WAR RESEARCH PROJECTS

A. Combustion of Hydrocarbons and the Pollution of the Atmosphere to Render Automotive Equipment Inactive.

B. Synthesis of Divinyl Sulfide from Acetylene.

by

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This thesis is submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Master of Science.

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FOREWORD

This thesis is essentially a report on the work done on War Research projects during the past year. It consists of two parts:

A. The Combustion of Hydrocarbons and Pollution of the Atmosphere to Render Automotive Equipment Inactive.

B. The Synthesis of Divinyl Sulfide from Acetylene.

Work was started during the fall of 1939 on the Oxidation of Hydrocarbon - Alcohol mixtures, but was early discontinued in favor of a war research project, the Synthesis of Divinyl Sulfide. This problem developed into a long time project and was temporarily abandoned in favor of the problem on the Combustion of Hydrocarbons and Pollution of the Atmosphere to Render Automotive Equipment Inactive.

M.Sc. Chemistry.

JAMES D. B. OGILVIE

WAR RESEARCH PROJECTS

PART A.

Pollution of Atmosphere to Render Automotive Equipment Inactive.

Some 197 compounds were tested to determine whether they would cause knocking when added to the air intake of a 1933 Chevrolet engine. Those which were found to cause knocking were examined semi-quantitatively using the audibility of knock as the criteria of effectiveness. Chloropicrin was found to cause slight knock at a concentration of three parts per million of air. Other compounds found effective in concentrations less than one part in 2000 were: iso-amyl nitrite, t butyl nitrite, n butyl nitrite, ethyl nitrate, t butyl nitrate, acetoacetic ester and thionyl chloride.

PART B.

Synthesis of Mustard Gas from Acetylene.

The reaction of hydrogen sulfide and acetylene was carried out homogeneously in the gas phase and over an alumina catalyst at various temperatures. Complex liquid products were obtained but the presence of divinyl sulfide was not definitely established. The reaction between ethylene dichloride and hydrogen sulfide did not appear to be appreciable. The problem was discontinued in favor of other research since it did not appear to be of practical value.

PART A.

Combustion of Hydrocarbons and Pollution of the Atmosphere to Render Automotive Equipment Inactive.

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INTRODUCTION.

It is known that the combustion of hydrocarbons with oxygen or air, as well as decomposition may be inhibited or accelerated by the addition of relatively small amounts of foreign substances. Such substances as mercury dimethyl and lead tetra ethyl inhibit the oxidation of hydrocarbons; others like nitrogen peroxide and isoamyl nitrite accelerate the oxidation. In internal combustion engines similar phenomena occur. There are anti-knock compounds, which inhibit the early phases of combustion at low temperatures and pro-knock compounds which promote this oxidation and cause the phenomenon of knock, which will be discussed later.

It seems possible that such phenomena could be made use of to render automotive equipment inactive. The accelerators or pro-knock compounds would act by overheating the engine parts and destroying the bearings; the inhibitors by choking or stalling the engine.

In the past, the addition of anti-knock and pro-knock compounds has been made to the fuel. It seems that similar effects should result if they were introduced into the cylinder in the air stream.

If the air could be polluted with a sufficient concentration of pro- or anti-knock compounds, it is possible that aeroplanes, tanks, or other automotive equipment could be rendered inactive by passing through an area so treated.

It is the purpose of this investigation to determine the concentration in the air, of various compounds, necessary to render the equipment inactive. Only pro-knock compounds have been considered to date. However the effect of combustion inhibitors as well as abrasive smokes, and gum-forming accelerators is to be investigated at some future time.

A brief review of the mechanisms of the combustion of hydrocarbons is essential as an introduction and explanation of this work.

COMBUSTION OF HYDROCARBONS

I. Chemical Phenomena Associated with Combustion

During the nineteenth century the greater part of the research on hydrocarbon combustion was done, principally with a view to determining whether one or other of the elements constituting the hydrocarbon molecule burned preferentially.

Bone and his collaborators (1) (2) showed that a whole series of intermediate compounds are formed during combustion. It was then realized that hydrocarbon combustion was a reaction of considerable complexity. A consideration of the equation:

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$$

shows that the probability of one propane molecule colliding with five of oxygen is vanishingly small. Thus a series of intermediate reactions is expected.

The obvious method of approaching a complete understanding of the combustion is to attempt to isolate the intermediate products by suddenly chilling the reaction mixture at various stages of the reaction. This information must be supplemented by various physico-chemical studies as the intermediate compounds of great importance are not stable enough to permit their isolation. Use has been made of the kinetics of the reaction and of the significance of such phenomena as chemiluminescence, the induction period, wall effects, and the effect of positive and negative catalysts.

By chemical analysis of intermediate products, such substances as alcohols, aldehydes, organic peroxides, ethylene oxide, etc., have been isolated as well as the oxides of carbon, hydrogen, and the lower hydrocarbons. A theory of combustion has been built up entirely from these results by Bone and his associates.
This will be discussed later (3).

A study of the kinetics of the reaction shows:

(a) Practically all combustion reactions take place by a chain mechanism.

(b) Increasing the fuel concentration has greater effect on rate than increased oxygen concentration, so propagation of chains seems to be with chain carrier and fuel molecule.

(c) There is evidence that chains are initiated at the walls.

(d) Increase of surface slows the reaction down.

(e) The temperature coefficient indicates that a very complicated sequence of events is involved in the chain. The higher hydrocarbons undergo different kinds of combustion at different temperatures.

(f) Combustion, with the possible exception of that of the more unsaturated hydrocarbons, is auto-catalytic.

(g) The chain carriers are probably too short-lived to be isolated. (3).

A study of the chemiluminescence occurring below the ignition point of hydrocarbons indicates that some very active molecule or radicals are produced, such as $\equiv$ CH, -OH, etc., spectroscopic studies of the luminescence indicate the presence of aldehydes, ethers and similar compounds which may be identified.

An induction period occurs in practically all combustion reactions. No appreciable reaction is shown by analysis but the mixture must be sensitized in some way during this period.

Combustion reactions are very susceptible to action of positive and negative catalysts. Negative catalysts (anti-knock) prevent slow combustion prior to the arrival of the flame and positive catalysts (pro-knock) greatly facilitate combustion.

A. Combustion Characteristics of Typical Mixtures (2)

1. H_2 and CO - Each of these is a very simple case. For Hydrogen, water and H_2O_2 are the only inter-

mediates which have been isolated. There is abundant evidence of a chain mechanism, and no chemiluminescence is observed. With carbon monoxide there is no slow combustion before 600°C. i.e. CO is a stable intermediate in the low temperature region. The slow combustion shows chemiluminescence.

2. Paraffins - In accordance with what has been said about the two regions of combustion of higher hydrocarbons, the paraffins are conveniently classified into methane and ethane, propane as an intermediate, and those from butane up.

The products isolated in the slow combustion of methane and ethane are: aldehydes, acids, oxides of carbon, and steam. Alcohols are also formed at high pressures (1-14). These are predictable from Bones' hydroxylation theory.

Propane also yields alcohols at high pressures and aldehydes, alcohols, acids, etc. at ordinary pressures. Under suitable conditions, however, organic peroxides are formed, and also propene. Excess fuel catalyses the reaction while excess oxygen or diluents, e.g. nitrogen, cause retardation. No marked chemiluminescence occurs.

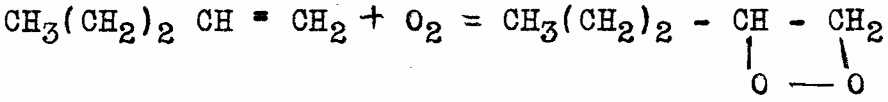
The higher paraffins from butane upwards show two characteristic modes of ignition. The reactions are very difficult to investigate chemically since the large number of possible intermediates, as would for instance occur in successive hydroxylations, are difficult to interpret and apply to any theory. This is somewhat simplified by the fact that it is the end methyl group on the longest chain which reacts first.

The slow oxidation of hexane at 300° yields aldehydes, chiefly formaldehyde, and peroxides with the reaction of alcoxy peroxides ($ROO-CH_2OH$).

The kinetics of both pentane and hexane have been investigated. Owing to the complicated molecules involved, interpretation of rate of pressure rise, etc. in terms of any specific mechanism is difficult. For pentane, heated at a steady rate from 210°C. an induction period is observed. An increase of pressure results in corresponding increase in rate. The concentration of pentane to oxygen is 1:1 for optimum rate. The addition of an inert gas increases the velocity and lowers the temperature of combustion. Increased concentration of fuel has greater effect on rate than corresponding increases in oxygen concentration.

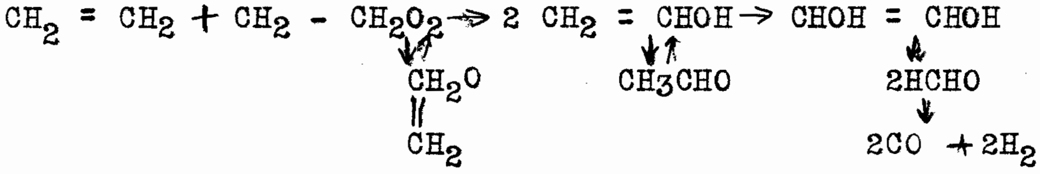
All of the higher hydrocarbons show chemiluminescence to a marked degree. Anti knocks inhibit the oxidation at low temperature.

3. Olefines - The combustion of olefines is much better understood owing to the greater certainty about the primary step. Amylene, by merely bubbling oxygen through it at room temperature, reacts as follows:



$$\begin{tikzcd}[column sep=small] CH_3(CH_2)_2\ CH = CH_2 + O_2 = CH_3(CH_2)_2 - & CH \arrow[d, no head] & - & CH_2 \arrow[d, no head] \\ & O & \text{—} & O \end{tikzcd}$$

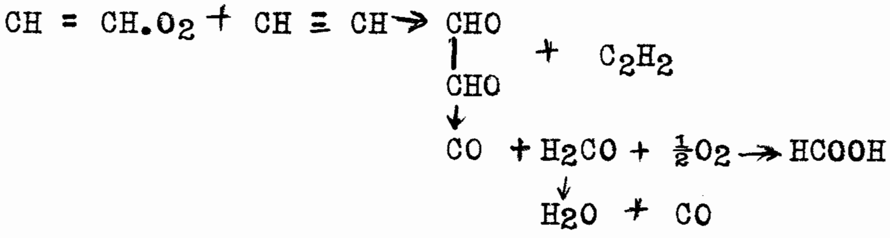
At higher temperatures the marked pressure drop, which occurs at first, is due to formation of a peroxide similar to the above. This peroxide, on collision with a second fuel molecule, decomposes:



$$\begin{tikzcd} CH_2 = CH_2 + CH_2 - CH_2O_2 \arrow[r] \arrow[d, shift right] & 2\ CH_2 = CHOH \arrow[r] \arrow[d, shift right] & CHOH = CHOH \arrow[d] \\ CH_2O \arrow[u, shift right] \arrow[d, equal] & CH_3CHO \arrow[u, shift right] & 2HCHO \arrow[d] \\ CH_2 & & 2CO + 2H_2 \end{tikzcd}$$

Olefines also show an induction period. The absence of strong chemiluminescence and the relatively small influence of aldehydes added to the combustion mixture suggests an oxidation mechanism differing from that for the paraffins. This difference is important for it renders improbable the theory of hydrocarbon oxidation that all paraffins lose hydrogen and become unsaturated.

4. Acetylenes - Glyoxal is readily isolated in the oxidation of acetylenes. The rate of the oxidation is proportional to the square of the glyoxal concentration and is independent of the oxygen concentration. This supports the scheme



$$\begin{array}{llll} \mathrm{CH = CH.O_2} + \mathrm{CH \equiv CH} \rightarrow & \mathrm{CHO} & & \\ & | & + \mathrm{C_2H_2} & \\ & \mathrm{CHO} & & \\ & \downarrow & & \\ & \mathrm{CO} & + \mathrm{H_2CO} & + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{HCOOH} \\ & & \downarrow & \\ & & \mathrm{H_2O} + \mathrm{CO} & \end{array}$$

The formation of peroxides has also been reported.

5. Alcohols - The oxidation of these early intermediates in hydrocarbon combustion is of considerable theoretical importance. With regard to alcohols the general evidence is that they do not accelerate the combustion of hydrocarbons at low temperatures when mixtures are used. The oxidation products are probably the same as for paraffins at higher temperatures except that no peroxides have been isolated even with higher alcohols.

6. Aldehydes - The oxidation of aldehydes is of great importance since the addition of aldehydes to combustion mixtures reduces the induction period considerably, and increases the rate of reaction. The effect of anti knocks on aldehydes is the same as on paraffins. Aldehydes also show chemiluminescence spectroscopically identical with that for the paraffins. The kinetics of aldehyde oxidation definitely show a chain mechanism. Acids and per acids are the chief oxidation products.

