1080	1080	1080
Mol Fr. ethane	0.37	0.37	0.37	0.37	0.37	0.37
Temperatures, °C						
1	556	550	550	550	553	546
2	440	440	442	443	445	445
3	552	553	553	553	550	550
4	--	--	--	--	--	--
5	513	522	518	517	517	510
Ave. temp., °C	540	540	540	540	540	540
Anal. of prod. % by vol.						
CO_2	1.3	0.8	0.5	0.3	0.0	0.1
C_2H_4	13.7	13.1	12.2	12.4	12.1	11.4
O_2	3.8	4.8	3.7	3.0	2.2	1.3
H_2	21.4	12.3	11.6	11.8	11.3	11.6
C_2H_6*	35.8	60.0	61.1	65.1	68.5	70.0
CH_4*	24.4	9.6	10.0	7.4	5.8	5.8
Conversion, %	21.5	19.7	16.6	17.5	16.9	15.3
Selectivity, %	41.5	68.8	63.5	73.5	78.5	78.8

*Calculated

TABLE 4

Effect of Oxygen---Basis: one minute

Run 9

Oxygen added, %	5.0	11.9	9.3	7.5	0.0
Vol. ethane, cc	1045	1045	1045	1045	1045
Vol. steam, cc	1145	1210	1240	1185	1280
Space velocity	10.6	11.0	11.1	10.8	11.2
Vol. prod., cc	1120	1330	1170	1180	1090
Mol Fr. ethane	0.47	0.46	0.46	0.47	0.45
Temperatures, °C					
1	540	545	550	545	545
2	425	425	427	437	437
3	540	538	541	548	548
4	--	--	--	--	--
5	505	511	515	515	507
Ave. temp., °C	540	540	540	545	545
Anal. of prod. % by vol.					
CO_2	0.2	0.7	0.3	0.4	0.1
C_2H_4	17.6	16.5	17.4	17.8	15.9
O_2	2.2	5.3	4.1	3.6	1.6
H_2	15.3	14.9	15.1	16.2	14.9
C_2H_6*	54.5	49.4	50.5	51.2	63.2
CH_4*	10.3	13.4	12.9	10.8	4.4
Conversion, %	17.5	19.9	18.3	18.9	15.1
Selectivity, %	61.8	56.8	55.5	61.1	82.6

*Calculated

TABLE 5

Effect of Space Velocity---Basis: one minute

Run 4

Space vel.	9.8	9.8	8.1	8.1	6.3	6.3	11.7	11.7
Vol. ethane, cc	1900	1900	1585	1585	1230	1230	2290	2290
Vol. steam, cc	0	0	0	0	0	0	0	0
Vol. oxygen, cc	99.7	98.7	80	80	62	62	116	116
Vol. prod., cc	2100	2100	1820	1820	1488	1530	2540	2490
Temp., °C								
1	577	570	562	558	552	556	578	578
2	422	418	418	417	420	420	422	430
3	552	540	545	545	552	556	542	548
4	535	535	535	530	537	540	542	548
5	497	503	500	503	502	506	548	556
Ave. temp., °C	545	540	540	540	540	540	540	540
Anal. of prod. % by vol.								
CO_2	0.0	0.6	0.0	0.5	0.1	0.7	1.1	1.0
C_2H_4	11.2	11.6	11.8	11.5	13.5	14.1	10.3	6.6
O_2	2.8	1.0	1.4	1.3	2.0	2.6	0.8	3.8
H_2	7.7	6.2	7.3	6.2	9.5	11.3	6.2	2.9
C_2H_6*	69.0	69.3	68.9	70.2	65.7	62.5	68.9	78.6
CH_4*	9.3	11.3	10.7	10.0	9.2	8.7	12.7	7.1
Conversion, %	10.5	11.0	11.8	11.4	14.8	16.1	9.4	4.9
Selectivity, %	55.7	51.6	55.0	56.2	63.8	66.5	44.0	47.0

