THE STUDY OF THE OXIDATION OF PROPANE AND BUTANE IN THE VAPOR PHASE WITH OXYGEN AND AIR IN THE PRESENCE OF AN ELECTRICAL DISCHARGE

by

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CONTENTS.

Page

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HISTORICAL

The study of the oxidation of gaseous hydrocarbons of the simple homologous alphatic series has been conducted from the several points of view; but regardless of this fact the information is none the less important, for the field is large and its importance great.

Lob[1] found, while studying the action of a silent electrical discharge upon moist methane, that the following products and types of products were produced: carbon dioxide, carbon monoxide, hydrogen, C_nH_{2n} and C_nH_{2n+2}. The hydrogen produced occupied about 35-45 per cent of the gaseous volume. A colorless insoluble solid compound having the emperical formula of $C_9H_{16}O$, was deposited on the sides of the apparatus. The formation of this solid compound was very slow. This compound was not affected by boiling with alkalies or dilute acids, but concentrated sulfuric acid decomposed it. In a similar work, Hiedman[2] found a brown deposit on the walls of a highly polymerized nature.

The scrub water through which the exhaust gas was bubbled was found to contain traces of esters of alphatic acids such as butyric, capric and heptylic acids. Wl Leob[3] noticed from his own experimental data and also from experimental data of other research men, that in all systems subjected to the silent electrical discharge in which the possibility of acetic acid formation exists, the production of butyric acid has also been observed. He also found that

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1. Lob: Ber. 41, 97-90 (1908)

2. Hiedman: Ann. Physik. (5) 2, 221-23 (1929)

3. Leob: Berlin Biochem Z. 20, 126-33

as acetaldehyde is converted into methane and carbon monoxide, it is very difficult to decide whether in the decomposition of the aldehyde, acetic acid is the primary product or methane and carbon monoxide are immediately responsible for the butyric acid formation. Since CH_4 is transformed to H_2 and C_2H_2, which on addition of water changes to acetic acid, there is the possibility that C_2H_2 and H_2O may likewise be responsible for butyric acid formation.

Briner and Durand[1], while studying the chemical action of an electric discharge at low temperatures, found that the action of the spark upon a mixture of nitrogen and hydrocarbons results in the formation of carbon, hydrogen, hydrogen cyanide, ammonia and higher hydrocarbons. The formation of ammonia being predominant if the hydrocarbons are saturated, and the reverse if the hydrocarbon is unsaturated. The action of a wave discharge upon a mixture of nitrogen and hydrocarbons results in the exclusive production of higher hydrocarbon compounds.

Other experimentors[2] have found that methane, when treated both in the pure state and diluted with hydrogen, gave higher unsaturated hydrocarbons such as acetylene and ethylene. The hydrocarbons above methane in the series gave the corresponding unsaturated compounds. Pryanishnikov[3], while studying the effects of an electric discharge

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1. Briner and Durand: J. Chim. Phys. 7, 1-30 (1909)
2. Fujio: Bull. Chem. Soc. Japan 5, 249-60 (1930)
   Fischer and Peters: Z Physik. Chem. Abt. A 141, 180-94 (1929)
   Fischer and Peters: Brenstoff Chem. 10, 108-13 (1929)
3. Pryanishnikov: Ber. 61B, 1358-63 (1928)

upon the gases of the ethylene series, found that the electrical discharge tends to produce polymerization of the unsaturated hydrocarbons. This tends to explain the presence of a residue in the electrical discharge apparatus.

Lind and Glockler[1] have done some very interesting work upon the condensation of ethane into a liquid. They found that the silent, the corona and the high frequency discharges, all cause the condensation of ethane to a liquid, with the liberation of other gases.

The average molecular weight of the liquid product has been regulated between 105 and 467, by controlling the time that the first products, either gas or liquid, are allowed to remain in the discharge tube. The more secondary action takes place, the higher the molecular weight will be because of further condensation.

Continuing their work on the chemical effect of an electrical discharge on methane, ethane, propane and butane, Lind and Glockler[2] have shown that there is a parallelism between the reaction products of an electrical discharge on the hydrocarbons and condensation of the same hydrocarbons caused by α rays from radon. The empirical composition of the liquid product obtained by the aid of an electrical discharge is $C_nH_{1.8n}$, from the gaseous phase and also from the combustion of the liquid.

Experiments have shown that by the α ray condensation of methane, ethane, propane and butane, a liquid compound is obtained, the emperical composition of which is $C_nH_{1.8n}$.

1.Lind and Glockler: J. Am. C. S. 50, 1767-72 (1928)

2.Lind and Glockler: Trans. Am. Electrochem. Soc. 52, 37-47 (1929)

Lind and Glockler: J. Am. C. S. 51, 2811-22 (1929)

When air or oxygen is subjected to an electrical discharge, ozone[1] is produced in varying amounts, depending upon the existing conditions. Briner[2] and his co-workers have shown that below 150°C the oxidation of butane and propane by oxygen is negligible, but ozone produces an appreciable amount of aldehydes and acids. At a higher temperature, the ozone appears to function as a catalyst because the combined oxygen is that attributed to oxygen alone plus the effect calculated for ozone, on the assumption that the action of ozone increases with the temperature at a constant rate.

Lind[3] has proposed three theories to account for the chemical action of electrical discharge upon gaseous hydrocarbons. They are:

1. The photochemical theory, whereby it is assumed that the radiations produced during the discharge are responsible for the chemical action produced.
2. The static ion theory, wherein it is assumed that the ions serve as clustering centers and that chemical effects are produced on neutralization of the clusters, using part or all of the energy of ionization as activating energy.
3. The kinetic ion theory, where it is assumed that the ions impart kinetically a critical activating energy to the molecules which react.

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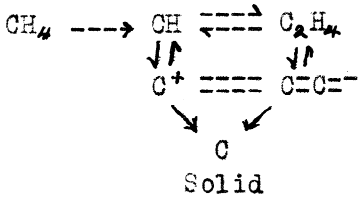
[1] Fischer: Z. Physik Chem. 104, 74-89 (1923)
Kruger: Nernst Festschrift 240-256
Briner and Durand: Compt. Rend 145, 1272-4 (1909)

[2] Briner and Carceller: Helv. Chim. Acta 18, 973-81 (1937)
Briner, Carceller and Adler: Swiss 182, 957. June 2, 1936

[3] Lind: Science 67, 565-9 (1928)

Lind claims to have reasons to support both the static ion and the clustering theory.

Peters and Wagner[1] studied the mechanism of the action of the electrical discharge on methane with the aid of a spectroscope. The spectrum analysis of the arc in the discharge, before the color change was observed upon increasing the electrical charge, shows the band of the CH, N and CN groups. This is taken to show the progression in radicals from $CH_3 \dashrightarrow CH_2 \dashrightarrow CH$. Polymerized saturated hydrocarbons are thus formed at low pressure and low charge, while C_2H_4 and C_2H_2 are formed at high pressure. Solid hydrocarbons result from the reaction of $=C=C=$ groups with reactive hydrogen. The mechanism is as indicated:



A. de Hemptinne[2] has shown that Faraday's law holds with fair approximation for chemical effects produced by an electric discharge in gases at low pressure.

It has been found that the silent discharge in dry air[3] forms N_2O and N_2O_5 as well as O_3. Secondary action of O_3 on N_2O_5 produces a small amount of a highly colored gas, giving a characteristic absorption spectra.