B. The Oxidation of the Lower Hydrocarbons

(a) Slow Combustion (1,2,4)

A slightly more extended study of the oxidation of the lower hydrocarbons seems advisable since it is mainly from the study of these reactions that the various theories of combustion have been built up. In addition the theories will be much more readily understandable after consideration of these simple oxidation reactions.

1. Methane - At atmospheric pressure, slow oxidation begins at a temperature of about 420 C. The products are oxides of carbon, water and small amounts of formaldehyde, and formic acid. There is a well

defined induction period followed by rapid reaction. The most reactive mixture is 2:1 hydrocarbon to oxygen. Increased pressure or temperature shortens the induction period and increases the rate of reaction. Thy hydrocarbon concentration affects the combustion much more than the oxygen concentration. Increasing the surface retards the reaction. Addition of a trace of formaldehyde or other intermediates greatly reduces induction period and increases the rate.

At low pressures the reaction can be followed at much higher velocities. There is an induction period and then an abrupt inflammation. There are three explosion limits.

At high pressures the reaction is much the same except that considerable quantities of methanol may be isolated.

2. Ethane - At atmospheric pressure, as with methane, the most reactive mixture is a ratio of ethane to oxygen of 2:1. Addition of acetaldehyde or formaldehyde increases the rate considerably. Products are acetaldehyde, formaldehyde, formic acid, a

a peroxide or per acid, oxides of carbon, and steam. During the induction period very little oxygen is used and no intermediate products are detectable. Aldehydes and peroxides appear together. There is no separation of carbon or hydrogen. Carbon, hydrogen and oxygen balances indicate C_2H_6O or some less oxygenated ethane is present, and that fact that it accumulates as oxygen is used up suggests it is a primary product.

At high pressures, ethane, methanol and acetic acid are found.

3. Ethylene - At atmospheric pressure the products which may be isolated are ethylene oxide, acetaldehyde, formaldehyde, a peroxide, oxides of carbon, steam and in special circumstances glyoxal, and dioxy methyl peroxide. The 2:1 ratio of hydrocarbon to oxygen is again the most reactive. The rate is also dependent much more on the ethylene concentration than on the oxygen. The addition of third substances has an effect also: nitric oxide eliminates the induction period, ethylene oxide reduces it slightly,

acetaldehyde and formaldehyde have little effect. A material balance indicates presence of C_2H_4O isomers, as oxygen is used up. Formaldehyde and formic acid reach a maximum before the pressure rise ends and peroxide formation follows accumulation of formaldehyde. The pressure decreases as the reaction nears completion, when the primary product is accumulating. This suggests that the formation of the latter involves a decrease in volume.

4. Acetylene - Acetylene - oxygen mixtures interact at temperatures from 250°C up; formaldehyde and carbon monoxide form simulatneously at an early stage, probably as a result of the decomposition of unstable $C_2H_2O_2$. Formic acid, carbon dioxide, steam and a trace of acetaldehyde are also found in the products. Glyoxal is also reported. There is an induction period. The rate is accelerated by excess acetylene, retarded by excess oxygen.

(b) Explosive Combustion (4)

Under the more drastic conditions of explosive combustion, secondary thermal decomposition of the intermediate products come into play at an earlier stage and play a more conspicuous part in the combustion. Here, on account of the complexities we can only account for the main happenings in a general way. A brief discussion of the thermal decomposition of alcohols and aldehydes is necessary since these intermediate products will decompose at the high temperatures of explosive combustion. Their modes of decomposition may vary with temperature and at the increased temperatures of flames show wide differences as the composition of the explosive mixture is near one or other of the explosion limits. The extent of such decompositions depends upon the pressure, a fact which may greatly influence the course and temperature of the combustion.

At low temperatures alcohols decompose to steam and an unsaturated hydrocarbon; at higher temperatures to hydrogen and the corresponding aldehydes. In intermediate ranges both may occur and also secondary decompositions may result. For example, the decomposition of ethanol may occur:

(1) $C_2H_5OH \Rightarrow C_2H_4 + H_2O \rightarrow C_2H_2 \quad H_2$ and/or $2C + 2H_2$

(2) $"\quad \rightarrow H_2 + CH_3CHO \rightarrow CH_4 + CO$ and/or $C \quad 2H_2 + CO$

Between 400 - 600 C. aldehydes with one CHO group and one or more other carbon atoms gives carbon monoxide and a saturated hydrocarbon, i.e. for acetaldehyde

$$CH_3CHO \longrightarrow CH_4 + CO.$$

At higher temperatures carbon, hydrogen and carbon monoxide result. Formaldehyde decomposes to carbon monoxide and hydrogen at all temperatures in this range. Glyoxal decomposes at all temperatures to carbon monoxide and formaldehyde and eventually to carbon monoxide and hydrogen. Bearing this in mind the following features of explosive combustion are clear:

1. Methane - No separation of carbon or hydrogen occurs. Steam is formed, and no change in volume occurs.

2. Ethane - In this case a considerable deposit of carbon occurs and considerable condensation of water on cooling. There is a 50% increase in pressure. Analysis shows oxides of carbon, hydrocarbons, hydrogen, as well as the carbon deposit, and steam, as products.

3. Ethylene and Acetylene - No carbon deposition occurs. Products are similar to other cases, varying only in proportions. For ethylene the pressure is doubled, for acetylene increases 50%.

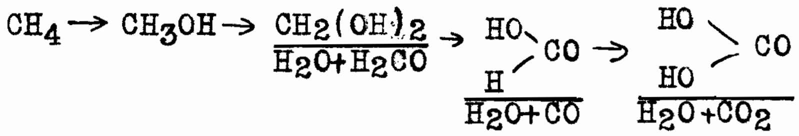
C. Theories of Hydrocarbon Combustion

(a) Hydroxylation Theory (1,2,4)

This theory was first introduced by Armstrong in 1874 and later developed by Bone 1898-1902. It presumes the oxidation to proceed by successive hydroxylations of the hydrocarbon molecule, followed by decomposition of these hydroxylated molecules. It is based largely on chemical analysis of the products, and does not postulate the existence of any compound capable of independent existence which cannot be isolated or identified.

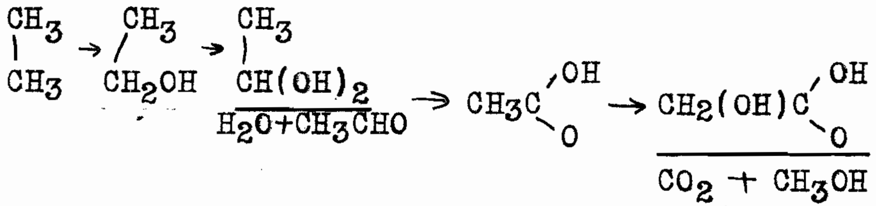
For the slow oxidation of the simple hydrocarbons, schemes are as follows:

(1) Methane



$$CH_4 \rightarrow CH_3OH \rightarrow \dfrac{CH_2(OH)_2}{H_2O+H_2CO} \rightarrow \dfrac{\begin{matrix}HO\diagdown\\ H\diagup\end{matrix}CO}{H_2O+CO} \rightarrow \dfrac{\begin{matrix}HO\diagdown\\ HO\diagup\end{matrix}CO}{H_2O+CO_2}$$

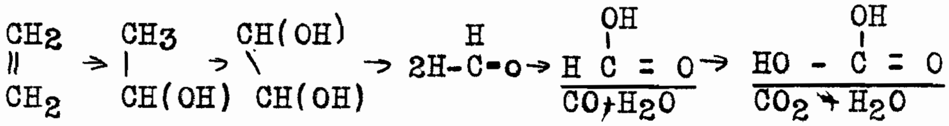
(2) Ethane



$$\begin{matrix}CH_3\\ |\\ CH_3\end{matrix} \rightarrow \begin{matrix}CH_3\\ /\\ CH_2OH\end{matrix} \rightarrow \dfrac{\begin{matrix}CH_3\\ |\\ CH(OH)_2\end{matrix}}{H_2O+CH_3CHO} \rightarrow CH_3C\begin{matrix}\diagup OH\\ \diagdown O\end{matrix} \rightarrow \dfrac{CH_2(OH)C\begin{matrix}\diagup OH\\ \diagdown O\end{matrix}}{CO_2 + CH_3OH}$$

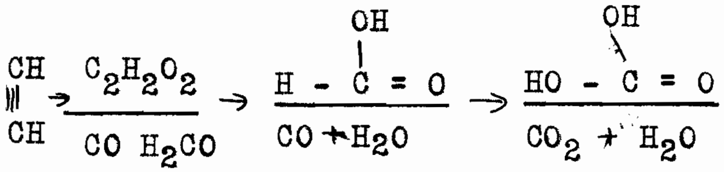
(see methane)

(3) Ethylene



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \rightarrow \begin{matrix}CH_3\\ |\\ CH(OH)\end{matrix} \rightarrow \begin{matrix}CH(OH)\\ \backslash\\ CH(OH)\end{matrix} \rightarrow 2H\text{-}\overset{H}{C}\text{=}o \rightarrow \dfrac{H\ \overset{OH}{\overset{|}{C}} = O}{CO+H_2O} \rightarrow \dfrac{HO - \overset{OH}{\overset{|}{C}} = O}{CO_2+H_2O}$$

(4) Acetylene



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} \rightarrow \dfrac{C_2H_2O_2}{CO\ \ H_2CO} \rightarrow \dfrac{H - \overset{OH}{\overset{|}{C}} = O}{CO+H_2O} \rightarrow \dfrac{HO - \overset{OH}{\overset{\backslash}{C}} = O}{CO_2+H_2O}$$

Except in the case of acetylene, the initial product is always an alcohol; then an unstable dihydroxy compound is formed which decomposes into water and an aldehyde. The aldehyde then yields a lower aldehyde or an acid and finally further hydroxylation of the acid and the subsequent breakdown of this product occurs. Secondary reactions arising from thermal decompositions, condensations or interactions of the intermediates may give rise to a variety of substances including lower hydrocarbons, peracids, free carbon and hydrogen.

This theory explains very satisfactorily the products which may be isolated during hydrocarbon combustion. It accounts for these from slow combustion and in a general way even in explosive combustion. Alcohols are not readily obtained at atmospheric pressure but can be isolated in large quantities at high pressure.

The theory does not specify any mechanism of initial oxygen attack. Indeed, the formation of the initial hydroxylated molecule would involve a ternary collision, which is very unlikely. It does not account for the initial induction period which occurs.

(b) Peroxidation Theory (4)

In view of the fact that peroxides occur during combustion, the suggestion has been made that the initial product of the combustion of a hydrocarbon is an alkyl peroxide or alkyl hydrogen peroxide. According to his view the oxidation of methane, for example, would proceed as follows:

$$CH_4 + O_2 \rightarrow CH_4(O_2) \quad \text{or} \quad CH_3O\text{-}O\text{-}H$$

$$CH_4(O_2) \rightarrow HCHO + H_2O$$

The formation of methanol at high pressures could result from the autoxidation of methane by its peroxide or by intramolecular change

$$CH_4(O_2) + CH_4 \rightarrow \begin{array}{l} 2\ CH_3OH \\ CH_4(O_2)_{CH_4} \rightarrow 2CH_3OH \end{array}$$

Alkyl peroxides are usually unstable endothermic liquids which readily explode giving a mixture of alcohols, aldehydes and fatty acids, and since their decomposition might give rise to oxygen atoms there is no difficulty in postulating a chain mechanism based on their initial formation and subsequent decomposition.

The induction period may be accounted for by assuming that, during the first stages of the oxidation, reaction only occurs at the walls, since surface has such a marked effect on the induction period.

The unstable peroxide, when first formed may revert to normal state and form a stable peroxide, or it may rearrange and give highly active products, i.e. for ethane

$$CH_3 - CH_3 + O_2 \rightarrow CH_3\ CH_3\ O_2 \rightarrow CH_3CHO + H_2O$$

The peroxide might also collide with a fairly active fuel molecule and react, producing active products. These products may in turn collide and activate other fuel molecules, setting up a reaction chain mechanism. The active aldehyde formed is assumed able to communicate their energy to activate other ethane molecules, and so on.

This theory explains the formation of aldehydes and a very active pro knock (which is not an aldehyde peroxide) very early in the combustion. It also explains, since the intermediate moloxide is unstable, why practically all hydrocarbons require a collision with a second fuel molecule for the reaction to proceed. It explains how combustion is totally inhibited by anti-knocks and does not even proceed to the aldehyde stage.

The peroxides isolated by Mondain Monvall and Quanquin, however, have only a very mild pro-knock activity, whereas the alkyl peroxides have considerable pro-knock activity.

