THE REACTION BETWEEN OXYGEN AND 2-BUTENE

Thesis

by

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INTRODUCTION

The oxidation of mono-olefin hydrocarbons has been a subject of study for many years. So far, only ethylene and propylene have been investigated. Lenher (1) has done the most recent comprehensive work on both these compounds. He made a careful examination of the intermediate oxidation products and found, in the case of the slow thermal oxidation of ethylene in small Pyrex vessels, formaldehyde, ethylene oxide, formic acid, glyoxal, the oxides of carbon, water and a substance supposed to be dioxymethyl peroxide. Evidence of the formation of hydrogen peroxide was also given. In the case of the oxidation of propylene under similiar conditions, the reaction products were acetaldehyde, formaldehyde, propionaldehyde, formic acid, acetic acid, carbon oxides, propylene oxide and a peroxide compound. It was shown that in the presence of oxygen the polymerization and pyrolysis of ethylene and propylene took place at lower temperatures than when the hydrocarbon was in the pure state. Lenher explained this by assuming the activation of the double bond by oxygen to be the primary process in the reaction.

It was thought that a study of the oxidation of 2-butene might help to clear up the mechanism of the oxidation of the mono-olefin hydrocarbons in general. It would be of interest to know whether the intermediate products of this reaction were of the same type as those found by Lenher for similiar oxidations.

EXPERIMENTAL

The reaction was studied by the flow method at atmospheric pressure. The 2-butene was prepared by heating 100 cc. Eastman's 1-butanol No. 50 with 100 cc. 95% sulfuric acid and 50 cc. water in a three-liter three-neck flask provided with a reflux condenser and a safety tube. Young and Lucas (2) have shown that 1-butanol when heated with 60% sulfuric acid (by volume) at a temperature of 140-160°C decomposes to give pure 2-butene.

The gas was led from the top of the condenser through three spiral wash bottles, each of approximately 200 cc. capacity. The first spiral wash bottle contained a 50% potassium hydroxide solution to remove traces of sulfur dioxide from the gas. The second and third wash bottles contained 40% sulfuric acid to absorb alcohol vapors. The gas was then passed through a tower containing soda lime and calcium chloride to a trap, cooled by ice and concentrated hydrochloric acid, where it was condensed and stored.

Before beginning an experiment, the 2-butene was volatilized at room temperature and the gas run into a 20-liter bottle displacing water. The proper amount of oxygen was then run in and the mixture of gases allowed to stand for a day. The mixture was analyzed at the end of this period. A small amount of nitrogen was always found to be present.

During an experiment, water was forced from a second 20-liter bottle into the first by gas pressure. The gas pressure was furnished by a tank of nitrogen and was adjusted with a diaphragm valve. The mixture of oxygen and 2-butene was pushed out of the bottle and through the apparatus at a constant rate by the entering water.

The mixture of gases was led through a flowmeter and a calcium chloride tower into the reaction vessel. The reaction vessel consisted of a vertical Pyrex tube of 7 mm. internal diameter. It was heated in a 30 cm. electric furnace, the temperature being determined with a Chromel-Alumel thermocouple. The hot junction of the thermocouple was located in a Pyrex tube adjacent to the reaction vessel at the center of the furnace.

The reaction products were cooled in a short water jacketed condenser and easily condensable substances removed in an ice trap. The gas was passed through two spiral wash bottles to remove water soluble material and then through a flowmeter. The gas for analysis was drawn from the stream immediately after it left the flowmeter.

All the experiments were made with an average gas velocity of 43 cc. per minute. The maximum variations in this figure were less than 10%. Assuming the entire length of the reaction vessel in the furnace to be up to the reaction temperature, the time of contact of the gas mixture was 16 seconds.

In preliminary experiments it was found that at temperatures above 500°C, carbon was deposited on the walls of the reaction vessel and material suspended in the issuing gas caused trouble in the second flowmeter. This indicated that polymerization and pyrolysis were the principal reactions and not oxidation, so the remainder of the experiments were done at lower temperatures. The results of these experiments are given in Table 1.