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1. Peters and Wagner: Brennstoff Chem, 12, 67-8 (1931)
2. Hemptinne: Bull. Acad. Roy. Belg. 5, 521-7 (1919)
3. Anon: Z. Angew. Chem. 25, 1324-6 (1912)

Briner and Durand[1] found that the silent discharge acting on air does not produce the oxides of nitrogen at a low temperature, ozone being the only product formed. The arc and the spark discharge produce, under the same conditions, the oxides of nitrogen and only a small quantity of ozone. According to Kruger[2], it seems probable that the mechanism of ozone formation by the silent electric discharge consists of splitting off a secondary electron from the oxygen molecule, and the consequent separation of the molecule into two atoms. Each atom then unites with an oxygen molecule to form a molecule of ozone.

Fischer[3] has shown that the ozone concentration increases almost proportionally to the energy of the current, and rapidly diminishes as the distance between the electrodes is increased. The ozone concentration also increases as the flow of gas through the tube becomes smaller, and vice versa. Glass and aluminum ozonizers of the same dimensions yield approximately the same concentration of ozone under the same experimental conditions; but the ozonizers with a brass electrode produce very small quantities of the anhydride of nitric acid (HNO_3), and no anhydride of nitrous acid (HNO_2) was formed.

The oxidation of hydrocarbons may be aided by the use of the

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1. Briner and Durand: Compt. Rend. 145, 1272-4
2. Kruger: Nernst Festschrift, 240-256
3. Fischer: Z. Physik Chem. 104, 74-89 (1923)

following catalyst[1]: CuO, Fe_2O_3, V_2O_5, UO_3, $Ni_3(PO_4)_2$, Na_2CO_3.

Juilard[2] found, contrary to statements in the older literature, that hydrogen (H_2) and silicon fluoride (SiF_4) decrease the formation of ozone from oxygen in ozonizers of the ordinary type.

The mechanism of the oxidation of the hydrocarbons has not been definitely agreed upon; but much work has been done on this subject, and several theories have been proposed. The slow oxidation of hexane[3] at 210°C by an anonymous experimentor gives a possible mechanism of the oxidation. During the reaction, moloxides (unsaturated intermediate oxidation products) and peroxides are probably formed first. They then undergo secondary reactions resulting in the formation of water, unsaturated compounds, fatty acids, carbon monoxides and other gases. Quantitative investigation of the reaction products show that in the addition to the formation of the moloxides and peroxides, the manner of oxidation of the hydrogen atom is important. The unsaturated intermediate product thus formed will take up oxygen, forming new secondary products. The decomposition of both the primary and secondary peroxides results in a series of further changes which may lead to the formation of aldehydes, peracids and other compounds.

Pope, Dykstra and Edgar[4] interpreted the results of their work on the vapor phase oxidation of octanes on the theory that

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[1] de Balaafsche: Fr. 784, 016 July 20, 1935

[2] Juilard: Bull. Sci. Acad. Roy. Belg (5) 12, 914-20 (1926)

[3] Techn. Hochschule Zurich. Helv. Chim. Acta.11, 881-97 (1928)

[4] Pope, Dykstra and Edgar: J. Am. C. S. 51, 1875-89 (1929)

the initial oxidation product of normal octane is octaldehyde, which in turn is further oxidized to aldehydes of successively smaller number of carbon atoms, carbon monoxide and some carbon dioxide being simultaneously formed.

Pease and Munro[1], in their study of "The Slow Oxidation of Propane", found that both the peroxides (other than peracid) and aldehydes may be important products of propane oxidation. Their results show:

1. Peroxides can not be essential to the chain propagation of reactions, since a very simple treatment of the reaction bulb (coated with potassium chlorides) almost entirely eliminates these peroxides, but only moderately decreases the total amount of reaction.
2. Organic peroxides, aldehydes (mainly formaldehyde) and alcohols (mainly methanol), which have been estimated quantitatively, are secondary products.
3. Acids, esters, acetals, acetone propionaldehyde and ethylene oxide are unimportant.
4. The early appearance of propylene in quantity without the equivalent of hydrogen, indicates its importance in the primary oxidation process.
5. The main reaction of hydrocarbons with oxygen has yet to be discovered.

Pease[2], in his study of "The Mechanism of the Slow Oxidation of Propane", found that methanol, formaldehyde, carbon monoxide and water are the primary products of the slow oxidation of propane.

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[1] Pease and Munro: J. Am. C. S. 56, 2034 (1934)

[2] Pease: J. Am. C. S. 57, 2296 (1935)

His results are interpreted in terms of Rices[1] radical-chain theory, on the assumption that methoxyl (CH_3O) and propyl (C_3H_7) groups are the chain carriers. Pease points out that similar mechanisms involving hydroxyl in place of the methoxyl groups, and producing water in place of the methanol, may apply to the oxidation of methane and ethane.

Since the oxidation of the saturated open chain hydrocarbons yields aldehydes as one of the oxidation products, attention has been drawn to the aldehyde oxidation reactions in hopes that the latter may throw some light upon the mechanism of hydrocarbon oxidation.

There exists some disagreement as to the nature of the reaction between acetaldehyde vapor and oxygen. According to Bodenstein[2] the reaction is homogeneous, and yields mainly pre-acetic acid. Hatcher, Steacie and Howland[3], on the other hand, find that the rate is increased by a glass packing (indicating wall reactions) and a complex mixture of products is obtained. Both Bodenstein and Hatcher with his colleagues, are inclined to regard the reaction as of the chain type; but for different reasons.

Under these conditions, Pease[4] undertook a re-investigation of the acetaldehyde oxygen reaction. He found that:

1. Peracetic acid is the preponderant product except where the reaction vessel is coated with potassium chloride.

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1. T. O. & K. K. Rice: The Aliphata Free Radicals. Johns Hopkins Press, Baltimore, Md. 1935

2. Bodenstein: Sitzber preuss Akad. Phys. Mal III 1 (1931)

3. Hatcher, Steacie and Howland: Can. J. Research 7, 149 (1932)

4. Pease: J. Am. C. S. 55, 2753-61 (1933)

2. The reaction is accelerated by broken glass packing, and also by coating the reaction vessel with potassium chloride.
3. The reaction is inhibited by ethyl alcohol vapor, but not by water vapor. Nitrogen, hydrogen and ethane do not affect the rate.
4. The initial rate is proportional to the square of the acetaldehyde concentration, and independent of the oxygen concentration. The reaction is auto-accelerated.
5. The reaction appeared to be the chain type, with chains starting on the walls and ending in the gas phase; but this is not definitely proved.

Guyot[1], in his process for the production of acetic acid from acetaldehyde, took precautions against the formation of peracetic acid. The vapors of acetaldehyde are oxidized by a gas rich in oxygen, in the absence of a catalyzer, and at once are brought to a temperature of about 100° C to destroy any peracetic acid present.

In their work on the oxidation of acetaldehyde by oxygen, Bowen and Tietz[2] showed:

1. When acetaldehyde is shaken with oxygen at ordinary temperature, a peroxide is formed.
2. The velocity of the reaction between the gaseous substances in ultra violet light is high; it is approximately proportional to the square root of the intensity of the light,

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[1] Gayot: U. S. 1,409,036. March 7, 1922. Can. 214, 163. Nov 8, 1921

[2] Bowen and Tietz: Nature 124, 914. 1929

proportional to the aldehyde concentration and independent of the oxygen concentration.