(c) Atomic Chain Theory (4)

The atomic chain theory postulated by Norrish differs from the above two theories in the first phase but agrees closely with the rest of the mechanism. The oxidation of a hydrocarbon molecule according to Norrish follows a simple chain mechanism involving a hydrocarbon radical and an oxygen atom.

For methane:

$$CH_4 + O \rightarrow CH_2 + H_2O$$

$$CH_2 + O_2 \rightarrow HCHO + O$$

This can continue until the chain is terminated by either

$$O + CH_4 + X \rightarrow CH_3OH + X^1$$

or $$O + \text{surface} \rightarrow \tfrac{1}{2} O_2$$

The oxygen atoms to start the chain are assumed to form by the production of formaldehyde through a surface reaction

$$CH_4 + O_2 \xrightarrow{\text{surface}} HCHO + H_2O$$

followed by $HCHO + O_2 \rightarrow (H_2CO_3) \rightarrow HCOOH + O$. Much of this atomic oxygen will remain adsorbed and ultimately recombine on the surface, the remainder passing out into the gas phase and generating reaction chains. The induction period would therefore be the time during which an equilibrium quantity of formaldehyde is being built up at the surface, and formaldehyde may be regarded as the initial product in the oxidation of methane.

The above equations illustrate the formation of methanol. Its formation may be expected to be most marked at high pressures and in high concentrations of inert gas.

For olefines, the corresponding mechanism would be

(1) Induction period

$$C_2H_4 + O_2 \rightarrow 2HCHO$$

$$HCHO + O_2 \rightarrow H\ COO\ H + O$$

(2) Reaction period

$$C_2H_4 + O \rightarrow H\ CHO + CH_2$$

$$CH_2 + O_2 \rightarrow HCHO + O$$

(3) Chains terminated by

$$O + C_2H_4 + X \rightarrow C_2H_4O + X^1$$

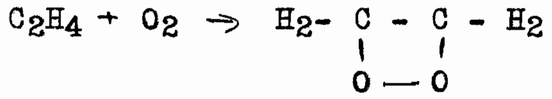
$$O + \xrightarrow{\text{surface}} \tfrac{1}{2}\ O_2$$

This theory postulates the propagation of reactivity by atoms and radicals, and not by an energy chain mechanism as in the peroxidation theory. It explains more clearly than the previous mechanism the kinetics of the reaction, and accounts for the induction period.

The presence of an inert gas should, according to this mechanism, increase the rate of combustion whereas the reverse is actually true. Again, at low temperatures the concentration of oxygen atoms would appear to be far too small for such a process to occur at all frequently in the gas phase. Neither is every collision with CH_4 and O efficient, so that further activation is required.

(d) Lewis Theory (4)

The first step in the oxidation of olefins is known with a fair degree of certainty to be

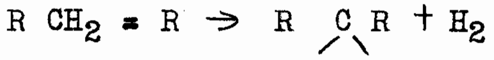


$$C_2H_4 + O_2 \rightarrow \begin{array}{l} H_2-C-C-H_2 \\ \qquad | \quad\;\; | \\ \qquad O - O \end{array}$$

This led Lewis and others to propose that the first step in the oxidation of a paraffin was reduction to the corresponding olefine:

$$RCH_2CH_3 \rightarrow R-CH = CH_2 + H_2$$

Berl and Winnaker modified this slightly and postulated:

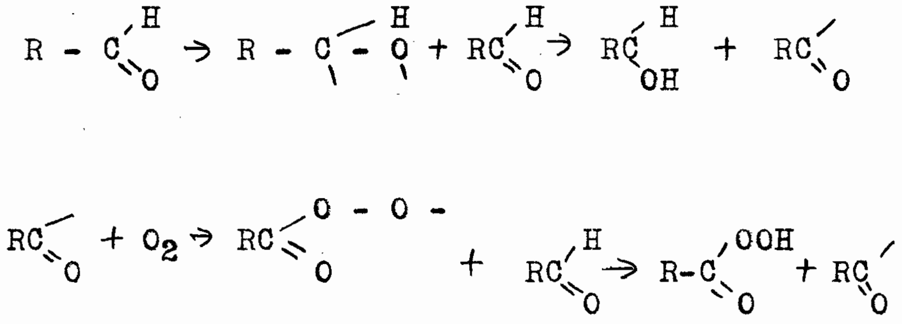


$$R\,CH_2 = R \rightarrow R\,\underset{/\ \backslash}{C}\,R + H_2$$

From the velocity at which carbon pyrolysis takes place and the energy required for the process of Berl and Winnaker both mechanisms seem unlikely in the low temperature region. Furthermore, the oxidation of olefines has been shown not to follow the same course as for paraffins, and no pro-knocks are formed so this hypothesis does not seem to meet all the facts. The occurrence of propene in the oxidation of propane may be due to the ending of a chain rather than the initial step.

(e) Ubbelohde's Theory (4)

The chain mechanism for paraffin hydrocarbons is probably closely bound up with that for aldehydes where the autoxidation is easier to study thermally or photochemically due to the much lower temperatures possible. According to Backstrom the chain mechanism for aldehyde oxidation is

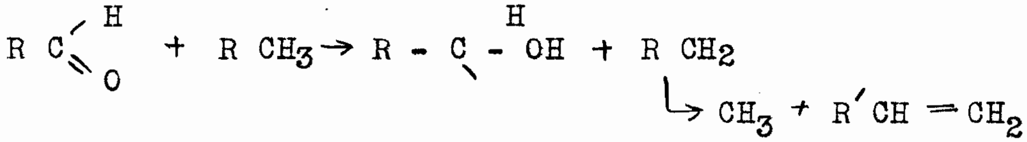


$$R-\underset{O}{\overset{H}{C}} \rightarrow R-C-\overset{H}{O} + R\underset{O}{\overset{H}{C}} \rightarrow R\underset{OH}{\overset{H}{C}} + R\underset{O}{C}$$

$$R\underset{O}{C} + O_2 \rightarrow R\underset{O}{\overset{O-O-}{C}} + R\underset{O}{\overset{H}{C}} \rightarrow R-\underset{O}{\overset{OOH}{C}} + R\underset{O}{C}$$

The chain carrier is essentially the $R-\underset{O}{C}$ radical. If the same radical is active in hydrocarbon oxidation the scheme might be:

I



$$R\underset{O}{\overset{H}{C}} + R\,CH_3 \rightarrow R-\overset{H}{C}-OH + R\,CH_2$$

$$\hookrightarrow CH_3 + R'CH=CH_2$$

II $R\,CH_2 + O_2 \rightarrow R\,CH_2\,.O_2$

$R\,CH_2\,.O_2 + R\,CH_3 \rightarrow R\,C\,H_2\,O\,O\,H + R\,C\,H_2$

$\downarrow$ $R\,C\,H\,O + H_2O$

$\hookrightarrow R\,CH_2O + OH + R\,CH_2$ (chain branching)

III $O\,H + R\,H \rightarrow R\,CH_2 + H_2O$

$R\,CH_2O + O_2 \rightarrow R\,O_2 + CH_2O$

This scheme has the advantage of explaining the following:

(1) The early appearance of formaldehyde and other aldehydes which act auto-catalytically.

(2) The appearance of a small amount of active pro-knock.

(3) Mechanism III of chain branching leading to ignition when conditions are suitable.

(4) The favorable effect of free alkyl radicals on combustion. Inhibitors probably stop the chain by colliding with R CH_2OO the product not being released again until it is oxidized.

II. Physico-Chemical Phenomena of Combustion

A. Inflammation

The combustion of hydrocarbons might occur in one of three ways depending on the conditions of temperature, pressure, composition of the mixture, and source of heat. It may occur slowly without the appearance of a flame as in the slow oxidation already discussed. At higher rates flame appears at which stage oxidation takes place fairly completely in a very short time. At still higher rates various other phenomena occur and in the limiting case, that of detonation, combustion takes place with exceedingly great rapidity and extreme violence.

(a) Ignition Phenomena (5)

At higher pressures the rate of reaction increases so rapidly that at a suitable temperature the heat of reaction can no longer be dissipated. In consequence, the conditions no longer remain isothermal and the reaction auto-accelerates, producing a very high temperature and the characteristic emission of light from fragments of molecules such as are present in flames. In the low pressure region the transition from slow combustion to ignition is much sharper owing to the fact that more chain carriers are produced than removed in unit time by chain branching rather than by gradual rise in temperature. Once the explosion sets in the rise in temperature due to the liberation of heat of reaction is very marked, and the characteristic luminosity observed in low pressure explosions is probably spectroscopically similar to that of flames though this has not been tested.

From the above the term ignition may be interpreted as meaning the state of hydrocarbon combustion which occurs with propagation of a flame, the ignition temperature of a hydrocarbon mixture being defined as the minimum value for inflammation to occur and be self propellant. The ease of ignition and ignition temperature are not constant for a particular hydrocarbon. They vary greatly with conditions, such as: (6)

(1) Position, intensity and nature of the source of ignition;

(2) Chemical nature of the inflammable constituents and their amount relative to the amount of oxygen available.

(3) Nature and amount of diluent gases.

(4) The presence or absence of oxidation catalysts.

(5) The initial temperature and pressure of the mixture and its state of motion.

(b) Inflammability (5,6,7)

An inflammable mixture is one through which flame can be propagated independently of and away from the source of ignition. With any particular inflammable gas there are, under given physical conditions, certain limits of composition, within which but not outside of which, self propagation of flame will take place after ignition has been effected. These are called the upper and lower limits of inflammation of the gas under the given conditions. In passing up a homologous series the range of inflammability narrows with increased molecular weight e.g. for methane limits are 5.4 - 14.8%, for hexane 1.2 - 4.2%. Endothermic combustibles like acetylene have a much wider range due to exothermic decomposition on combustion. The limits of inflammation depend also on the position of the source of ignition since the progress of the flame may be assisted or retarded by convection currents, according as the flame has to pass in an upward, horizontal or downward direction. If oxygen is used instead of air the upper limit is raised appreciably, and, obviously, increasing the concentration of diluent gases like nitrogen narrows the limits. An increase of temperature widens the limits. An increase of initial pressure may cause variable effects, depending on the nature of the mixture and the mode of ignition. With spark ignition the range is widened with pressure; with a heated surface there is generally an optimum pressure. The increased density facilitates ignition by compression and reduces the critical compression ratio for ignition to occur, so that heat losses are reduced. The effect of turbulence of the mixture is usually to make ignition more difficult, the turbulence tending to increase the rate of dissipation of heat. This is particularly noticeable in spark ignition. Once ignition is accomplished the limits are widened by turbulent mixtures. With the higher hydrocarbons a chemiluminescence may be observed for sometime before the actual ignition point is reached. This range is usually designated as that of "cool flames" and as has been previously mentioned aldehydes are present if the products are condensed out during this luminescence.

(c) Flame Movement (7)

In general there is not enough known about the movement of flames to get a true picture. Flame movement is only uniform under special conditions. Photographic methods are mainly used. A method using a sensitized paper on a revolving drum was introduced by Mallard and Le Chatelier, and improved by Dixon. More recently a snapshot method has been made use of. The rate and nature of flames varies widely with conditions (7,8) particularly with the freedom offered the products of the combustion. In general, the speed of the flame is governed by the nature and concentration of the inflammable gas, and the shape and size of the containing vessel. Temperature and pressure have little effect but movement of the gases ahead of the flame has considerable influence.

With an inflammable mixture in a tube closed at one end, the flame travel is uniform for a short distance. Each succeeding layer of unburnt gas is raised to its inflammation point by conduction and radiation from the adjacent burning layer and there is no appreciable movement of unburnt mixture as products are free to expand and escape from the open end. The rate of flame travel is then expected to be determined by flame temperatures, thermal conductivity and average rate of reaction in each layer during the heating up period. This is a conception of a fundamental flame speed. Such conditions are hard to realize since slight disturbances have a disproportionately large effect on the rate of uniform movement. If the mixture is ignited at the closed end of the tube the reaction products cannot escape the pressure rises and the flame accelerates. But in some circumstances the flame neither rises at constant rate nor at a constantly increasing rate, but takes a vibratory form of propagation, the amplitude of which may become locally very great. These vibratory flames may be exaggerated by effects of resonance due to the shape of the container, but probably have their origin in the chemical nature of the reaction; the rate of propagation may not be entirely uniform, but increasing in certain regions amongst favored molecules.

In mixtures of a certain composition containing not too much diluent gas the type of combustion suddenly changes after a prescribed length of flame travel, detonation occurs and thereafter flame is propagated at a very great rate.