All the gas analyses were done with an Orsat apparatus, using a hot copper oxide tube to determine hydrogen and carbon monoxide and a combustion pipette to determine the saturated hydrocarbons. Since in most of the experiments the saturated hydrocarbons were

Table 1

Effect of Temperature on Reaction of Oxygen with 2-Butene
Time of each Experiment, 100 minutes
Rate of Flow, 43 cc. per minute

Temp. °C	Analysis of Entering Gases O_2	C_4H_8	N_2	Condensate in cc. Oil Phase	Aqueous Phase	Rate of Flow Exhaust Gases cc. per min.
380	31.1%	62.3%	6.6%		0.1-	38
396	34.0	64.3	1.7		0.3	35
423	35.8	60.4	3.8		3.9	22
426	34.8	60.7	4.5		3.3	22
452	34.0	64.3	1.7		3.0	22
477	32.1	60.4	7.5	1.5	2.8	28
490	33.6	63.0	3.4	1.1	1.4	30

Temp. °C	Analysis of Gaseous Products CO_2	unsat.	O_2	H_2	CO	CH_4 C_2H_6	N_2
380	0.1%	61.8%	30.7%	0.1%	0.3%	0.3%	6.7%
396	1.9	58.6	32.6	0.0	1.2	1.1	4.6
423	2.7	60.8	11.3	0.0	15.3	1.9	8.0
426	2.6	62.4	14.8	0.2	10.4	1.4	8.2
452	1.5	57.9	12.7	0.2	13.8	3.2	10.7
477	1.0	54.9	10.6	0.8	15.3	5.6	11.8
490	0.8	50.5	3.5	2.0	25.0	12.3*	5.9

Temp. °C	Moles HCHO (?)	Moles Total Aldehyde	Moles Oxide	Equiv. Acid	Equiv. Peroxide
380	0.0049	0.0060			
396	0.0419				
423	0.0274	0.0395	0.00013	0.00329	
426	0.0275	0.0434	0.00064	0.00220	0.00162
452	0.0240	0.0268		0.00354	
477	0.0179	0.0226	0.00012	0.00085	0.00105
490	0.0182	0.0179	0.0	0.00073	0.00099

(*) 10.4% CH_4 1.9% C_2H_6

Table 1 (contd.)

Identification of 2,4-Dinitro Phenylhydrazones

Temp. °C	Derivatives Identified	Derivatives Unidentified
380	Acetaldehyde m.p.158.5°C	Orange needles m.p.155°C Yellow plates m.p.151-2°C
396	Acetaldehyde m.p.159-60°C Propionaldehyde m.p.150°C	Orange crystals m.p.150°C Long red needles m.p.155°C
426		Yellow plates m.p.147-8°C Orange crystals m.p.142°C
452	Acetaldehyde m.p.159-60°C Propionaldehyde m.p.148-8.5°C	
477		Long red needles m.p.142°C Yellow plates m.p.152.5°C

Note

The melting points were taken by noting the melting point of individual crystals with the aid of a magnifying lense. Only in the case of the mixed melting points were the crystals crushed. The derivatives identified were verified by mixed melting points in all cases.

The unidentified derivatives may be spatial isomers of those identified. The color of these crystals is not a distinguishing property as the acetaldehyde derivative m.p.159-60 C has been prepared both as flat yellow plates and flat orange needles.

Melting Points of 2,4-Dinitro Phenylhydrazones

Formaldehyde	162-3.5°C
Acetaldehyde	159.5-60.5°C
Propionaldehyde	150-51°C
n-Butyric aldehyde	122°C
Isobutyric aldehyde	182°C
Methyl ethyl ketone	115°C

present in very small quantities, their exact determination was impossible with the apparatus used, but it could be shown that in all cases they consisted almost entirely of methane and ethane.