3. A long chain mechanism of reaction is indicated.

The question of peracids and peroxides resulting from the oxidation of hydrocarbons has attracted much attention. Bone[1] has insisted on the view that all hydrocarbon oxidation proceeds via hydroxalation, the hydroxyl compound losing water to form aldehyde:

$$RCH_3 + O_2 \dashrightarrow RCH(OH)_2 \dashrightarrow RCHO + H_2O$$

Further oxidation then yields the lower aldehydes and carbon monoxide:

$$R'CH_2CHO + O_2 \dashrightarrow R'CHO + CO + H_2O$$

or acid:

$$2\ RCHO + O_2 \dashrightarrow 2\ RCOOH$$

Pope, Dykstra and Edgar[2] adopt essentially the same view, without specifying the intermediate hydroxyl compound. Bone has minimized the importance of peroxides as initial products, pointing out that aldehydes formed in the primary reaction could consequently react with oxygen and give peracid as a secondary product. Bone and Hill[3] show that in the oxidation of ethane, the peroxide (as determined with titanium sulfate) tends to follow aldehyde production and amounts to only about one-tenth of the latter. In a discussion of the subject of the oxidation of organic compounds with oxygen, including some literature data, Alfred Rieche[4] sum-

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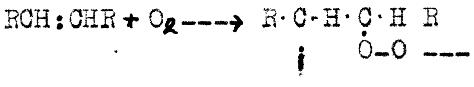
1..Bone and Townend: "Flame and Combustion in Gases", Mac millian and Company, 1927.
2. Pope, Dykstra and Edgar: J. Am. C. S. 51, 1875 (1929)
3. Bone and Hill: Proc. Roy. Soc. (London) A129, 434 (1930)
4. Rieche: Angun. Chem. 50, 520-4 (1937)

marizes the oxidation processes as follows:

1. In many cases, oxygen does not react with the double bond (in contrast with ozone) but enters between a C-H bond. This reaction seems to be the one which takes place most frequently.
2. The reactions between oxygen and organic compounds may be pictured as follows:

(1) $R{-}R + O_2 \longrightarrow ROOR$

(2) 

$RCH{:}CHR + O_2 \longrightarrow R\cdot \underset{|}{C}\cdot H\cdot \underset{\dot{O}-O\ ---}{C}\cdot H\ R$

(3) $R\cdot H + O_2 \longrightarrow R\ O\ O\ H$

(3a) $R\ C\ H\ O + O_2 \longrightarrow R\ C\ ({:}O)\ OOH$

(3b) $R\ C\ H_2C({:}O)\ R + O_2 \longrightarrow R\ C\ H\ (OOH)\ C({:}O)\ R$

(3c) $R\ C\ H_2OH + O_2 \longrightarrow R\ C\ H\ (OOH)\ O\ H$

(3d) $R\ C\ H_2O\ R + O_2 \longrightarrow R\ C\ H\ (OOH)\ O\ R$

Steacie and Plemes[1] have drawn four conclusions from many investigations of the kinetics of the oxidation of gaseous of hydrocarbons. They are as follows:

1. All oxidation reactions of gaseous hydrocarbons proceed by a chain mechanism.
2. The rate of reaction depends on some fairly high power of concentration of the original substance.
3. Packing the reaction vessel with material of which it is made, usually retards the oxidation markedly.
4. In all of these reactions there is a more or less pronounced induction

The oxidation of unsaturated gaseous hydrocarbons can be satisfactorily explained in a general way on the Bodenstein mechanism. While

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[1] Steacie and Plemes: Can. Chem. Met. 18, 216-17 (1934)

in the saturated hydrocarbon, the oxidation proceeds through a primary dehydrogenation, followed by a chain oxidation of the olefin.

While some workers favor the hydroxylation theory of oxidation, others leave no doubt as to the formation of the true peroxides, other than peracids. Thus Lenher[1] reported the formation of dioxymethyl peroxide ($HOCH_2 OOCH_2 OH$) from ethylene, and Mordain-Mornal and Quanquin[2] partially identified compounds of the type ROOH, ROOR'OH, and HOROOR'OH, in the oxidation of paraffins from pentane to octane. Mardles[3], by his study of the peroxidation of hydrocarbons during combustion in air, has been able to explain the presence of methanol in the combustion products of methane by the peroxidation theory (Mourea) as satisfactorily as by the hydroxylation theory of Bone.

Since peroxides and peroxide compounds are so frequently found among the oxidation products of hydrocarbons and hydrocarbon compounds, studies have been made of the peroxides. Fujimoto[4] has prepared di formal peroxide hydrate ($HOCH_2OOCH_2OH$) by the action of a 1500-volt silent electrical discharge upon a mixture of 64 percent methane and 35 percent oxygen. Medvedev and Alekseena[5], after much work and study of various reactions, succeeded in preparing iso-

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1. Lehner: J. Am. C. S. 53, 3737, 3752 (1931)
2. Mordain-Mornal and Quanquin: Ann. Chim. 15, 309 (1931)
3. Mardles: Nature 128, 116-7 (1931)
4. Fujimoto: Japan 110, 728. May 13, 1935
5. Medvedev and Alekseena: Ber. 65B, 133-7 (1932)

propyl and propyl hydroperoxide. Isopropyl hydroperoxide is a mobile liquid with an irritating odor. It boils at 107-109°C, and explodes on heating to a high temperature. It is missible in all proportions of water, alcohol and ether. It is relatively stable in quartz vessels and in neutral or acid aqueous solutions, but decomposes quickly in alkali solutions with the formation of acetone. The propyl hydroperoxide was not obtained in the pure form, but the barium salt was isolated.

In following up some previous work, Rieche and Hitz[1] undertook to prepare and purify some free methyl hydroperoxide (CH_3OOH). The dilute solution was obtained, but it was with much work that they finally succeeded in obtaining the pure methyl hydroperoxide. The compound is very soluble in water, and it boils between 38 and 40°C, with slight decomposition. It has an extraordinary penetrating odor, attacks the respirating organs, and produces deep burns on the skin which heal with difficulty. Even in vapor form, it destroys organic compounds and attacks mercury. On heating, it explodes very violently, and is also very sensitive to shock at high temperature. Methyl ethyl peroxide ($CH_3OOCH_2CH_3$) and hydroxydimethyl peroxide(CH_3OOCH_2OH) were also prepared. The hydroxydimethyl peroxide is an oil of penetrating odor which explodes violently on heating, does not solidify in an ice-salt mixture and shows typical peroxide reactions toward reducing agents.

Continuing his work on alkyl peroxides, Alfred Rieche[2] studied the hydroxyalkyl hydroperoxides. He found that in a mixture of alde-

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[1] Rieche and Hitz: Ber. 62B, 218-25 (1929)
Rieche and Hitz: Ber. 62B, 2458-74 (1929)

[2] Rieche: Ber. 64B, 2328-35 (1931)

hyde and hydrogen peroxide, there exists the equilibrium:

$H_2O_2 + 2RCHO \rightleftharpoons RCH(OH)OOH$ (hydroxyalkyl peroxide)

$RCH(OH)OOH + RCHO \rightleftharpoons RCH(OH)OO\ CH(OH)R$ (bis hydroxyalkyl peroxide)

so that one molecule of aldehyde and hydrogen peroxide do not always give the hydroxyalkyl hydroperoxide. The bis peroxide is the more stable product and tends to be formed in general, especially in water. In ethyl ether, the state of affairs is much more favorable to the formation of the hydroxyalkyl hydroperoxide, which under the proper conditions can be isolated in pure form. The preparation of the derivitives of the lower aldehydes offers special difficulties, and the lowest member of the series, $HOCH_2OOH$, has not been isolated. The α hydroxyethyl hydroperoxide has been prepared, but with much difficulty. The higher hydroxyethyl hydroperoxides are readily obtained in leaflet crystals with the following melting points:

Hydroxyheplyl hydroperoxide	$C_6H_{13}CH(OH)OOH$	40°
Hydroxyoctyl hydroperoxide	$C_7H_{15}CH(OH)OOH$	46°
Hydroxynonyl hydroperoxide	$C_8H_{17}CH(OH)OOH$	50-54°
Hydroxydecyl hydroperoxide	$C_9H_{19}CH(OH)OOH$	61°
Hydroundodecyl hydroperoxide	$C_{10}H_{21}CH(OH)OOH$	62°
Hydrododecyl hydroperoxide	$C_{11}H_{23}CH(OH)OOH$	65-67°

They are not explosive and merely decompose vigorously when super heated; they are insoluble in water, but are slowly decomposed by it in the cold.