(d) Pressure Development (5)

Under ideal conditions the rate of pressure development and the maximum pressure attained in gaseous explosions would always be characteristic of the given mixture, dependent only on the mode of combustion and the initial pressure. Unfortunately the development of explosions is influenced by the size and shape of the vessel, factors which also influence the conduction and radiation losses. Maximum pressure might be expected to synchronize precisely with the moment the flame reaches the walls, but this depends so much on circumstances that it is only with the fastest of explosions that this is even nearly so. Cooling by conduction or radiation during the explosion period results in a lowering of maximum pressure attained. Raising the initial temperature, at a given pressure, diminishes the time required for attainment of maximum pressure. Increased initial pressure causes varied effects depending on the mixture; the explosion time may be either decreased or increased. The fastest explosions occur with mixtures which contain a small excess of the combustible.

In general there are three phases to the explosion of a gaseous mixture - an induction period, followed by a period of rapid pressure rise, and then a cooling period.

(e) Flame Temperatures (5)

Both direct and indirect means of measurement of flame temperatures may be used. The direct methods, platinum resistance thermometers, etc., are limited in application by the melting points of the metals. Indirect methods, e.g. calculating temperature from the maximum pressure attained or by the spectral line reversal method, are much more convenient.

The flame temperature is markedly affected by the proportion of combustible gas in the mixture. The flame temperatures increase rapidly from the lower limit of inflammability and reach a maximum, then decrease toward the upper limit but not nearly so rapidly as with excess oxygen. The maximum flame temperatures for all hydrocarbons are similar, in the vicinity of 1900°. The maximum flame temperatures of ethylenes is greater than those of the paraffins, but within 100 of them. These maximum flame temperatures occur over a very narrow range of gas to air ratios, a small change in this ratio causing a sharp reduction in the flame temperature. Values have been calculated for the maximum flame temperatures of various mixtures, taking into account the specific heat and thermal conductivity of the gases at the high temperatures of the flame, and also dissociation. Even with these corrections, calculated values are still from 50 - 100° too high. This is attributed to radiation losses.

B. Detonation (7,8,9)

Detonations are generally set up by one of two or three methods. They may be set up by the flame itself; if the flame arrives in a denser region, in the crest of the compression wave which travels ahead of the flame, there is a great enhancement of rate, and combustion is propagated as fast as the wave, which adiabatically compresses the gas mixture as it passes through it. The sudden release of energy provides conditions which suddenly activates a large portion of molecules into reaction. It is also possible to start a detonation wave when a compression wave, reflected from the walls, catches up with the flame, or vice versa. Detonation occurs much more readily when ignition occurs near the closed end of a tube than at the open end due to the wave from the spark reflecting from the closed end. It may take three or four increases of flame velocity caused by flame or compression wave overtaking each other to cause detonation in some cases. The initiation of a detonation wave must be preceded by a condition in the gases ahead of the flame such that auto ignition can occur.

The main characteristic of detonation waves is their great speed which is greater than that of sound in the medium. This is because the great force of the detonation causes a tremendous pressure gradient between successive layers, whereas in sound waves only a small pressure change occurs.

As for inflammations, there are definite limits of composition, within which but not outside of which a detonation wave may be propagated. Detonation waves are influenced also by the diameter of the tube in which the wave is set up, and to a slight extent by the initial temperature, pressure, and the presence of inert gases or anti-knocks. The detonation wave generally travels with a uniform velocity which is dependent on the composition, decreasing near the detonation limits.

Detonation waves are not always propagated in straight lines. There is good evidence that it may be propagated helically near the walls of the tube. Such a wave is called the "spin" detonation wave. There is still doubt as to whether the whole body of the gas is rotating, or only part. Bone, Frazer and Wheeler are of the opinion that only the head of the detonation wave follows the helical path. The head of the wave travels faster than the body of of the gases, but its displacement from the end of the tube where ignition occurs must be the same as the wave in the main body of the gas. The fastest wave then must zigzag across the tube and the easiest path is a helical one. This phenomenom of spin is quite general in detonation waves.

During the initial stages of an explosion, combustion in the flame front is comparatively incomplete and combustion goes on behind it. In detonation, the chemical change occurs almost instantaneously and completely, in the flame front.

A phenomenon which occurs frequently in combustion and is often confused with detonation, is that of knock. Knock occurs when the last portion of the charge suddenly reacts. It has previously been brought into a sensitized condition by increased temperature by conduction and compression, and reaction is already partially complete in this region. It is of great importance in operation of internal combustion engines and will be dicussed there.

III Combustion in Internal Combustion Engines (8)

Combustion in internal combustion engines does not differ from that in laboratory equipment when the conditions of operation are considered. The combustion occurs at fairly high pressures and with a considerable degree of turbulence in the mixture. In addition to the instantaneous spark ignition the mixture is heated by compression and by contact with the hot cylinder walls before the spark ignition.

Essentially a mixture of a combustible hydrocarbon and air are admitted to the engine cylinder. This charge is compressed, and on nearing the completion of the compression stroke a spark passes through a portion of the mixture. After a slight delay, a flame travels through the compressed gas at a speed depending on a variety of factors. The rapid bluish flame burns the mixture as it courses through it, the burning taking place along a narrow flame front, the burnt product reaching a high temperature due to the heat of reaction, thereby causing a very rapid rise in pressure. The energy is utilized during the expansion stroke, the pressure being exerted on the piston.

The power output of such an engine depends on the volumetric efficiency and the compression ratio, the fuel economy on the compression ratio. Thus for maximum power and greatest economy of operation it is desirable to have as high a compression ratio as is consistent with the combustion characteristics of the mixture.

The flame speeds, relative to the cylinder-head walls usually range from 25 to about 250 feet per second, They are principally determined by the degree of turbulence, which in turn is largely a function of chamber design and engine speed. The compression ratio, charge density, and spark advance have little or no effect on the actual flame speeds. The temperature of the combustion chamber walls, the design, location and temperature of the sparking plugs and valves, together with the chemical composition of the fuel, the air-fuel ratio and charge temperature and dilution with exhaust gas, all have a greater or less effect on the flame speeds.

Combustion of the fuel is practically complete in the narrow flame front. In non-knocking operation, no extensive chemical change occurs in any region in the gas before the flame reaches that region. The products of the combustion are oxides of carbon and water, and traces of hydrocarbon due to chemical decomposition of fuel and oil on the cylinder walls may be found in the exhaust gases. During the cooling period behind the flame front readjustments occur in the equilibria;

$$2\ CO + O_2 \rightleftarrows 2\ CO_2$$

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

and $$H_2 + 2\ OH \rightleftarrows 2\ H_2O$$

from left to right in each case.

In normal combustion the pressure increases to its maximum value in a smooth continuous manner without pulsations or vibration. Its maximum value in modern engines is around 1000 lbs. per sq. in. per 0.001 sec.

IV. Knock in Internal Combustion Engines (8,10,11)

Mention has been made of the phenomenon of knock in static combustion systems. It is however mainly an engine phenomenon. Certain circumstances may cause the character of the combustion to change, accompanied by a knocking sound. Knock may be defined as an abnormally rapid explosion of a certain portion of the charge which is the last to burn in an internal combustion engine, resulting in the formation of pressure waves in the gas. It must be distinguished from pre-ignition and after firing. These are quite different from knock although they are of considerable importance in internal combustion engine performance.

The occurrence of knock in the engine is marked by flame and pressure characteristics quite different from those of normal combustion. These characteristics are confined to a portion of the charge which is the last to burn. This portion of the charge may vary from an undetectable small amount to at least three-quarters of the whole. The portion of the combustion which precedes knock is perfectly regular and is indistinguishable from that observed in the entire absence of knock.

The flame of knocking combustion seems to sweep through the whole charge almost instantaneously. Its velocity is in the neighborhood of 1000 ft. per sec., greater than the rate of normal flame travel but definitely less than that in a true detonation wave. The pressure rise is also high, and attains a maximum value of the order of 10,000 lbs. per sq. in. per 0.001 sec. This also is less than that of a true detonation wave. Pressure waves are set up due to the abrupt change from the normal rate of combustion to that of knocking type of combustion. It is these pressure waves, which on reflection from the cylinder walls set up a state of resonant vibration which causes the cylinder walls to vibrate, resulting in the audible sound associated with knock.

Since knock is due to the sudden and extremely rapid explosion of the last portion of the charge to burn, and that this portion is in a highly sensitized state due to partial combustion at the temperatures caused by the compression of the charge and conduction from the walls, it is obvious that any change in operating conditions which tends to increase the temperature of the charge or to lengthen its time of heating prior to ignition, increases its tendency to knock, High temperatures of the induction system, cylinder walls and pistons, carbon deposits, hot exhaust valves and presence of localized hot spots, low flame speeds and high flame temperatures, high compression ratio, low engine speeds and presence of pockets or dead spaces in the cylinder, all cause increased tendency to knock. Turbulence, and dilution by exhaust gases, and suitable placement of the spark-plugs decrease this effect. All these mechanical variables modify either the temperature or the time factor, or both.

The tendency to knock depends not only on the physical factors of time and temperature but also on the chemical composition of the charge. Here the significant variables are the chemical nature, concentration, and heat of vaporization and combustion of the fuel, the air - fuel ratio, the presence of compounds which act as pro- or anti-knock agents, and the degree of charge dilution by residual exhaust gas in the cylinder. These chemical factors influence the initiation rather than the propagation of the knocking flame.

Knock in engines must also be distinguished from "detonation", although there is considerable similarity between the processes. It is very doubtful if a true detonation wave could be propagated under the conditions in an engine cylinder.

An ordinary fairly heavily built engine suffers knock without much harm though the efficiency falls off as the intensity of the knock increases, and eventually pre-ignition sets in owing to carbon formation, heated plugs, and other troubles occasioned by the continuance of knock. A high-duty engine, however, such as used for aircraft, rapidly suffers from the effect of knock, and gumming, pitting and seizure soon result. Intense local attack of the metal of the cylinder head sometimes occurs. Besides the noise associated with knock, the limitation which the fuel sets on an engine's performance is thus very definite.

V. The Effect of Anti- and Pro-Knock on Combustion Susceptibility to Knock of Fuels (12,15)

Fuels vary greatly in their susceptibility to knock. Even two isomers may differ greatly in this regard. The paraffin hydrocarbons in general are much more prone to knock than corresponding olefines, and these in turn more than ring compounds. Increased knock susceptibility occurs with increase in chain length. Branched chain hydrocarbons are less susceptible than straight chain ones. In general the more compact and symmetrical the molecule, the less its knock tendency.

The knocking characteristics of any fuel vary considerably with conditions. To compare fuels their "octane rating" is used. Normal heptane is a fuel of very low anti-knock rating; iso octane is one of very high anti-knock rating; using various mixtures of these two as reference fuels any fuel which has the same knocking characteristics as a particular mixture of n heptane and iso octane has an octane number equal to the percentage of iso octane in the standard reference fuel. Fuels are also rated on their H.U.C.R. - highest useful compression ratio. Tests are carried out mainly on C.F.R. engines for this purpose.

Anti-Knock Compounds (13)

The addition of relatively small amounts of certain substances suppresses or greatly decreases knocking in an engine. Such substances are called anti-knock compounds. There are several of this type of compound which are really non-knock fuels, and the addition of 10 - 60% of the substance is required, as in benzene or aniline. Many nitrogen compounds are very effective anti-knocks, particularly the aromatic amines. Sometimes a concentration as low as 0.1% is effective. The heavy elements are generally quite active anti-knocks; substances like lead tetraethyl and iron carbonyl are effective in low concentrations. With these, the anti-knock properties are due to the element itself, rather than the compound as a whole.

The effectiveness of anti-knock compounds varies greatly with the conditions. It may be measured by engine tests.

Combustion studies show that anti-knocks act by inhibiting oxidation in front of the flame, as it passes through the mixture.

Anti-knock compounds are regularly used in commercial fuels. Lead tetraethyl is the one most widely used.

Pro-Knock Compounds (14)

The addition of pro-knock compounds to a fuel, promotes knock in the engine. As with anti-knocks the effectiveness of the pro-knock varies a great deal with the compound and with conditions. Ozone is particularly effective in causing knock. Organic nitrites, nitrates and nitro compounds are also very effective. The higher halogens are good pro-knocks, the effect decreasing with increased molecular weight; iodine, actually, is an anti-knock. Organic peroxides are usually extremely potent knock inducers. This might be expected since peroxides are formed during the preliminary stages of combustion. Pro-knock compounds are known, also, to decrease the self ignition temperature of hydrocarbons. In general highly oxygenated organic compounds are the most potent pro-knocks.

Both anti-knock and pro-knock compounds differ from catalysts in that they are used up, and their effectiveness ends when they are used up. When both are added to a fuel each tends to offset the effects of the other.