The water in the spiral wash bottles always gave a good iodoform test and a positive test for aldehydes with Schiff's reagent. The condensate consisted of one phase at temperatures below about 455°C. At higher temperatures the condensate consisted of two phases. The upper phase was a yellow oil, density ca. 0.9. It had a very penetrating odor, boiled over a range of 75 -185°C leaving a residue of tar in the distilling flask, and very rapidly decolorized a solution of bromine in carbon tetrachloride. The lower phase consisted mainly of water. When diluted with more water, a small quantity of light yellow oil separated. This aqueous phase gave a good iodoform test and reacted acid to litmus. It gave a positive test for hydrogen peroxide with a solution of titanium tetrachloride in dilute hydrochloric acid (3) and a positive test for formic acid when heated with powdered mercuric oxide (4a). It gave a positive test for an olefin oxide when added to a saturated solution of manganous chloride (4b).

The aqueous phase increased in acidity when left standing at room temperature. In some cases a constant slow evolution of gas was noted, but it was formed in such small quantities that it could not be identified. This is analogous to the phenomenon observed by Lenher (1). He explained it by assuming the presence of dioxymethyl peroxide, $CH_2OHOOCH_2OH$, which decomposes to give hydrogen and formic acid (5).

$$CH_2OHOOCH_2OH \rightarrow H_2 + 2HCOOH$$

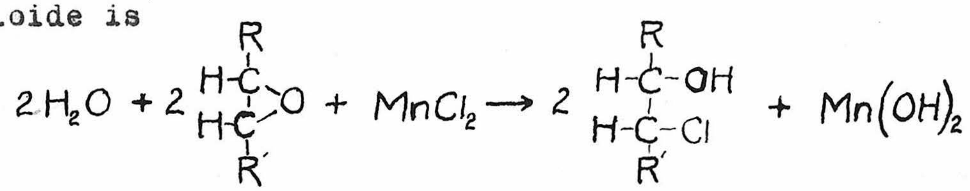
The formaldehyde was determined by the cyanide method (6). This method has been found to be good in the presence of acetone, paraldehyde and acetaldehyde; but for these experiments its correctness is questionable. This will be discussed further when the identification of the carbonyl compounds formed is taken up.

The total aldehyde present was determined by the bisulfite method (7). Both in the determination of formaldehyde and total aldehyde, aliquot portions were taken of the aqueous phase of the condensate and of the wash water.

The acid present in the aqueous phase of the condensate was determined by titrating an aliquot portion with 0.1n. NaOH. During this titration the solution was cooled by ice to decrease the rate of decomposition of the peroxide. Even with these precautions, the end point shifted slowly.

An excess of 0.1n. NaOH was then added to the solution and the mixture left standing for about four days at 10°C to decompose the peroxide. At the end of this period, the peroxide was determined by titrating to neutrality with 0.1n. HCl. The moles of peroxide were equivalent to one-half the difference between the moles excess alkali added and the moles acid used in this titration.

To determine the olefin oxide, an excess of solid manganous chloride was dissolved in the solution, and the mixture left standing at room temperature for about ten days. The reaction of an olefin oxide with manganous chloide is



$$2H_2O + 2\begin{matrix}R\\ |\\ H-C\\ |\\ H-C\\ |\\ R'\end{matrix}\!\!>\!O + MnCl_2 \longrightarrow 2\begin{matrix}R\\ |\\ H-C-OH\\ |\\ H-C-Cl\\ |\\ R'\end{matrix} + Mn(OH)_2$$

The precipitated manganous hydroxide was determined by titration with 0.1n. HCl. In all these titrations, phenol red, pH range 6.8-8.4, was used as the indicator.

For identifying the carbonyl compounds present in the wash water, 2,4-dinitro phenylhydrazine was used (8). A 3% sulfuric acid solution was saturated with this reagent and added in excess to a quantity of the wash water. In all cases a voluminous yellow precipitate of the 2,4-dinitro phenylhydrazones was formed after a few minutes. This precipitate was collected, dried and the components separated by fractional crystallization from alcohol.

The derivatives of acetaldehyde and propionaldehyde were separated in a pure state by this method. These compounds were identified both by microscopic comparison of the crystals with crystals of the pure substance and by mixed melting points. The acetaldehyde was present in much the larger quantity. No evidence was found for the presence of formaldehyde, methyl ethyl ketone, or glyoxal in the wash water.