Continuing the study of alkyl peroxides, Rieche, in co-operation with R. Miester[1], has studied Elhylidene peroxides. The per-

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1. Rieche and Miester: Ber. 64B, 2335-40 (1931)

oxides in which two peroxide groupings are joined through a carbon atom, are best designated as alkylidene peroxides. Of those derived from aldehydes $(R\,C'HOO-)x$ only three were hitherto known, i.e. $(C_6H_5C'\,HOO-)x$ and $(CH_3C'HOO-)x$ $(C_2H_5C'HOO-)x$. The ethylidene compound $(CH_3C'HOO-)x$ had been previously obtained by Wieland and Wingler[1] from $(CH_3CH(OH)\cdot O)_2$ as a viscous, exceedingly explosive resin. Rieche and Miester have observed its formation in several other ways, and have studied its properties.

The ethylidene peroxide, when freshly prepared, is a very viscous oil of only a faint odor and not particularly sensitive, so that it can be handled with comparative safety. After standing for several days in a closed vessel, or for one hour in the air, it becomes more viscous and sticky, and finally becomes very sensitive and dangerous, far more so than CH_3OOCH_3. Further hitherto unknown alkylideneperoxides have been obtained by Rieche and Miester[2], by the elimination of water from bis (hydroxyethyl) peroxide. By further reactions of bis peroxide, they isolated and identified a peroxide compound which they call perparaldehyde. This perparaldehyde is paraldehyde in which one of ring oxygens is replaced by the -O*O* groups. It has only a faint odor, is insoluble in water and easily soluble in almost all organic solvents. It is hydrolyzed by hot dilute sulfuric acid to three molecules of acetaldehyde and one molecule of hydrogen peroxide.

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[1] ..Ann: 431, 301-22 (1923)

[2] Rieche and Meister: Ber. 65B, 1274-9 (1932)

Two sets of workers[1] were studying the reactions of diacyl peroxides about the same time, and their papers were published the smae year. Their results agree very well. They have shown that diacyl peroxides decompose when heated to give a hydrocarbon and carbon dioxides: $RCOO \cdot OOCR \xrightarrow{\Delta} RR + 2CO_2$.

The reaction may take place by the intermediate formation of carbon dioxide and the free radicals R, which polymerize to form R R. More than one type of reactions may take place at the same time when the diacyl peroxide is decomposed by heat.

On continuing their studies of alkyl peroxides, Rieche and Meister[2] found that the power of formaldehyde (HCHO), to add to hydrogen peroxide, is not limited to the addition of two molecules of formaldehyde. By very careful work they were able to prepare three complicated peroxide compounds. The first compound, bis (hydroxymethyl) peroxide bis (hydroxymethyl) ether has the formula $(HOCH_2OCH_2)_2O_2$. It is an oil with the consistency of liquid paraffin, easily soluble in water, and not particularly explosive. The second compound is believed to be pertrioxymethylene, $CH_2(O.CH_2)_2 \cdot O_2$; it is insoluble in water and quite explosive, detonating with a loud report when superheated in a test tube, and forming a white sublimate of polyoxymethylene. The third compound, after very careful handling, was analized and assigned the structure of tetraoxymethylene diperoxide, $O_2(CH_2OCH_2)_2\ O_2$. This compound is exploded with tremendous violence by friction, shock or heat.

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[1] Fichter and Erlenmeyer: Helnetica Chim. Acta 9, 144-52 (1926)

[2] Rieche and Meister: Ber. 66B, 718-27 (1933)

Rieche and Meister[1], continuing their study of alkyl peroxides, turned their attention to the simpler members of the groups. Up to this time numerous hydroxyalkyl hydroperoxides had been prepared by the addition of H_2O_2 to aldehydes, but it had been found impossible to obtain the simplest member of this group of compounds; namely, hydroxymethyl hydroperoxide ($HOCH_2OOH$). When ether and solution of formaldehyde and hydrogen peroxide were brought together, and the ether evaporated, there remained unstable oils of varying composition.

It has been found that the trouble lay in the fact that the solutions of formaldehyde contained the hydrate of formaldehyde. With a solution of specially prepared anhydrous formaldehyde, hydrogen peroxide gives hydroxymethyl hydroperoxide as a relatively stable oil of medium consistency, not sensitive to friction but exploding with extreme violence when heated in a flame.

Rieche[2] studied the autoxidation of ether in order to determine the explosive character of ether, since numerous instances had been cited where violent explosions of ether residues had been caused by heat on friction. He found that the formation of peroxides is greatly accelerated by light (ultra violet rays), and by the presence of aceteldehyde. Formaldehyde has a similar effect, but to a lesser degree. Thus he claims that the high degree of explosiveness noted in ether residues can be due only to alkylidene peroxides. Such compounds may result directly from the oxidation of the ether molecule, or from dioxyalkyl peroxides with the sepa-

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1. Rieche and Meister: Ber. 68B, 1465-73 (1935)
2. Rieche: Z. Angem. Chem. 44, 896-9 (1931)

ration of acetaldehyde and water, or from oxyalkyl hydroperoxides with the separation of water.

According to Schwaz and Heinrich[1], there are two types of peroxides, the false and the true. The true peroxides have the -O-O- bridge within the molecule, while the false peroxides have the H_2O_2 attached to the molecule.

Roessler[2] has found that peroxide solutions may be made more stable by the addition of tin compounds, such as Na_2SnO_3 after the pH of the peroxide solution has been properly adjusted.

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1. Schwaz and Heinrich: Z. Anorg. Allgem. Chem. 223, 387-92 (1935)
2. Roessler: Ger. 610, 185 March 7, 1935.

THEORETICAL

The study of the oxidation of propane and butane in the vapor phase, with oxygen and air, in the presence of an electrical discharge, was undertaken. The oxidation product obtained, was found to contain aldehydes and peroxides along with other compounds. This lead to the study of the oxidation of aldehydes by air and oxygen, since aldehydes and peroxides were found in the same solution. Acetaldehyde, butyraldehyde and heptaldehyde were used for oxidation study, and each yielded a peroxide compound.

The saturated aliphatic hydrocarbons are rather stable compounds. They do not readily react with oxygen of the air or pure oxygen, at normal conditions of temperature and pressure, without the aid of an outside force.

Lob[1], while studying the action of a silent electrical discharge upon moist methane, found that the following compounds were produced: carbon dioxide, carbon monoxide, hydrogen, higher saturated and unsaturated hydrocarbons, and traces of esters of higher aliphatic acids, such as butyric, capric and heptylic. It would seem that the longer chain hydrocarbon was built up from methane and then possibly oxidized through various steps, finally to give the acid. Leob[2], Briner, Durand[3], Fujio[4], Fischer and Peters[5] obtained results to agree with those of Lob.