EXPERIMENTAL

The engine available for this work was a 1933 Model Master Chevrolet. Data pertaining to this engine is as follows:

Rating - 65 Brake Horsepower at 2800 R.P.M.
Piston displacement -206.9 cu. in.
Compression ratio - 5.2
Order of firing - 1-5-3-6-2-4
Octane rating, ordinary gasoline - 65
ethyl gasoline - 78
Carburettor-------Carter - $1\frac{1}{4}$" size.
Fuel consumption per hour at
maximum load------41.5 lbs/hr.
------ 0.7 lbs/B.H.P./hr.(approx)
Air consumption per hour at
maximum load-----1800 cu.ft./hr.(approx).

The load was applied by a Heenan-Froude hydraulic brake. The cooling water temperature was measured by a thermometer inserted through the radiator cap. A revolution counter supplemented the speedometer in measuring the speed.

Throughout all trials, the engine was operated under full load, at maximum throttle, the speed being maintained at approximately 10 miles per hour.

I. Gas Technique

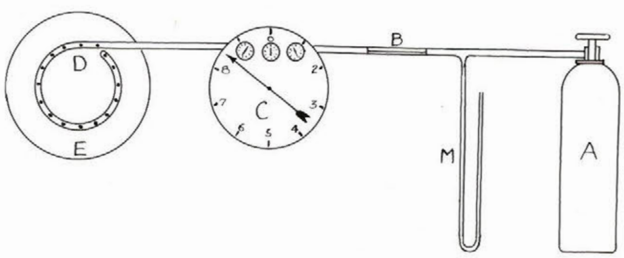
A six foot length of seven inch diameter stove pipe was connected horizontally to the top of the air filter by a right angle bend. A venturi meter was placed at the outer end of this pipe to measure the air consumed by the engine. This system was made air tight.

The gas was introduced directly from the cylinder into the main air stream by a copper tube bent into a circular shape, two thirds of the diameter of the main air stream pipe. Perforations, of negligible resistance to the flow of the gas were made in the tube, facing upstream. Diffusion may be assumed complete, since 2-3 seconds are required for the gas to reach the engine. The amount of gas was measured by a wet gas meter of the rotary type to 0.001 cu. ft. A calibrated capillary flow meter, with a dibutyl phthallate manometer connected to it, was used to obtain a quick indication of the gas rate, for adjustment of the valve on the cylinder.

Readings were taken of; the gas flow, air consumption, cooling water temperature, room-temperature, engine speed, revolution counter, brake load, and the state of operation of the engine.

II Vapor Technique

(a) The great majority of the compounds tested were expected to be without effect. Hence in order that a large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number of compounds could be used, the following technique for rapid testing was used; a can, with a removable cover, had the bottom taken off and a large hole cut in the cover. A piece of cheesecloth was spread over the top of the can, and held in place by the cover. This was placed on a support, in a horizontal position, directly in front of the venturi meter, so that the air entering the engine passed through the cheesecloth. About one cc. of the liquids was placed on the cheesecloth by an eye dropper. The air stream carried the vapor into the engine. The method was found to be quite sensitive, especially for liquids with fairly high vapor pressures. The use of high boiling liquids would in practice, be limited by their low vapor pressures. Two hundred and forty organic liquids were tested in this way.

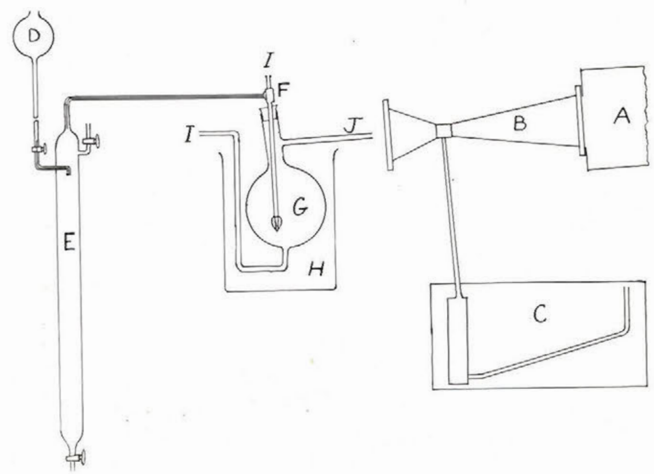
(b) For those compounds which had a noticeable effect on the state of operation of the engine, a quantitative technique was developed to find the critical concentration for a given effect. It was attempted to introduce vapors into the air stream by bubbling part of the air through a system of traps containing the liquid. This was unsatisfactory. Only a small fraction of the total air could be passed through a convenient bubbling system, and this was insufficient to vaporize the required concentration of liquid in the air stream. There was also the difficulty of determining the degree of saturation of the air passed through the bubblers.

A second method was to boil the liquid in an evaporator, measuring the pressure of the vapor on a manometer. The vapor passed through an electrically heated superheater tube to prevent any entrained liquid escaping with the vapor. The vapor was discharged into the mixing chamber through a calibrated capillary orifice. A stream of air carried the vapor from the mixing chamber into the main air stream. This was discarded because of the condensation of vapor in the orifice, and the large fluctuations of pressure in the evaporator.

The third method eventually proved satisfactory. The liquid was displaced from a burette through a capillary tube sealed into the top of the burette, by dropping mercury at constant rates into the burette.

The constant rate was easily maintained, provided the mercury reservoir was at a sufficient height that changes in the head were negligible. The amount displaced was readily determined from the burette readings over a measured time interval. The rate could be varied by a stopcock regulating the flow of the mercury. Several methods of evaporating the liquid were attempted before a satisfactory means was found. An electrically heated evaporator, at a high enough temperature for immediate evaporation of the liquid, caused decomposition of several compounds. An atomizer did not give fine enough droplets, and condensation in the air intake of the engine resulted. However, a combination of a flash evaporator and atomizer was very satisfactory. The complete set up is shown in figure II. The mercury in the reservoir D is allowed to drop, at a rate regulated by the stopcock, through the capillary tubing into the burette E which contains the liquid. The liquid is displaced through a capillary tubing into atomizer F. The fine stream of droplets impinges on the walls of the flask G which is heated in an oil bath H. A stream of air I is introduced into the bottom of the flask to assist the evaporation of the liquid. The bath temperature was maintained at all times below the decomposition point of the material, and usually at its boiling point. The air and vapor were discharged through the tube J into the main air stream at the mouth of the venturi meter.

Readings were taken over a measured time interval of; burette, room temperature, oil bath temperature and the venturi meter, as well as the usual engine readings of cooling water temperature, brake load, and speed. The technique was to gradually increase the rate of introduction of the liquid, until the first audible knock occurred. A set


D
I
F
A
B
I
J
G
E
H
C

of readings were taken at constant conditions at this rate. The rate was then increased in stages at which different effect were noticed, and finally until a dangerous knock ensued. Readings were taken at each stage.

III Oxygen Mixtures

The oxygen was passed directly from the cylinder through the liquid in a flask immersed in a water bath at about 100°F., the stream of vapor and air being directed into a main air stream entering the engine.

RESULTS

I GAS TESTS:-

Gas	Concentration parts/1000 of air	Effect
Oxygen	6.5	Slight increase in knock.
	19.0	Bad knock, intermittent "spit".
	30.0	Very bad knock.
Hydrogen	0.5	Slight decrease in knock.
	10.0	Engine sound dead, operation unsteady.
Methane	5.0	Increased vibration.
Butane	15.0	Slightly uneven torque, - choking.
Iso butane	18.0	Slight vibration, uneven torque, load dropped 15%.
Ethylene	30.0	No effect.
Propylene	15.0	Less knock, uneven torque, load down.
Acetylene	20.0	Less knock, load down slightly.
Carbon dioxide	15.0	Slight decrease in load.
Nitrogen	9.	Torque uneven.
	18.	Torque uneven.
Hydrogen sulfide	15	No effect
Sulfur dioxide	15	No effect.
Ammonia	18	Less knock, decreased load, uneven torque.
Ethylene oxide	6.5	No effect.

II Liquid Tests.

(a) Rapid tests.

Compound	Effect
1. Hydrocarbons.	
(a) Saturated.	
n Octane	No effect
Cymene	No effect
Isoamyl benzene	No effect
Diphenyl methane	No effect
o Xylene	No effect
m Xylene	No effect
p Xylene	No effect
Mesitylene	No effect
Diphenyl ethylene	No effect
Cetene	No effect
Tetrahydro naphthalene	No effect
Paraffins - 18 C	No effect
- 42 C	No effect
- 186 & 90 C	No effect
(b) Unsaturated	
Dicyclopentadiene	No effect
Caprolene	No effect
Styrene	No effect
Octylene	No effect
Cyclohexene	No effect
Pinene	No effect
Safrol	No effect
Phenylcyclohexene	Definite knock
2. Halides.	
Ethyl chloride	No effect
Ethyl bromide	No effect
Ethyl iodide	No effect
Chloroform	Very slight knock
Propyl iodide	No effect

Compound	Effect
Bromoform	Slight knock at high concentrations.
Methylene chloride	Load drops at high concentrations.
Methylene bromide	No effect
Ethylene dichloride	No effect
Tetra chloro ethane	No effect
Penta chloro ethane	No effect
Di chloro ethylene	No effect
Tri chloro ethylene	No effect
Tetra chloro ethylene	Very slight trace of knock
Propylene bromide	Loss of load, uneven torque
Tri methylene bromide	No effect
Allyl bromide	Slight drop in load
n Butyl iodide	No effect
Iso amyl chloride	No effect
Iso amyl bromide	No effect
Iso amyl iodide	No effect
Fluoro benzene	Drop in load
Chloro benzene	No effect
Bromo benzene	No effect
Iodo benzene	No effect
Chloro toluene	No effect
Chloro naphthalene	No effect
Bromo naphthalene	No effect
Phenoxyethylbromide	No effect
3. Alcohols	
(a) Saturated	
Methyl alcohol	No effect
Tertiary butyl alcohol	No effect
Iso amyl alcohol	No effect
Methyl ethyl carbinol	No effect
Diethyl carbinol	No effect
Tertiary amyl alcohol	No effect
Secondary butyl alcohol	No effect
Cyclohexanol	No effect
Phenylethyl carbinol	No effect
Furfural alcohol	No effect
Pinacolone	No effect
Tetrahydrofurfural alcohol	No effect

Compound	Effect
(b) Unsaturated	
Allyl alcohol	No effect
Cinnamylalcohol	No effect
Terpineol	No effect
Methacrolein	No effect
Methyl Ethyl acrolein	No effect
(c) Halogenated	
Chlorohydrin	No effect
Dibromohydrin	No effect
Ethylene bromohydrin	No effect
Propylene chlorohydrin	No effect
(d) Others	
Diacetone alcohol	No effect
Ethanol amine	No effect
4. <u>Aldehydes</u>	
Acetaldehyde	No effect
Paraldehyde	No effect
Butylaldehyde	Barely noticeable knock
Isobutyl aldehyde	No effect
Formaldehyde 50%	No effect
Acetyl aldehyde	No effect
Benzaldehyde	No effect
Phenyl propaldehyde	No effect
Tolyl aldehyde	No effect
Hydrocinnamic aldehyde	No effect
Salicylaldehyde	No effect
Aldol	No effect
Cinnamic aldehyde	No effect
Acetaldol	No effect

Compound	Effect
5. Ketones	
Acetone	No effect
Diisopropyl ketone	No effect
Methyl isoamyl ketone	No effect
Methyl hexyl ketone	No effect
Acetophenone	No effect
Cyclopentanone	No effect
Cyclohexanone	No effect
Propiophenone	No effect
Methyl vinyl ketone	No effect
p Bromo acetophenone	No effect
p Fluoro acetophenone	No effect
Diethyl ketone	No effect
6. Diketones	
Acetonyl acetone	No effect
Acetyl acetone	No effect
7. Acids	
Isobutyric acid	No effect
Isovaleric acid	No effect
Perchloric acid	No effect
chloro acetic acid	No effect
Bromo propionic acid	No effect
Bromo butyric acid	No effect
Thioacetic acid	No effect
Glyoxallic acid	No effect
Eugenol	No effect
Isoeugenol	No effect
8. Anhydrides	
Acetic anhydride	No effect
9. Acyl Halides	
Acetyl chloride	No effect
Propionyl chloride	No effect
Oxalyl chloride	No effect
Benzoyl chloride	No effect
Phenacetyl chloride	No effect
p chloro benzoyl chloride	No effect