*Calculated

TABLE 6

Effect of Space Velocity---Basis: one minute

Run 6

Space velocity	3.5	9.5	10.9	17.5	22.6	29.6	6.75#
Vol. ethane, cc	310	750	820	1440	1780	2420	923
Vol. steam, cc	395	1170	1370	2140	2760	3520	790
Vol. oxygen, cc	15.5	37.5	41.0	72.0	89.0	121.0	28.4
Vol. prod., cc	300	1200	1260	1770	2040	2690	973
Temperatures, °C							
1	513	532	532	543	545	550	531
2	442	422	433	438	440	448	430
3	537	537	538	542	530	525	540
4	--	--	--	--	--	--	--
5	450	498	512	550	558	560	480
Ave. temp., °C	540	540	540	540	540	540	540
Mol Fr. ethane	0.43	0.38	0.37	0.40	0.38	0.40	0.41
Anal. of prod. % by vol.							
CO_2	0.0	0.0	0.1	0.4	0.6	1.0	0.0
C_2H_4	28.4	19.1	17.0	10.8	6.3	3.9	20.9
O_2	1.2	1.9	1.7	2.3	2.6	3.5	1.2
H_2	26.7	16.8	13.5	7.7	2.6	2.1	17.6
C_2H_6*	33.9	52.4	57.8	67.8	77.6	79.1	49.4
CH_4*	9.8	10.8	10.2	10.9	10.2	10.2	10.9
Conversion, %	28.0	20.4	19.0	8.8	3.8	1.3	21.0
Selectivity, %	66.2	64.0	65.5	45.5	29.7	12.4	63.4

*Calculated
#From Run 7

TABLE 7

Effect of Space Velocity---Basis: one minute

Run 10

Space velocity	5.6	10.4	16.5	18.7	15.5	23.3
Vol. ethane, cc	548	1000	1600	1725	1435	2040
Vol. steam, cc	564	1060	1665	1980	1642	2590
Vol. oxygen, cc	38.8	70.7	113	121	101.2	141
Vol. prod., cc	1094	1393	1845	1835	1603	2085
Temperatures, °C						
1	560	600	613	608	600	618
2	465	470	473	473	470	477
3	592	592	592	577	577	577
4	--	--	--	--	--	--
5	505	575	617	603	588	615
Ave. temp., °C	590	590	590	590	590	590
Mol Fr. ethane	0.48	0.47	0.47	0.45	0.45	0.43
Anal. of prod. % by vol.						
CO_2	6.0	0.4	0.4	1.3	0.9	0.9
C_2H_4	24.7	29.3	19.9	13.3	15.2	12.2
O_2	1.0	2.1	2.8	3.7	3.3	4.2
H_2	53.3	30.0	17.0	12.5	13.2	9.7
C_2H_6*	2.5	26.3	49.5	58.1	57.3	63.8
CH_4*	12.5	11.9	10.4	10.0	10.1	9.2
Conversion, %	50.7	41.7	22.0	12.4	15.9	10.5
Selectivity, %	56.2	71.5	65.7	53.5	60.3	53.5

*Calculated

TABLE 8

Effect of Pressure---Basis: one minute

Run 5

Mol Fr. ethane	0.428	0.137	0.542	0.717	0.322
Vol. ethane, cc	1207	500	1875	2460	1100
Vol. steam, cc	1555	3110	1490	840	2250
Vol. oxygen, cc	60.3	27.4	98.7	125	55
Space velocity	13.8	17.7	16.9	16.8	16.7
Vol. prod., cc	1500	775	2020	2780	1300
Temperatures, °C					
1	563	557	572	580	543
2	426	437	430	445	437
3	536	536	534	537	540
4	536	536	534	541	547
5	525	530	545	563	545
Ave. temp., °C	535	535	535	540	540
Anal. of prod. % by vol.					
CO_2	0.2	0.3	0.5	0.8	0.8
C_2H_4	10.7	8.4	8.0	4.4	7.3
O_2	1.9	1.0	2.0	2.9	2.1
H_2	7.3	6.6	3.8	0.2	2.0
C_2H_6*	69.3	72.3	76.2	85.3	79.7
CH_4*	10.5	10.2	9.6	6.4	8.2
Conversion, %	11.5	11.2	6.4	2.5	6.4
Selectivity, %	55.0	56.0	43.7	36.0	50.0

*Calculated

TABLE 9

Effect of Reaction Temperature---Basis: one minute

Run 7

Ave. temp., °C	500	560	600	650
Vol. ethane, cc	1520	1520	1520	1520
Vol. steam, cc	2020	1760	1760	1760
Vol. oxygen, cc	57.3	57.3	57.3	57.3
Space velocity	16.0	14.7	14.7	14.7
Mol Fr. ethane	0.37	0.4	0.4	0.4
Vol. prod., cc	1540	1540	1585	1645
Temperatures, °C				
1	522	550	573	602
2	412	442	470	492
3	500	568	606	651
4	--	--	--	--
5	487	558	600	651
Anal. of prod. % by vol.				
CO_2	0.0	0.4	0.2	0.2
C_2H_4	10.7	14.1	18.3	19.7
O_2	3.3	2.3	1.5	1.9
H_2	9.4	11.5	13.3	15.8
C_2H_6*	64.8	60.1	57.7	53.5
CH_4*	11.8	11.5	9.0	8.9
Conversion, %	8.8	12.5	17.7	20.2
Selectivity, %	42.4	57.5	66.5	68.5

*Calculated