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1. Lob: Ber. 41, 87-90 (1908)
2. Leob: Berlin Biochem. Z. 20, 126-35
3. Briner and Durand: J. Chim. Phys. 7, 1-30
4. Fujio: Bul. Chem. Soc. Japan 5,249-60 (1930)
5. Fischer and Peters: Z. Physik Chem. Abt. A, 141, 180-94

The gas used in these experiments was the commercial pyrofax gas which is a mixture of about 3 per cent butane and 97 per cent propane. The liquid product which formed in the reaction chamber was collected in a cup at the bottom of the chamber. This liquid was a mixture of compounds. It contained formaldehyde and higher aldehydes, acids, a peroxide and polymerized compound. As Leob[1] found from his own experimental work, these acids which are found in the liquid may contain acetic acid, butyric and possibly higher aliphatic acids. The peroxide is very unstable, and will decompose if left standing at room temperature. Instead of decomposing into smaller components, it may react with something else in the mixture, possibly an aldehyde, to give one or more molecules of an acid. Rieche and Hitz[2] have found that the peroxides in a solution react with other compounds in the same solution, and thus lose their original identity as peroxides. If kept on ice, the peroxide may remain for at least twenty four hours. The brown polymerized product in the liquid has similar characteristics to those of a brown polymerized product which forms on the walls of the reaction chamber of the elctrical discharge apparatus. Hiedman[3] reports on a similar brown deposit which formed on the walls of his electrical discharge reaction tubes. He reported the deposit to be of a highly polymerized nature. Nitrogen from air does not

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1. Leob: Berlin Biochem. Z. 20, 126-35

2. Rieche and Hitz: Ber.62B, 2458-74, (1929)

3. Hiedman: Ann Physik (5) 2, 221-23 (1929)

cause this brown deposit, because when pure oxygen is mixed with the hydrocarbon gas and this mixture run through the elctrical discharge apparatus for the same period of time and under the same conditions of temperature and pressure, the same type of brown deposit is formed on the walls of the reaction chamber. If the liquid, which drips from the walls of the reaction chamber into the collection cup, is allowed to evaporate in the air, the brown deposit is left. When, at the end of a run, the reaction chamber is not cleaned out, but is allowed to stand with some of the compounds in it until the next run, the brown deposit is much more readily formed. Thus it appears that once the polymerization of the certain compounds in the liquid has started, the reaction increases.

This brown deposit may be explained as the polymerization of the unsaturated hydrocarbon compounds, for it has been found that the action of an electrical discharge[1] upon hydrocarbon gases tends to produce unsaturated hydrocarbon compounds of the ethylene and acetylene type; and Pryanishnikov[2] has shown that the silent electrical discharge produces polymerization upon unsaturated hydrocarbons.

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[1] Lob: Ber. 41, 97-90 (1908)
Leob: Berlin Biochem. Z. 20, 126-35
Fujio: Bul. Chem. Soc. Japan 5, 249-60 (1930)
Fischer and Peters: Z. Physik Chem. Abt A, 141, 180-94
Fischer and Peters: Brennstoff Chem. 10, 108-13 (1929)

[2] Pryanishnikov: Ber. 61B, 1358-63 (1929)

The second liquid product obtained from the oxidation process is that which is condensed from the gases that come from the reaction chamber. This liquid contains water along with the volatile liquids whose vapors were caused to condense by the freezing mixture of the cooling bath. Fujimoto[1], using a glass ozonizer and 15,000-volts, has prepared a liquid product from a mixture of a 64 percent methane and 35 percent oxygen. This liquid product was composed of about 50 percent diformal peroxide hydrate ($HOCH_2 OOCH_2 OH$), 10 percent formic acid, small amounts of methyl alcohol, formaldehyde, methyl formate and water. Thus when propane and butane are used, similar reactions are expected and corresponding compounds should be formed. The secondary reactions and the chain reactions are to be considered, for they further complicate the composition of the liquid. Moloxides[2], which is the name given for unsaturated intermediate oxidation products, and peroxides are probably formed first, in the oxidation of hexane at 210° C, then they undergo secondary reactions resulting in the formation of water, carbon monoxide, fatty acids, unsaturated compounds and gases. Briner and Carceller[3],have shown that below 150° C the oxidation of propane and butane by oxygen is negligible, but ozone produces an appreciable amount of aldehydes and acids. Now in a system where the propane and butane are subjected to the action of an electrical discharge, at the same time being mixed

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[1] Fujimoto: Japan 110, 728 (May 13, 1935)

[2] Techn Hochschule Zurich. Helv, Chem. Acta 11,881-97 (1928)

[3] Briner and Carceller: Helv. Chim. Acta 18, 937-81 (1937)

with oxygen and ozone, the reaction is expected to be modified; but, at the same time, it should be more vigorous. Chain reactions should further complicate the expected reactions. Steacie and Plemes[1] have reached the conclusion that all oxidation reactions of gaseous hydrocarbons proceed by a chain mechanism.

The scrub water through which the exhaust gas was bubbled, was found to contain acids and aldehydes. Lob[2], while working with methane in a similar apparatus, found the scrub water to contain esters of aliphatic acids, such as butyric, capric and hypletic. Leob[3] noticed from his own experimental data,and also from that of other research men, that in all systems subjected to the silent electrical discharge in which the possibility of acetic acid formation exists, the production of butyric aicd has also been observed. It does not seem that the vapors of the compounds dissolve in the water and thus remain, but rather that some reactions take place within the water solution.

Aldehydes and peroxides were found among the oxidation products of propane and butane and, since they react together to form other compounds, the question of their relation to the mechanism of the hydrocarbon oxidation seemed to be in order. The method of attack was through the study of oxidation and peroxide formation of aldehydes. In the oxidation of acetal-

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1. Steacie and Plemes: Can. Chem. Met. 18, 216-7 (1934)

2. Lob: Ber. 41, 87-90 (1908)

3. Leob: Berlin Biochem. Z. 20, 126-35

dehyde for the production of acetic acid, the problem of per compounds, especially the peracetic acid formation, has given much trouble. For when a large amount of peracetic acid collects, a violent explosion occurs.

Guyot[1] has patented a process whereby acetaldehyde vapor is oxidized without the aid of a catalyzer, and at once brought to a temperature of 100°C to destroy any peracetic acid present. Thus we should expect peroxide compounds to be more stable at low temperatures.

The fact that acetaldehyde is easily oxidized even in air, has been definitely verified by many investigators, but the mechanism of the reaction is still subject to much discussion. Bodenstein[2] claims that when acetaldehyde vapor is oxidized by oxygen in a suitable apparatus, the reaction is homogeneous and yields mainly peracetic acid. Hatcher, Steacie and Howland[3], on the other hand, find that the rate of reaction is increased by a glass packing (indicating wall reaction) and a complicated product is obtained. Both seem to regard the reaction as belonging to the chain type, but for different reasons. Pease[4], in a reinvestigation of the acetaldehyde oxidation reaction, found that the reaction is accelerated by broken glass packing and also by coating the walls of the reaction chamber with potassium chloride. When potassium

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1. Guyot: Can. 214, 163 November 8, 1921
2. Bodenstein: Sitzber preuss. Akad. Phys- Math III 1,(1929)
3. Hatcher, Steacie and Howland: Can J. Research 7, 149 (1932)
4. Pease: J. Am. C. Soc. 55, 2753-61 (1933)

chloride was used to accelerate the reaction, no peracetic acid was found in the product. The writer found that by packing the reaction chamber with pieces of glass, the reaction was increased. Thus checking the work of Pease, Hatcher, Steacie and Howland.

Bone[1] has insisted on the hydroxyl theory of oxidation for aldehydes, while Pope, Dykstra and Edgar[2] take essentially the same stand; but they do not specify any special intermediate products. Bone, in supporting the hydroxyl theory of oxidation, states that aldehydes are formed by the primary oxidation reaction, and the peroxides and peracids are formed by oxygen and aldehydes as secondary reactions.