Compound	Effect
10. <u>Esters</u>	
(a) Organic acid.	
Ethyl ortho formate	No effect
Methyl acetate	No effect
Isopropyl acetate	No effect
Isoamyl acetate	No effect
Methyl phenyl acetate	No effect
Ethylphenyl acetate	No effect
propyl propionate	No effect
Isopropyl benzoate	No effect
Diethyl oxalate	No effect
Acetylene decarboxylic ester	No effect
Oxyisobutylic ester	No effect
Monopropyl mallonate	No effect
Triacetic	No effect
Ethyl valerate	Slight knock
Vinyl acetate	No effect
Ethylidene diacetate	No effect
Acetol acetate	No effect
(b) Halogenated Organic Esters	
Ethyl chloroacetate	Barely noticeable knock
Chlorethyl acetate	No effect
Bromo ethyl butyrate	No effect
(c) Keto-esters	
Acetoacetic ester	Noticeable knock
Acetone dicarboxylic ester	No effect
Ethyl acetone dicarboxylic ester	No effect
diethylacetone dicarboxylic ester	No effect
Dimethyl acetone dicarboxylic ester	No effect
Ethyl benzoyl formate	No effect

Compound	Effect
(d) Other Organic	
Diazo acetic ester	Marked knock
(e) Inorganic acid esters	
Diethyl carbonate	No effect
n Butyl nitrite	Very pronounced knock
Tertiary butyl nitrite	Quite bad knock
Amyl nitrite	No effect
Ethyl nitrate	No effect
Tributyl phosphate	No effect
Dimethyl sulfate	No effect
Di ethyl sulfate	No effect
Methyl sulfate	No effect
Methyl borate	Very slight trace of knock
n Butyl chlorcarbonate	No effect
Ethyl chlorcarbonate	No effect
11. Amides	
Formamide	No effect
12. Ethers	
Diethyl ether	Marked knock
Di-isopropyl ether	Slight knock at high concentration
n Dibutyl ether	No effect
Isoamyl ether	No effect
Diphenyl ether	No effect
Methyl n-butyl ether	No effect
Methyl t-butyl ether	No effect
Ethyl t-amyl ether	Barely noticeable knock
Guiacol	No effect
Dioxane	No effect
Methyl cellosolve	No effect
Mesityl oxide	No effect
Cresol ethyl ether	No effect

Compound	Effect
Resorcinol diethyl ether	No effect
Benzyl ethyl ether	No effect
Furfuryl ethyl ether	No effect
Phenetol	No effect
Acetal	No effect
Dichloroethyl ether	No effect
Chloroacetal	No effect
Ethyl chloro acetal	No effect
13. <u>Sulfur compounds</u>	
Isoamyl sulfide	Very slight knock
Benzyl mercaptan	No effect
Benzene sulfo-chloride	No effect
Methyl p toluene sulfonate	No effect
Carbon disulfide	Decrease of load
14. <u>Phenols</u>	
Phenol	No effect
Cresol	No effect
Cresylic acid	No effect
Chlorophenol	No effect
vo Bromo phenol	No effect
15. <u>Nitro compounds</u>	
Nitro benzene	No effect
Nitro methane	slight trace of knock
Nitro ethane	No effect
1 Nitro propane	No effect
2 Nitro propane	Possibly slight trace of knock
Chloropicrin	Very bad knock
Bromopicrin	Definite knock

Compound	Effect
16. Nitriles etc.	
Aceto nitrile	No effect
Propronitrile	No effect
Benzonitrile	No effect
Naphthonitrile	No effect
Capro nitrile	No effect
Lacto nitrile	No effect
Phenylisothiocyanate	No effect
o Tolyl isothiocyanate	No effect
Allyl isothiocyanate	No effect
p Chlor-Tolyl cyanide	No effect
Phenyl azide	Loss of load
17. Amines	
Methyl amine	No effect
Di isobutyl amine	No effect
Propyl amine	No effect
Mono amyl amine	No effect
Di isoamyl amine	No effect
Piperidine	No effect
Pyridine	No effect
Isophorone	No effect
Pyrrol	No effect
Xylidine	No effect
2-amino-1,3,dimethyl benzene	No effect
2 amino cymene	No effect
Dimethyl aniline	No effect
Pyridine acetate	No effect
Quinoline	No effect
18. Miscellaneous	
Bromine	Fairly bad knock
Hydrobromic acid	No effect
Hydriodic acid	No effect
Silicon tetra ethyl	No effect
Nitrogen peroxide	Noticeable knock
Nitrosyl chloride	Bad knock

Compound	Effect
Phosphorus trichloride	Slight knock
Phosgene in toluene	Drop in load
Hydrazine hydrate	No effect
Phenyl hydrazine	No effect
Ethylene oxide	No effect
Thionyl chloride	Slight,knock,decrease in load.

(b) Quantitative Tests-

Compound	Concentration Parts/1000 of air by volume	Effect
Methylene chloride	1.0	Slight knock
Bromoform	10.0	No effect
Tetra chloro ethylene	10.0	No effect
Propylene bromide	10.0	No effect
Butyraldehyde	3.0	Slight knock
Acetoacetic ester	0.2	Slight knock
	2.0	Definite knock
Ethyl chloro carbonate	10.0	No effect
n Butyl nitrite	0.008	Slight knock
	0.010	Definite knock
	0.169	Very bad knock
t Butyl nitrite	0.006	Slight knock
	0.045	Bad knock
iso Amyl nitrite	0.004	Slight knock
	0.044	Bad knock
	0.088	Very bad knock
Ethyl nitrate	0.056	Slight knock
	0.160	Very bad knock
t Butyl nitrate	0.011	Slight knock
	0.110	Definite knock
	0.180	Bad knock
Isopropyl ether	1.50	Slight knock
	4.50	Still slight knock
Ethyl t Amyl ether	9.00	Slight knock
Nitro methane	1.2	Slight knock
	3.2	Bad knock
2 Nitro propane	0.5	Slight knock
	2.1	Bad knock
Chloropicrin	0.003	Definite knock
	0.007	Bad knock
	0.021	Very bad knock
Bromopicrin	0.014	Definite knock
	0.040	Bad knock
Thionyl chloride	0.346	Bad knock

III Oxygen Mixtures

In all cases when oxygen was passed through the liquid, the knock tendency of the compound increased. The magnitude of the effect varied with the liquid concerned.

DISCUSSION

Compounds which have been found effective are: chloropicrin, iso-amyl nitrite, t-butyl nitrite, n-butyl nitrite, brompicrin, ethyl nitrate, t-butyl nitrate, acetoacetic ester, and thionyl chloride. Chloropicrin produced an effect in the engine at a concentration of 3 parts in 1,000,000; thionyl chloride at 4 parts in 10,000. A concentration of 1 part in 5000 in the air is possible, depending on the cost, availability, and method of polluting the air with the material. Could any of the above be put to use, it is likely that they would be effective in rendering automotive equipment inactive. If a concentration greater than 1 part in 5000 is obtainable the following substances amy be considered: Methylene chloride, butyraldehyde, iso propyl ether, ethyl tertiary amyl ether, nitro methane and 2-nitro propane. Compounds which were effective in the rapid tests, but which were not available for quantitative tests, are: iso-amyl sulfide, ethyl chloro acetate, phenyl cyclo hexene, phosphorous tri-chloride, bromine, nitrogen peroxide, and nitrosyl chloride.

Nitrites, nitrates, and nitro compounds seem most effective; the nitrite slightly more so than the nitrate or nitro compounds. Highly oxygenated molecules seem to have the greatest pro-knock characteristics.

The effectiveness seems to decrease with increased length of hydrocarbon chain, and to increase with the branching of the chain. Although iso amyl nitrite is more effective than t-butyl nitrite, the t-butyl nitrite molecule is much more compact and symmetrical than the iso-amyl nitrite, and might not be expected to be as powerful a pro-knock agent.

The presence of halogen atoms in the molecule seems to increase its pro-knock properties, chlorine being more effective than bromine in this regard. Halogens are reported as being effective pro-knocks, their effectiveness decreasing with increased molecular weight.

These results are supported by the observations of others mentioned in the introduction, page (42).

The engine used in this work was operated at low speed, under full throttle, maximum load, and with the octane selector advanced as far as possible. Thus the engine was in a critical condition regarding its susceptibility to knock. If tests are to be continued on this engine, it is essential that the above work be done on an aero-engine under working conditions. This will show whether the results obtained above and on further work are applicable in actual practise. The engine is heavily built and has a relatively low compression ratio. High duty aircraft engines are much more seriously affected by knocking.

Compounds containing two or more functional groups are expected to yield even more satisfactory results, particularly if a peroxide group be included. Many organic peroxides are known to be very effective in producing knock in engines. Peroxides would be particularly advantageous. Other vapors may be filtered from the air stream, but the peroxides would liberate their oxygen, which is a highly effective pro-knock.

It is hoped to carry on this work on an aero-engine, approximating working conditions.

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PART B

THE SYNTHESIS OF MUSTARD GAS FROM ACETYLENE

I PREPARATION OF DIVINYL SULFIDE

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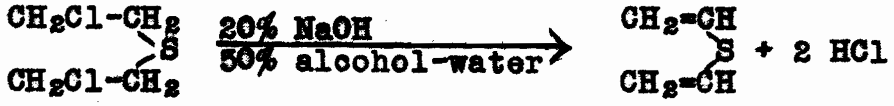
INTRODUCTION

The hydrolysis of mustard gas ($\beta\beta'$ dichloro-diethyl sulfide) in 20% alkali solution, yields under appropriate conditions mainly divinyl sulfide (1).



$$\begin{matrix}CH_2Cl-CH_2\\ \quad >S\\ CH_2Cl-CH_2\end{matrix} \xrightarrow[\text{50\% alcohol-water}]{\text{20\% NaOH}} \begin{matrix}CH_2=CH\\ \quad >S\\ CH_2=CH\end{matrix} + 2\ HCl$$

Divinyl sulfide is also formed as a result of a side reaction in the manufacture of acetylene (3). If, therefore, mustard gas could be prepared from divinyl sulfide and if divinyl sulfide could be prepared in quantity from acetylene, it would be possible to prepare mustard gas from acetylene as the starting material. The problem thus resolves itself into two distinct parts:

I The preparation of divinyl sulfide from acetylene

II The synthesis of mustard gas from divinyl sulfide.

This paper deals mainly with the former.

Throughout the problem, the commercial aspect of the reactions had to be considered. The object was to find a synthesis of mustard gas which was capable of commercial application in competition with present methods of manufacture.

Commercial Manufacture of Mustard Gas (11)

The earliest method of manufacture was that of Victor Meyer (7) in Germany. It may be represented by means of the following equations.

(1) $C_2H_4 + HOCl \rightarrow CH_2ClCH_2OH$

(2) $CH_2ClCH_2OH + Na_2S \rightarrow (HOCH_2CH_2)_2S + 2\ NaCl$

(3) $(HOCH_2CH_2)\ S + 2HCl \rightarrow (ClCH_2CH_2)_2S + 2\ H_2O$

The yields from this process are much lewer than in later processes and it is more expensive. Details of the mamufacture are given in the Journal of Industrial and Engineering Chemistry 1919, page 821.

A method, first introduced by Guthrie (8), using ethylene and sulfur chloride is mainly used to-day. It was developed chiefly by Pope and his collaborators (9)(10). Ethylene is bubbled through an excess of sulfur chloride, kept at a temperature between 30-35°C. by refrigeration. The reaction may be represented as follows:

$$2\ C_2H_4 + S_2Cl_2 \rightarrow \begin{matrix} CH_2Cl-CH_2 \\ \quad\quad\quad\; S \\ CH_2Cl-CH_2 \end{matrix} + S$$

The sulfur remains in colloidal suspension.

The advantages of this process are that it is cheap, since neither the ethylene nor sulfur chloride are required to be very pure and that the product is satisfactory for filling gas shells without purification.

The bulk of the mustard gas prepared in the United States is by the Levinstein method. It is quite similar to Pope's method. Here the ethylene is pumped into refrigerated lead tanks at 40 lbs. per sq. in pressure. The sulfur chloride is introduced in sufficient quantity to cover the nozzles of the ethylene inlet pipes. The ethylene is passed in at such a rate as to give rapid reaction. The sulfur chloride used is gradually replaced. The temperature is not allowed to rise above 35°C. In this process the sulfur deposited is allowed to settle out. This method is also cheap and allows large scale production.

Preparation and Properties of Divinyl Sulfide

Divinyl sulfide $(CH_2{=}CH)_2S$, molecular weight 84, is, according to Heilbron, a colorless mobile oil, which readily polymerizes to a translucent jelly, soluble in chloroform, partly soluble in benzene and convertible by alcohol or acetone into a gum. It is insoluble in water and most other organic solvents. Beilstein and Richter list the boiling point as 101°C. and density as 0.9125. These constants were obtained for divinyl sulfide from natural sources. Bales and Nickelson (1) give the boiling point as 85°C. which is accepted as being correct. Vapor density by the Victor Meyer method, on the freshly distilled liquid gives results for the molecular weight of 2 to 3 percent higher than the theoretical due to polymerization. Holm and Kennedy (3) list the boiling point as 83.5-84°C. They obtained a yellow oil possessing a garlic like odor. Their molecular weight determinations by the freezing point method showed 84.7 in benzene and 87 in acetic acid.