The fact that formaldehyde could not be shown to be present places the determinations of formaldehyde given above open to question. No explanation can be given for this contradiction.

Olefin oxides tend to rearrange to carbonyl compounds at high temperatures (9). If butylene oxide were present, the existence of some methyl ethyl ketone in the wash water would be expected. This could not be shown to be true; perhaps, because of the small quantity present.

DISCUSSION

From Table 1 it can be seen that reaction between oxygen and 2-butene is just beginning to take place at 380°C with the time of contact used. The reaction has not increased much between 380°C and 396°C, but between 396°C and 423°C a much larger increase is evident. The yield of reaction products in the condensate appears to have reached a maximum somewhere within this latter range. The determination of the oxide, acid and peroxide could not be made at the lower temperatures because the condensate was negligible.

As the amount of intermediate oxidation products decreased, the amount of polymerization and pyrolysis increased. This is shown by the appearance of an oil phase in the condensate and an increase in the unsaturated gases in the product. The increase in the unsaturated gases appeared between 452°C and 477°C and is shown by Table 2.

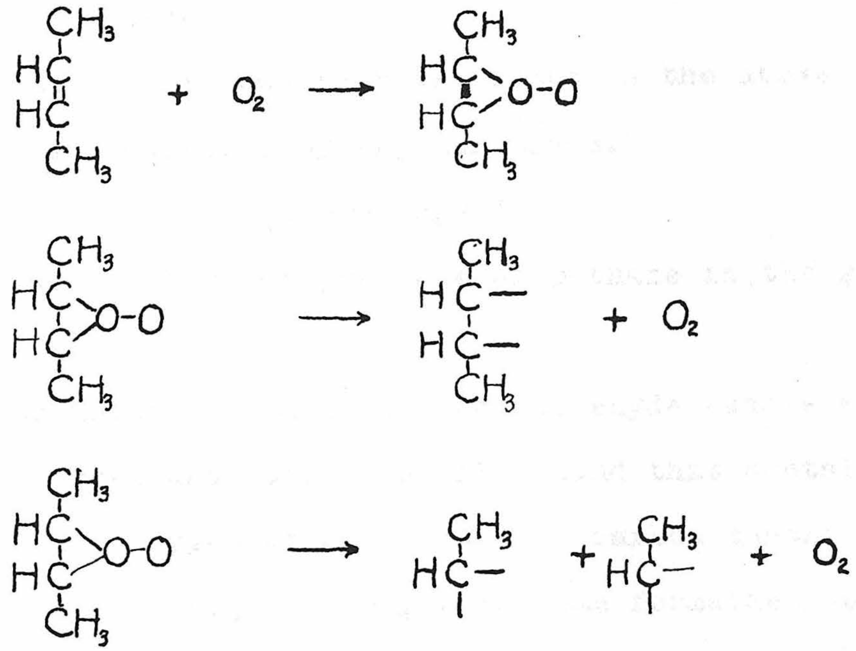
Table 2

Temperature °C	cc. of unsat. gas per min. in product
380	2~~1.6~~ 3.5
396	20.5
423	13.4
426	13.7
452	12.8
477	15.4
490	15.2

The second column of Table 2 was calculated by multiplying the fraction of unsaturated gas in the product by the rate of flow of the exhaust gas in cc. per minute.

The experiment was made of passing pure 2-butene through the Pyrex tube at 486°C and it was found that the formation of condensable polymerization products was negligible. Wheeler and Wood (10) passed pure 2-butene through a quartz tube at 600°C and found 35% of the gas to have decomposed or polymerized.

The formation of decomposition and polymerization products at temperatures below 500°C, as shown by the increase of unsaturates in the gaseous product and the appearance of an oil phase in the condensate, indicates that oxygen must facilitate these reactions. The best explanation for this is the one given by Lenher (1) to explain a similiar phenomenon in the case of the reaction between ethylene and oxygen. He assumed that the C=C bond is activated or opened up by oxygen.