Bone and Hill[3], from their study of the oxidation of ethane, show that the peroxide formation tends to follow the aldehyde production and amounts to only about one-tenth of the latter. But if this were a secondary reaction, why should only a fractional part of the aldehyde be oxidized to the peroxide ? Other investigators support the peroxide theory. Mardles[4] explains the presence of methanal in the combustion of methane by the peroxidation theory as satisfactorily as by the hydroxylation theory of Bone. Lenher[5] reported the formation of dioxymethyl peroxide ($HOCH_2\ OOCH_2\ OH$) from ethylene, and Mordain-Mornal and Quanquin[6]

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[1] Bone and Townend: "Flame and Combustion in Gases", Macmillian and Company (1927)

[2] Pope, Dykstra and Edgar: J. Am. C. Soc. 51, 1875 (1929)

[3] Bone and Hill: Proc. Roy. Soc.(London) A 129, 434 (1930)

[4] Mardles: Nature 128, 116-17 (1931)

[5] Lenher: J. Am. C. Soc. 53, 3737, 3752 (1931)

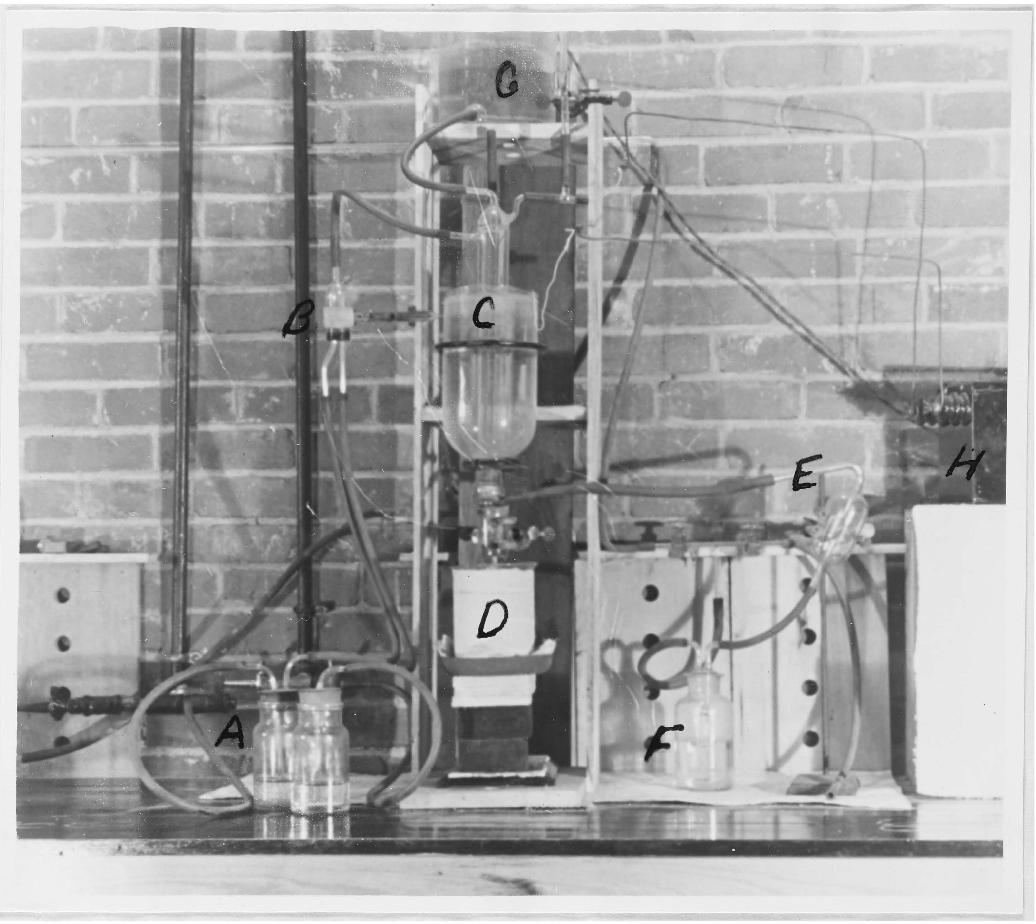
[6] Mordain-Mornal and Quanquin: Ann. Chim. 15, 309 (1931)

partially identified compounds of the types: ROOH, ROOR' OH, HOROOR' OH in the oxidation of paraffins from pentane and decane.

The information gathered from the study of the oxidation products of aldehydes, especially the peroxides, should be of much value in a study of the products formed when hydrocarbons are oxidized. Acetaldehyde is easily oxidized, but correspondingly the peroxide and per compounds are unstable. When a higher aldehyde is used instead of acetaldehyde, it should be harder to oxidize; but the peroxide or per compound should be more stable. Butyraldehyde should give peroxides or per compounds which are more stable than those of acetaldehyde. Likewise, heptaldehyde peroxides or per compounds should be more stable than those of butyraldehyde.

EXPERIMENTAL

The following apparatus was used to oxidize propane and butane in the vapor phase with oxygen and air in the presence of an electrical discharge:



The apparatus shown in the preceding picture consists of:

A. Gas indicator bubbling bottles, to indicate the flow of hydrocarbon gas and oxygen or air in the apparatus.

B. Mixing chamber for gases before going to the reaction chamber.

C. Reaction chamber. The water electrodes, between which the electrical spark jumps, serve as temperature stabilizers for the reaction chamber.

D. Condensation chamber. This contains a small cup to catch the drip liquid from the reaction chamber and the condensation proper, which is cooled by an ice-brine mixture.

E. Expansion chamber. The purpose of this chamber is to prevent the water of the scrubbing tower from being sucked back into the condensation chamber.

F. Scrubbing tower, which is used to remove soluble products from the exhaust gas.

G. Water reservoir. This is to supply circulation of water for the inner electrode of the electrical discharge reaction chamber.

H. Source of high voltage current, a 110- 15,000-volt transformer.

OPERATION OF THE APPARATUS

The operation of the above-mentioned apparatus may be briefly described as follows:

1. Air is turned on, and the apparatus is completely swept out. Then the air is adjusted at the desired bubble rate.
2. The current is turned on the transformer by a conveniently arranged control switch.
3. The gas is turned on and adjusted properly; usually about one-fifth the rate of the air, or the same rate of oxygen when it is used instead of air.

Before the apparatus is started, the ice-brine bath should be prepared and put in place, and all joints tested to make sure that they are secure.

There is enough water in the outer electrode (if put in while cool) to keep the outer side of the reaction chamber cool for three or four hours. The water in the inner electrode circulates, by the force of gravity, to and from the reservoir tank; thus keeping the inner side of the reaction chamber cool. If the reaction chamber is allowed to become hot, frequent explosions take place within the apparatus, and brown deposits are formed faster on the walls of the reaction chamber. The reaction chamber should be thoroughly cleaned after each run.

CHEMICALS USED

Propane and butane were used as a mixture of the two hydrocarbons. This was done because of the convenient and abundant supply of the gas- pyrofax, the gas in the laboratory gas line. Pyrofax is the trade name of a fuel gas put on the market by Carbide and Carbon Chemicals Corporation. It is supposed to contain about 97 percent normal propane, 3 percent butane and a trace of ethyl mercaptan to give the gas an odor.