Divinyl sulfide is prepared readily from sulfilimine ($C_{11}H_{13}O_2NS_2$) but it is much more convenient to prepare it by the hydrolysis of mustard gas.

Helferich and Emmet Reid (2), investigating the hydrolysis of mustard gas found that with NaOH in 50% aqueous alcoholic solution, in the cold, they obtained a high boiling oil which they suggested might be a polymer of divinyl sulfide. With sodium ethylate they obtained an easily polymerizable oil which might have been divinyl sulfide.

Bales and Nickelson, (1) made a thorough investigation of the hydrolysis of mustard gas. They confirmed the presence of divinyl sulfide and found that the best conditions for highest yields was 20% sodium hydroxide in 50% aqueous alcoholic solution. The hydrolysis product had a pronounced garlic like odor and on distilling off the alcohol, the odor was confined to the distillate. On pouring the distillate into water, a clear colorless light oil separated. After thorough washing with water and drying over calcium chloride, the yield of oil was about 26% of the weight of the mustard gas. The liquid was found to distill largely at 83-87°C. and on further fractionation the bulk of the liquid distilled at 85-86°C. In glass stoppered bottles it polymerized in upwards of 48 hours to an opaque jelly, somewhat soluble in carbon disulfide, but insoluble in alcohol, ether, benzene, carbon tetra chloride, or chloroform. Analysis showed the percentage composition to agree closely with that expected from the formula for divinyl sulfide. The hydrolysis may be represented:

$$(CH_2Cl-CH_2)_2S + 2NaOH \rightarrow (CH_2=CH)_2S + 2NaCl$$

This, now, is the usual method for the preparation of divinyl sulfide.

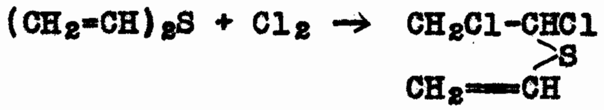
Divinyl sulfide has been found to occur during the manufacture of acetylene from calcium carbide (3), by the dry method. In this, just enough water is dropped on to the carbide for reaction to occur, in contrast to the wet method where a sludge of carbide and water is used. At present, approximately 60 lbs. of divinyl sulfide are obtained per million cubic feet of acetylene produced. It occurs along with hydrogen sulfide and other organic sulfides, mercaptans, and phosphines. It may be recovered by freezing out in traps, cooled by immersion in a dry ice-acetone mixture at about -80°C. through which the acetylene is passed. It may also be removed by absorption in chloramine T solution or by adsorption on charcoal.

Reactions of Divinyl Sulfide.

The reactions of divinyl sulfide have been investigated by Helfench and Reid (2), Bales and Nickelson (1), Mann and Pope (4), Alexander and McCombe (6) and Holm and Kennedy (3). Their results are summarized below:

1. Reaction with halogens.

(a) Chlorine (6) <u>one</u> mol of chlorine in carbon tetra chloride solution will add to form a brownish oil, having a boiling point of 84-5°C. at 20 mm. of mercury. It is α β dichloro vinyl sulfide



Alcoholic potassium hydroxide reacts with this addition product to give a monochlor divinyl sulfide:

This latter compound has a boiling point of 123-4°C. at 760 mm. pressure

- <u>two</u> mols of chlorine in carbon tetra chloride will add under the same conditions to give tetra chloro diethyl sulfide, a pale yellow liquid boiling at 132-3° at 15 mm. This tetra chloro diethyl sulfide, dissolved in benzene and heated with slightly more than one mol of triethyl amine yields α β dichloroethyl β' chloro vinyl sulfide

having a boiling point of 103-4° at 20 mm.

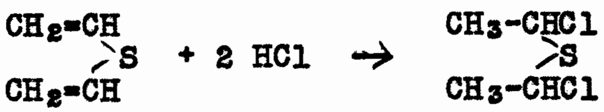
(b) Bromine and Iodine (6). These yield undistillable fuming oils. The liquid turns dark in color and persistent fumes of HBr and HI are liberated respectively.

2. Reaction with halogen acids.

(a) Hydrogen chloride (1). When divinyl sulfide is boiled with concentrated hydrochloric acid under reflux, it blackens, and apparently complete decomposition results.

When dry hydrogen chloride is passed into liquid divinyl sulfide, it is absorbed quietly and readily without appreciable evolution of heat. It yields clear colorless liquid, having a pungent and objectionable smell and persistent odor, and boils at 58.5-59.5°C. at 15 mm. The smoothness and ease of the reaction and sharpness of the boiling point of the product indicates simple addition. If sufficient hydrogen chloride is available the dichloro derivative is former, but the mono addition product results from the addition of but one mol of hydrogen chloride. The mono addition product boils at 36° at 15 mm.

The dihalogen addition product reacts violently with nitric acid. It decomposes on distillation at atmospheric pressure with the evolution of copious fumes of hydrogen chloride, the liquid distilling between 125-140°C. This dihalogen addition compound is entirely free from vesicant properties. It must, therefore, be αα'dichloro diethyl sulfide,



$$\begin{matrix} CH_2{=}CH \\ \quad >S \\ CH_2{=}CH \end{matrix} + 2\ HCl \rightarrow \begin{matrix} CH_3{-}CHCl \\ \quad >S \\ CH_3{-}CHCl \end{matrix}$$

an isomer of mustard gas. It can be seen from this that no ordinary method of chlorinating divinyl sulfide will produce mustard gas, but rather the $\alpha\alpha'$ isomer. It seems that the vesicant properties possessed by mustard gas are due to the chlorine atoms being in the β and β' positions

(b) Hydrogen bromide (1). This reacts very similarly to hydrogen chloride. When hydrogen bromide is passed into divinyl sulfide in the liquid state, both mono and di bromo addition products may be obtained depending on the amount of hydrogen bromide added. The boiling point of α bromo ethyl vinyl sulfide and $\alpha\alpha'$ dibromo diethyl sulfide are 50.5°C. and 87°C. at 15 mm., respectively. As in the case of hydrogen chloride, the bromine adds in the $\alpha\alpha'$ positions.

Mixed di- addition products may be produced by addition of one mole of hydrogen bromide to α chloro ethyl vinyl sulfide. This yields α chloro α' bromo diethyl sulfide having a boiling point at 15 mm. of 78°C.

(c) Hydrogen iodide. When dry hydrogen iodide gas is passed into divinyl sulfide, ready adsorption occurs as with the other hydrogen halides, but with considerable darkening of the solution. Distillation at 15 mm. results in rapid decomposition, finally with explesive violence (1)

When divinyl sulfide is warmed in alcoholic solution with a concentrated solution of hydriodic acid, a crystalline derivative is obtained. It is β β' di-iodo diethyl sulfide and melts at 56-60°C. (6). This is quite different from the addition of the other hydrogen halides which takes place with the halogens in the α and α' positions. This β β' di iodo compound is the iodine analogue of mustard gas. However, it is a solid, its vapor pressure is low and it is non-vesicant.

3. Reactions of Halogen Addition Compounds.

All of these α halogen addition compounds deposit a small quantity of fine, white, silky needle-like crystals around the stopper of the bottle which contains them. When α α' dichloro diethyl sulfide is treated in alcoholic alkali solution, with sodium phenoxide in alcoholic solution, crystals similar in appearance are obtained, and when the α α' dichloro diethyl sulfide is treated with ethylene chlorohydrin, similar crystals are obtained which have been identified as β tri-thio acetaldehyde and have a melting point of 125°C. (1)(4).

4. Reaction with Phenol and Thiophenol (6).

These two compounds add to divinyl sulfide to form β addition products e.g. $(S\ Ph\ CH_2\ CH_2)_2\ S$. This is solid having a melting point of 57°C.

5. Reaction with Aniline (6).

In sodium hydroxide or sodium methoxide, aniline gives only polymerization products.

6. Reaction with Nitric Acid (1).

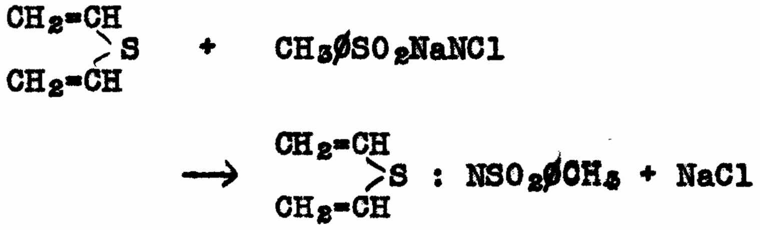
This reacts on both the liquid divinyl sulfide and its polymer with extreme violence.

7. Reaction with Perbenzoic acid (6).

This gives divinyl sulfoxide, a liquid boiling at 86-87°C. at 18 mm. pressure.

8. Chloramine T (5,3).

Freshly distilled divinyl sulfide, when added to a 10% aqueous solution of chloramine T and heated to 30°C., readily forms a solid derivative, a sulfilimine. The crystals are white, hexagonal prisms, which on recrystallization from alcohol melt at 92.9-93.4°C.



$$\begin{matrix}CH_2{=}CH\\ \quad >S\\ CH_2{=}CH\end{matrix} \quad + \quad CH_3\phi SO_2NaNCl$$

$$\longrightarrow \begin{matrix}CH_2{=}CH\\ \quad >S\\ CH_2{=}CH\end{matrix} : NSO_2\phi CH_3 + NaCl$$

__Reactions of Acetylene with Hydrogen Sulfide__.

Very little has been done on reactions of acetylene with sulfur compounds. The reaction of acetylene with hydrogen sulfide has been investigated catalytically to a slight extent in both the gas phase and in solution.

Chichibabin and Bagdassarjang (12) found that acetylene and hydrogen sulfide in the gaseous phase and in the presence of an alumina gel catalyst at 400°C., gave a yield of 35% of pure thiophene. Ethyl mercaptan, secondary butyl mercaptan and a mixture of α and β ethyl thiophenes were also present as well as other compounds not identified.

Margaret G. Tomkinson (13) further investigated the reaction by trying various oxide, sulfide, and sulfate catalysts. Alumina gel, Al_2O_3, was found to be the most effective. This reaction of hydrogen sulfide with acetylene, in the gas phase at 400°C. over an alumina gel catalyst is the chief method to-day for preparing pure thiophene.

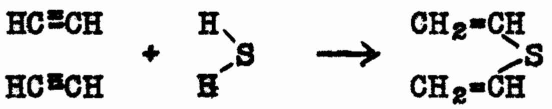
In aqueous solution (14) acetylene and hydrogen sulfide will react in the presence of potassium hydrogen sulfide as a catalyst at 100°C. and 10-20 atmospheres pressure, to give α tri thio aldehyde.

In diethylene glycol (14) again with potassium hydrogen sulfide as catalyst, ethyl mercaptan and vinyl ethyl sulfide are obtained. With an excess of acetylene, the main product is the diethyl ester of ethane dithiol.

Proposed Methods of Synthesis of Divinyl Sulfide

Several methods have been suggested as possible means of synthesis of divinyl sulfide and mustard gas from acetylene among these are:

(1) The homogeneous gas phase reaction between hydrogen sulfide and acetylene. The two reactants might combine directly to give divinyl sulfide under suitable conditions



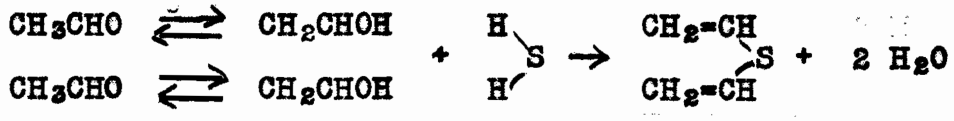
Temperature, pressure and concentration might be varied to find the optimum conditions for the reaction.

(2) Above reaction, catalytically - Several catalysts might be tried. The acetylene and hydrogen sulfide in the presence of a suitable catalyst might yield divinyl sulfide. Also the effect of steam might be investigated to approximate conditions in the manufacture of acetylene where divinyl sulfide is formed. It also must be remembered here that hydrogen sulfide and acetylene over alumina gel at 400°C. yields thiophene.

(3) Acetylene with a sulfur containing catalyst. Acetylene might be passed over a catalyst containing sulfides or sulfates or both and yield divinyl sulfide. In the manufacture of acetylene, the acetylene might react with hydrogen sulfide produced, or with the sulfur in the solid catalyst directly. Various conditions of temperature and pressure might be employed.

(4) Ethylene-chloride and hydrogen sulfide - the homogeneous gas phase reaction might yield mustard gas and if the reaction went, would probably eliminate the difficulty of getting the chlorine atoms into the β and β' positions. Ethylene chloride is readily made from acetylene.