The butylidene and ethylidene residues may react with 2-butene molecules to give higher mono-olefins. No analysis was made of the unsaturated portion of the gaseous product or of the oil phase in the condensate so no definite statement can be made as to the particular compounds formed.

The reaction between oxygen and 2-butene seems to follow two paths. The first is the oxidation at the double bond to form acetaldehyde.

$$CH_3CH{=}CHCH_3 + O_2 \rightarrow 2\ CH_3CHO$$

This probably predominates at the lower temperatures. The second is the formation of the addition complex as discussed above.

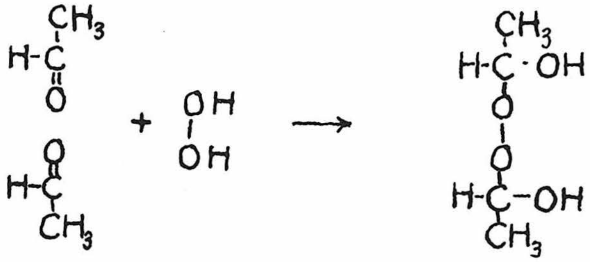
Some of the acetaldehyde formed in the above manner is decomposed by thermal means.

$$CH_3CHO \rightarrow CH_4 + CO$$

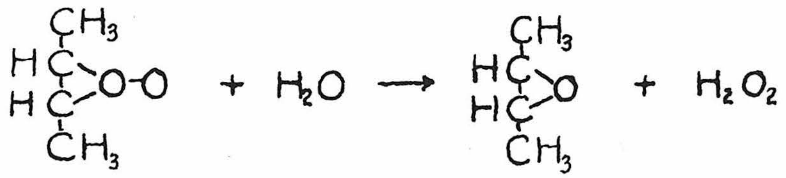
This accounts for the presence of methane in the gaseous product.

Undoubtedly some of the acetaldehyde reacts with oxygen. Bone and Stockings (11) found that acetaldehyde reacts with oxygen at 450°C to give carbon monoxide, methane and hydrogen, along with some formaldehyde.

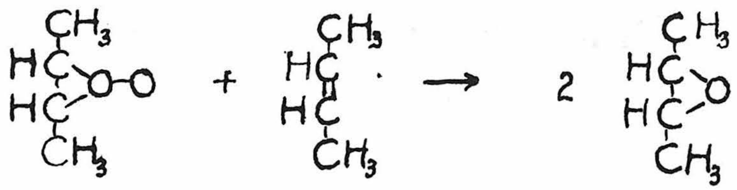
A part of the acetaldehyde reacts with hydrogen peroxide to form the peroxide compound, probably dioxyethyl peroxide.



The hydrogen peroxide is formed by the reaction between the addition complex and water.



The addition complex may also react with a molecule of 2-butene to give butylene oxide.



The oxide probably rearranges to give methyl ethyl ketone which on oxidation gives propionaldehyde and formic acid.