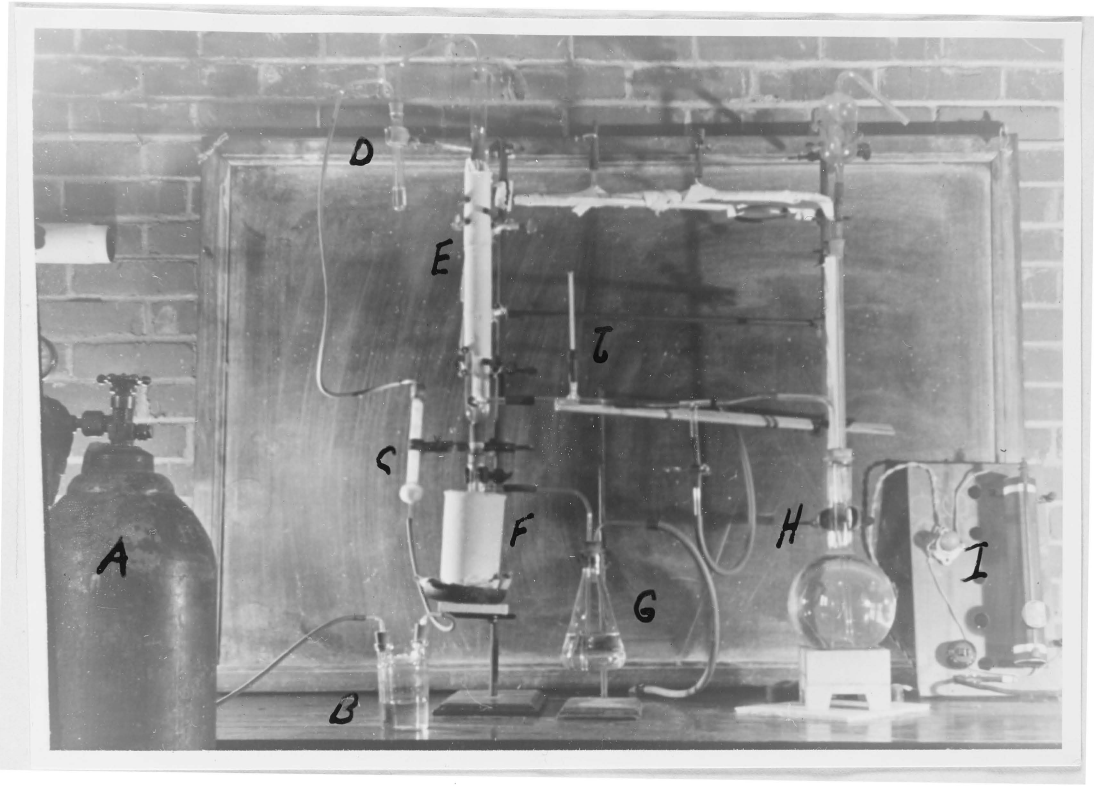
OXYGEN USED

The oxygen used was from a regular pressure tank of ogygen obtained from Air Reduction Sales Company.

AIR

The air used came from the compressed air line in the laboratory.

The following apparatus was used to oxidize acetaldehyde and butyraldehyde, in the vapor phase, with oxygen and air.



The apparatus, as shown in the preceding picture, consists of:

A. Oxygen tank for oxygen supply. When air was used instead of oxygen, the compressed air line was the source of air.

B. Indicator bubbling bottle, through which oxygen or air (when the latter was used) was bubbled to indicate the rate of flow.

C. Filter for removing large particles of moisture.

D. Aldehyde container, from which the aldehyde vapors were constantly carried off by oxygen or air.

E. Reaction chamber. This chamber was kept at a temperature of 75-85°C by a gravity circulating system of hot water.

F. Condensation chamber, cooled by an ice-brine bath.

G. Scrubbing tower to remove soluble components of the discharge gas.

H. The water heating unit, which furnishes the hot water for the gravity circulating system. The hottest water goes up the tube and into the top of the water jacket, aorund the reaction chamber; while the cooler water comes from the bottom of the water jacket and is taken to the bottom of boiler flask. A third tube leading straight up from the boiler flask to a trap bulb, takes care of the expansion of the water.

I. Control board, consisting of switch, rheostat and pilot light, to control the amount of current going to the hot plate under the boiler flask.

J. Thermometer, with which to read the temperature of the water coming from the water jacket of the reaction chamber

OPERATION OF THE APPARATUS

The apparatus mentioned above is operated as follows:

1. The current is turned on the hot plate. After the system has become hot, the rheostat is adjusted so that the water in the boiler flask just does not boil.

2. The ice-brine mixture is put in the condenser system

3. Aldehyde is put in the aldehyde container. The gas tube is adjusted so that the incoming air or oxygen is about one-half inch above the surface of the liquid.

4. The tubing is attached and the air or the oxygen is turned on. The valve is so adjusted that the bubble rate is about 140 bubbles per minute from a 0.4-m.m. glass tube

The apparatus may run for several hours or even longer if necessary. Usually the amount of aldehyde which is put in will last for about three hours

The reaction chamber is washed and dried after it has been used each day. It may be easily washed with hot water while it is still hot, and dried by putting air through the chamber with a suction pump.

CHEMICALS USED

The chemical used was acetaldehyde from Will Corporation; N-butyraldehyde (practical), from Eastman Kodak Company.

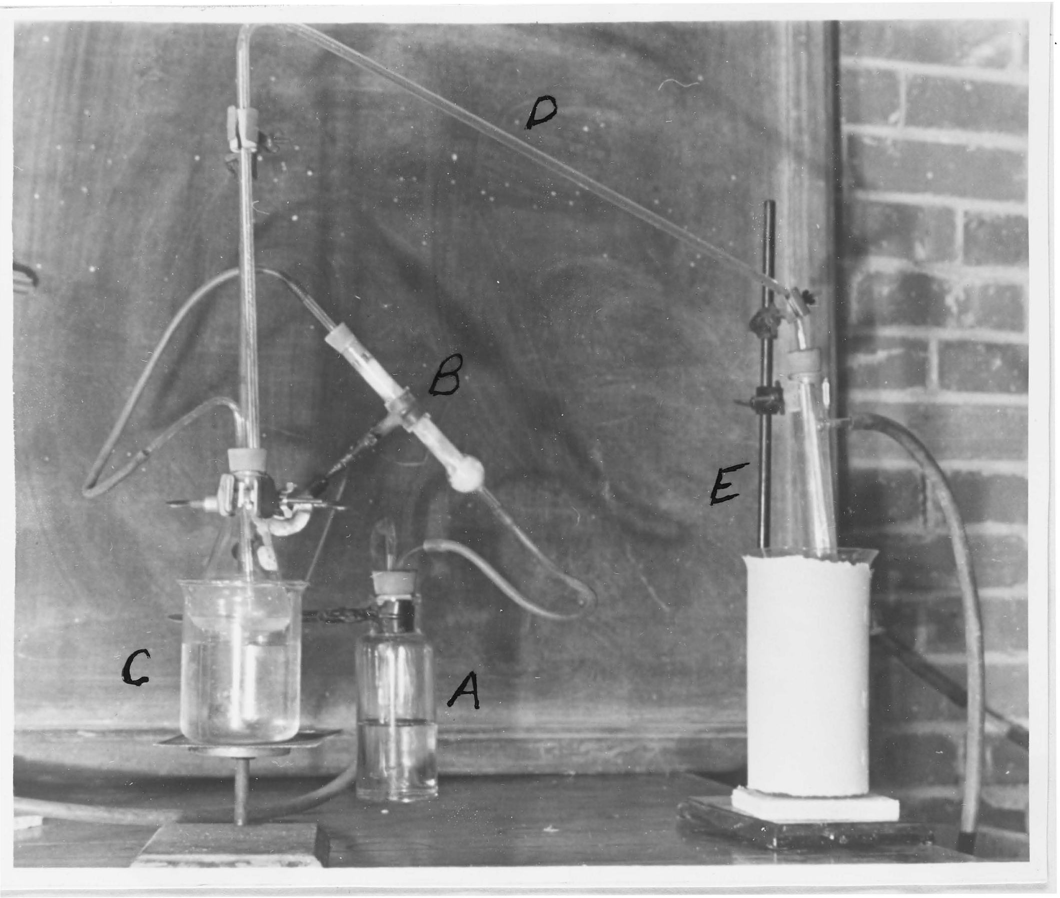
OXYGEN USED

The oxygen used was the same as that previously mentioned.

AIR USED

The air used came from the laboratory compressed air line.

The following apparatus was used to oxidize heptaldehyde in the vapor phase, with oxygen and air:



Due to the nature of heptaldehyde (b.p. 155 C), this apparatus was found to be more satisfactory for conducting the vapor phase oxidation, than was the apparatus used for acetaldehyde and butyraldehyde.

The apparatus, as shown on the preceding page, consists of the following parts:

A. Indicator bubbling bottle.

B. Filter.

C. Aldehyde container flask, heated by a beaker of boiling water.

D. Reaction tube. The oxidation reaction continues while the chemical is in the tube.

E. Condensation chamber, cooled by ice water.

OPERATION OF THE APPARATUS

The following steps describe in brief the operation of the forementioned apparatus:

1. Water in the beaker (D) is heated to boiling, and the ice and water are out in the container (E).

2. Tube joints are checked, both the intake and discharge tubes.

3. Air, or oxygen, is turned on, and the valve is adjusted to the bubble rate of about 140 bubbles per minute from a 0.4-m.m. glass tube.

CHEMICALS USED

The chemical used in this operation was heptaldehyde (technical), procured from Eastman Kodak Company.

OXYGEN AND AIR

Both the oxygen and **air** used in this operation were obtained in the same way as that for the preceding experiment.

ANALYSIS OF THE PRODUCTS OBTAINED FROM THE OXIDATION OF PROPANE AND BUTANE

The liquid collected in the cup just below the reaction chamber, we shall call "A", is composed of the liquid compounds which form in the chamber and drip into this cup. "A" has a very sharp odor, a straw color, and somewhat resembles a very light machine oil. It is soluble in water, acetone, sodium carbonate solution and dilute acid solution. It is soluble in concentrated sulfuric acid, and after a moment a reaction takes place, giving a brown color to the solution. Upon standing, "A" slowly gives off a gas and the straw color gradually deepens. When a portion of it is evaporated to dryness, a brown resinous substance is left. This substance is soluble in water and acetone, but insoluble in ether. "A" does not add bromine in a carbon tetrachloride solution, is oxidized by alkali potassium permanganate solution, gives a positive iodoform test, does not give a visible and characteristic reaction with a saturated solution of sodium bisulfite, and gives a strong positive test with the Fuchsin-aldehyde reagent and the fehling solution reagent. It does not give a precipitate with a clear saturated solution of lime water. It liberates iodine from an acid potassium iodide solution immediately. "A" contains an acid or a mixture of acids and a sample, when titrated with 0.1 normal sodium hydroxide solution, using phenolphthalin as an indicator, is found to contain 16.3 percent acid which reported as acetic acid. "A" contains peroxides, since it gives a strong positive test for peroxides when a freshly prepared solution is tested with titanium sulfate. A solution of "A", after standing for a while, does not give the peroxide test with titanium sulfate.

The liquid collected in the condensation chamber, we shall call "B", is composed of the liquids condensed from the gas which comes from the reaction chamber. It is a clear, colorless watery liquid with a sharp aldehyde odor. The solubility of "B" is about the same as that of "A", with the exception that the reaction with concentrated sulfuric acid after solution is not as great. "B" does not leave a brown residue upon evaporation to dryness as does "A". This liquid "B" reacts with: bromine in tetrachloride, alkali potassium permanganate, sodium bisulfite, fuchsin aldehyde reagent, fehling solution, saturated solution of lime-water, and potassium iodide solution about the same as does the "A" liquid. "B" contains an acid as does "A", but when a sample of "B" was titrated against 0.1 normal solution hydroxide, using phenolphthalin as an indicator, it was found to contain only 4.3 per cent acid reported as acetic acid. "B" contains peroxides, as indicated by the titanium sulfate test; but not as much as does "A". Upon standing, the peroxides in "B" decompose; thus a solution of "B" which has been standing for a while, does not give the titanium sulfate peroxide test. When determined by distillation, the boiling points of the components of "B" range from approximately 45°C up to and above 100° C.

The Use of Oxygen and Air: There was no marked difference upon the products "A" and "B" when oxygen was used in place of air in the oxidation process. The air-pyrofax gas ratio was 5 to 1, while the oxygen-pyrofax gas ratio was 1 to 1.

The discharge gas scrub water gives a positive test with fuchsin aldehyde reagent, indicating the presence of aldehydes. The sodium hydroxide test for acetaldehyde indicates the presence of traces of acetaldehyde, by titrating for acid, as was done for "A" and "B", a sample of the scrub water was found to contain 0.1 percent acid.

PARTIAL ANALYSIS OF THE PRODUCTS OBTAINED FROM THE VAPOR PHASE OXIDATION OF ACETALDEHYDE, BUTYRALDEHYDE AND HEPTALDEHYDE

A. When acetaldehyde was oxidized, as previously described, both with air and with oxygen, the following results were obtained: The product was a clear, colorless solution, with a sharp aldehyde acid odor, very soluble in water and giving an acid reaction with litmus. It immediately liberates iodine from an acid potassium iodide solution, and it gives a positive peroxide test with titanium sulfate solution. If the product is allowed to stand for several hours at room temperature before testing, the peroxide test is negative. But if the solution is kept on an ice-brine mixture, the peroxide will remain for a much longer period of time. The residue acetaldehyde solution has a light straw color, is acid to litmus, contains clear small needle shaped crystals, immediately liberates iodine from a potassium iodide solution, and gives a strong positive test for peroxides with titanium sulfate solution. The peroxide in the residue aldehyde solution is much more stable than the peroxide solution of the condensed product. It will remain for at least 48 hours.

B. When butyraldehyde was oxidized, as previously described, both with air and with oxygen, the following results were obtained: The condensed product resembled the pure butyraldehyde very closely in physical characteristics. It is acid to litmus and liberates iodine from potassium iodide solution, but it does not give a positive test for peroxides with titanium sulfate. The residue aldehyde is acid to litmus, liberates iodine from a potassium iodide solution; nut does not give a positive test for peroxides with titanium sulfate.

C. When heptaldehyde was oxidized, as previously described, both with air and with oxygen, the following results were obtained: The condensed product resembled the oxidized aldehyde with the exception of a stronger and sharper odor. It is acid to litmus, liberates iodine from potassium iodide solution, gives the positive test for, peroxides with titanium sulfate solution. The residue aldehyde contains a small amount of white precipitate, is acid to litmus, liberates iodine from a potassium iodide solution, and gives a strong positive test for peroxides with titanium sulfate solution. This peroxide is reasonably stable and remains in the residue aldehyde solution for several days.

CONCLUSIONS.

When propane and butane (pyrofax) are oxidized in the vapor phase with oxygen and air in the presence of an electrical discharge, acids, aldehydes, peroxides, and a highly polymerized substance are found among the products. The peroxide is unstable at room temperature, but is reasonably stable at 0°C. Either oxygen or air may be used in the oxidation process with apparently the same results, so long as the actual oxygen-hydrocarbon ratio is 1 to 1.

The next step is to isolate and to identify the peroxide and then to determine whether the peroxide is a primary or a secondary product.

Upon oxidation with air or oxygen, acetaldehyde, bytyraldehyde and heptaldehyde give a peroxide as one of the oxidation products. These peroxides are unstable at room temperature; but are rather stable when kept in an ice-brine bath. The peroxide of heptaldehyde is the most stable of the group.

The next step is to isolate and to identify the peroxides, and to determine the mechanism by which they are formed.

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