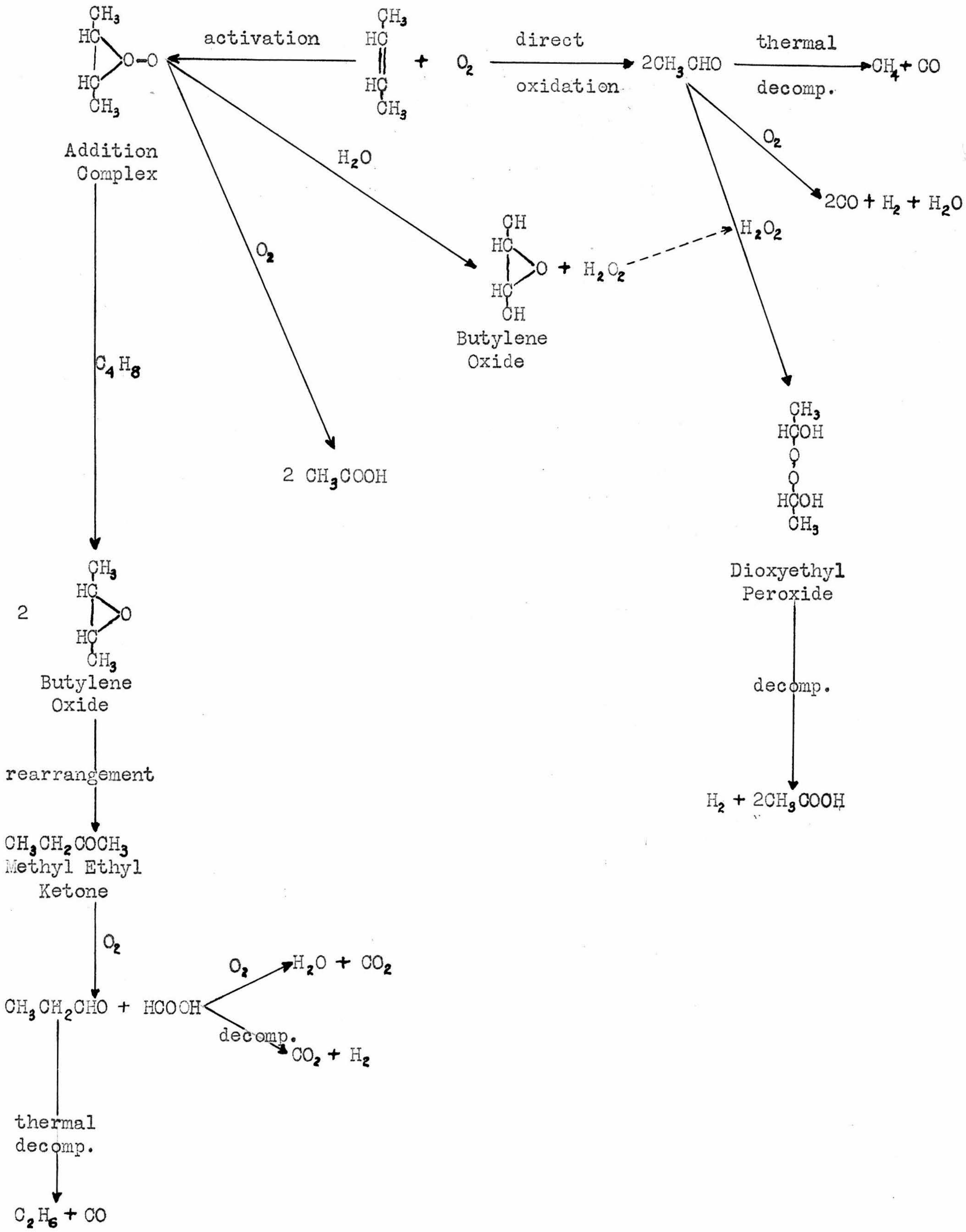
$$CH_3CH_2COCH_3 + O_2 \rightarrow CH_3CH_2CHO + HCOOH$$

The ethane in the gaseous product is formed by the thermal decomposition of the propionaldehyde.

$$CH_3CH_2CHO \rightarrow C_2H_6 + CO$$

The various reactions and phenomena in the oxidation of 2-butene can perhaps best be considered by a schematic representation of the course of the whole reaction. This scheme accounts for all the observed products of reaction and their formation in a stepwise sequence of consecutive reactions.

The Reaction between 2-Butene and Oxygen



SUMMARY

The slow thermal oxidation of 2-butene was studied in small Pyrex vessels over a temperature range 380-490° C.

The principal reaction product was acetaldehyde. Other products were propionaldehyde, formic acid, an olefin oxide, hydrogen peroxide, an organic peroxide, the oxides of carbon and water. At temperatures above 450° C, the polymerization and decomposition of 2-butene became an important reaction.

A scheme of the mechanism of the oxidation of 2-butene has been outlined. The activation of 2-butene, probably by the formation of an addition complex, is used to explain the formation of the olefin oxide and the polymerization at low temperatures.

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