(5) Acetaldehyde and hydrogen sulfide. These, under suitable conditions might react:



$$\begin{array}{lcl} CH_3CHO & \rightleftarrows & CH_2CHOH \\ CH_3CHO & \rightleftarrows & CH_2CHOH \end{array} + \begin{array}{c} H \\ H \end{array}\!\!>S \rightarrow \begin{array}{c} CH_2{=}CH \\ CH_2{=}CH \end{array}\!\!>S + 2\,H_2O$$

This would, of course, introduce an extra step into the syntheses, that of preparing acetaldehyde from acetylene, but this is already done on a large scale commercially.

(6) Ethylene oxide. This can also be prepared from acetylene. It is known to form thiodiglycol which gives quantitative yields of mustard gas on treatment with hydrogen chloride. However, to prepare the ethylene oxide, the chlorohydrin is an intermediate step and it is known that mustard gas can be prepared from the chlorohydrin as was done in the old Victor Meyer method.

Thus far only the homogeneous gas phase hydrogen-sulfide - acetylene reaction and the catalytic reactions of acetylene and hydrogen sulfide, and acetylene with the sulfate catalyst have been investigated. The reaction between ethylene chloride and hydrogen sulfide was also attempted.

Determination of Divinyl Sulfide.

From a consideration of the reactions of hydrogen sulfide and acetylene carried out by Chichibabin and Bagdassarjang (12) and Margaret G. Tomkinson (13) the product of any reaction where divinyl sulfide is expected, might be expected to be very complex. Therefore in the determination of divinyl sulfide tests must be used which are specific for divinyl sulfide and give results in the presence of thiophenes, mercaptans and organic sulfides. Many of these latter compounds have boiling points very close to that of divinyl sulfide and cannot be removed by distillation.

The reaction with halogens (6) does not make a conclusive test as it is difficult to add just the correct amount of halogen to cause complete reaction. Further only chlorine forms stable products. With halogen acids (1,6) the same difficulties are encountered. The crystalline derivative with hydriodic acid (6) is difficult to obtain. Phenol and thiophenol (6) also react to give solid derivatives which are much preferable to liquid derivatives provided they can be obtained in a very pure state.

Chloramine T, when mixed with divinyl sulfide readily forms a solid derivative melting at 92.9-93.4°C. (3,5). This is the best method of identifying divinyl sulfide as it is quite specific and the crystals are readily obtained from alcohol.

The presence or absence of thiophene, boiling point 84°C., can be detected by using a solution of isatin in concentrated sulfuric acid (15). A blue color results if thiophene is present.

Most of the mercaptans and organic sulfides will be separated from any divinyl sulfide by fractional distillation.

HOMOGENEOUS GAS PHASE REACTION BETWEEN C_2H_2 AND H_2S

Apparatus and Experimental Procedure

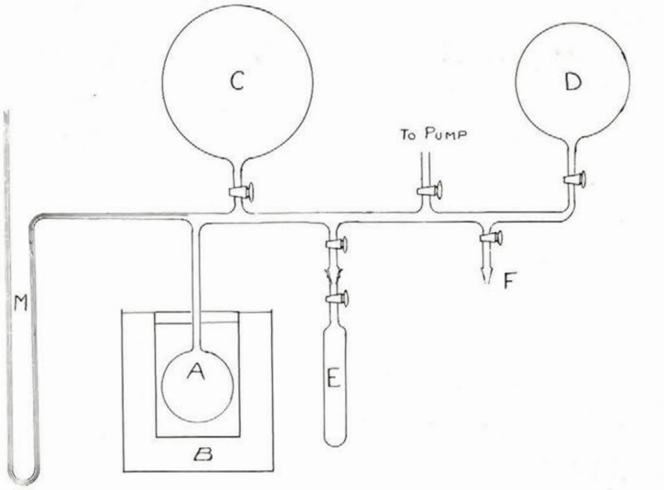
The experimental work on this reaction was done in a modification of the usual constant volume type, using a pyrex reaction vessel A. of 1500 cubic centimeters capacity, in an electric furnace B. The reacting gases were stored in large bulbs C. and D. and drawn into the evacuated reaction vessel. The hydrogen sulfide was admitted first since it is stable at the temperatures used whereas acetylene would polymerise slightly. The ratio of hydrogen sulfide to acetylene by volume was 1:2, the total pressure being about 50-75 cms. of mercury. As the reaction proceeded its course was followed by pressure changes which were recorded on the mercury manometer M. The furnace temperature was varied for the different runs by means of a rheostat and maintained constant to ±1°C. throughout each run by manual control of the rheostat. The temperature was measured using a chromel-alumel thermocouple connected to a millivoltmeter-potentiometer. The products were condensed out in the trap E which was surrounded by liquid air in a Dewar vessel. Residual gases were pumped off through the ground joint F by means of a Toeppler pump and stored over mercury in a gas holder. The trap was then surrounded by a dry-ice acetone mixture in a Dewar-vessel and the trap and its contents allowed to warm up to -80°C. Any gaseous material condensible in liquid air but not in dry ice-acetone mixtures were removed by another Toeppler pump and stored over mercury in a gas holder. Vacuum was obtained by means of a Langmuir pump in series with a Hyvac oil pump, fitted with a gas exit connection to dispose of obnoxious gases.

Runs were made at 125°C., 275°C., 375°C. and at 25° intervals to 500°C. A record of pressure change with time was kept.

Results.

At 125°C. no visible reaction occurred. At 275°C. a 15% pressure decrease was recorded in 6 hours. At 375°C. the same pressure change was accomplished in 3 hours. The rates gradually increased with temperature until at 500°C. a pressure change of 30% was recorded in 30 minutes.

Each run to a 20% pressure change yielded 0.2-0.5 ccs. of a pale yellow oil, which was solid at -80°C. and


C
D
TO PUMP
M
F
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E
B

darkened on standing at room temperature. In addition, a small amount of a dark brown gum was found in the bottom of the trap, and along the glass tubing connecting the furnace and the trap. The amount of the gum formed seemed to increase as the temperature was raised.

Approximately 50 runs of about 3 hours duration were made at temperatures between 375 - 400°C. and initial pressures from 65 - 75 cms. of mercury.

Distillation of the products at 10°C. under reduced pressure into a receiver at -183°C. resulted in the separation of a product which was colorless liquid at room temperature. The residue was the dark brown gum previously mentioned. It had an odor of the highly aromatic coal tar type and was soluble in benzene.

A boiling point determination was made on the distillate. About two-thirds of the liquid boiled at 84°C. some at 88°C. and a small amount at 96-98°C. An attempt was made to take the index of refraction of a sample of the larger fraction but the oil was too volatile for the Abegg refractometer available.

This behaviour coincides with the known behaviour of divinyl sulfide after such treatment, and indicates the presence of this compound in the reaction products.

Bromine added vigorously with the evolution of a slight amount of heat. Fumes of hydrogen bromide were given off, which persisted even after standing for a month.

In addition to the oil, there appeared to be a volatile fraction which boiled considerably below room temperature. However, it was not present in sufficient quantity to permit of its isolation and identification.

There was also considerable carbon deposition on the walls of the reaction vessel, when it was dismantled, but it is not known whether this occurred during every reaction or only during those at the higher temperatures.

A distillation of the residual gases was found impossible on a Podbielniak still, since acetylene sublimes rather than melts, and blocked the capillary at the bottom of the column. A combustion analysis was attempted also, but an explosion wrecked the combustion apparatus. A further attempt was planned but has not yet been carried out.

A sample of the oil was dissolved in a 10% aqueous solution of chloramine T and heated to 30°C. A brownish amorphous solid was precipitated, which on recrystallization from alcohol was white and melted at 135-137°C.

Although divinyl sulfide reacts with chloramine T in an analagous manner, the melting point of the solid on recrystallization from alcohol is quite different, being about 93°C. This evidence indicates that the reactive substance in the products is not divinyl sulfide.

Other tests planned are an isatin test to confirm the presence or absence of thiophene as well as a check test with chloramine T for divinyl sulfide and the complete analysis of the residual gases.

Discussion.

Acetylene and hydrogen sulfide do react at approximately atmospheric pressure and at temperatures above 250°C., the rate increasing with rise in temperature. Very likely this is due in part to the increased polymerization of acetylene at these higher temperatures. Acetylene begins to polymerise at around 300°C. and the rate increases with rise in temperature. The increased amount of gum deposited in the glass tubing and the trap at higher temperatures shows that the acetylene polymerizes in the presence of hydrogen sulfide. Thus the temperature at which the reaction is practical is limited by this polymerization as well as by the difficulties and expense of using high temperatures in an industrial process.

It cannot be definitely stated what the reaction products actually are. The fraction boiling at 84°C. might be divinyl sulfide, although, from consideration of the results of Chichibabin and Bagdassarjang (12) with the reaction at 400°C. over alumina gel it is not unlikely that it is thiophene. A check test with chloramine T will confirm the presence or absence of divinyl sulfide and the isatin test the presence of thiophene. The 88°C. fraction might be isobutyl mercaptan since that also is obtained in the acetylene-hydrogen sulfide reaction over alumina at 400°C.

Even a consideration of the results obtained to date seem to indicate that this method would not be at all suitable for a commercial process. The rate of reaction is quite slow, the yield is at most 40% if the 84° fraction is divinyl sulfide and quite complex products would have to be removed. Moreover the temperatures for even these slow rates are probably much too high for large scale operations.

Further work is necessary to make more definite conclusions, but it is very doubtful if a successful commercial process is possible with this reaction even if the main product is divinyl sulfide.

CATALYTIC REACTION OF HYDROGEN SULFIDE AND ACETYLENE

Apparatus and Experimental Procedure.

The apparatus used in this work was one using a flow system. The gas mixture was stored in a large glass bulb. The reaction vessel was a one inch diameter pyrex glass tube, heated in an electric furnace which was regulated and controlled similarly to the furnace used in the homogeneous reaction. The reaction vessel was packed with the catalyst. The gas mixture was drawn through the reaction vessel and then through a calibrated capillary flowmeter into an evacuated trap immersed in liquid air in a Dewar vessel. The unreacted gases were allowed to escape as the trap warmed up to room temperature. The catalysts used were calcium oxide and calcium sulfate and a mixture of the two. Stoichiometric proportions of acetylene and hydrogen sulfide were used, i.e. 2:1 by volume. Runs were made at 125°C. and 300°C. and the rate of flow was two ccs. of the gas mixture per second.

Results and Discussion.

No reaction took place at 125°C. or at 300°C. The catalyst was unchanged at the end of the experiment. Only a slight amount of moisture remained in the trap after it warmed up to room temperature.

This method may be rejected without further consideration, particularly in view of the fact that with a large number of catalysts and at higher temperatures (12), thiophene is produced in large yields.

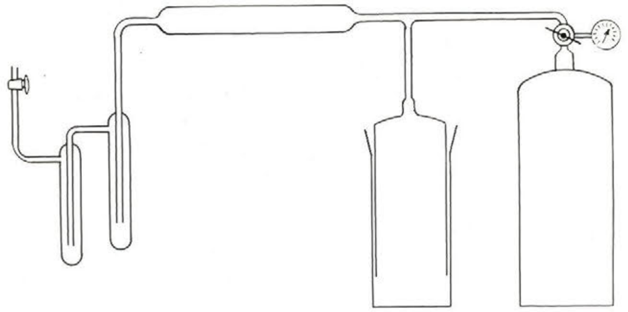
CATALYTIC REACTION OF ACTEYLENE WITH SULFUR IN CATALYST

Apparatus and Experimental Procedure

A flow system was also used in the investigation of this reaction. The reaction vessel and electric furnace used were similar to those used in the acetylene-hydrogen sulfide catalytic reaction. The acetylene was admitted to the reaction vessel directly from the cylinder. A five-litre gas holder was connected by a T joint to the acetylene line to guarantee a constant flow and pressure of acetylene through the reaction vessel. The products were drawn through two traps in series, each of which was immersed in a dry ice - acetone mixture, by expansion into a large glass bulb which had been previously evacuated. A scratched stopcock between the reaction vessel and the trapping system was used to regulate the flow of material from the furnace.

The catalyst used was alumina gel, made as follows: Metallic aluminum was dissolved in concentrated sodium hydroxide solution. The mixture was neutralized slowly with concentrated sulfuric acid and the resulting precipitate washed with a little water to remove some of the excess sodium sulfate. It was then filtered by suction on a Buchner funnel and dried in an oven at 100-110°C. overnight. The reaction vessel was packed with the catalyst in pieces about the size of a pea. Since the catalyst was washed with only a small amount of water considerable quantities of sodium sulfate would be included in the solid. The catalyst was activated by heating it for four hours at 425°C. in a stream of nitrogen, one cubic centimeter per second.

Runs were made at temperatures ranging from 360°-490°C. The catalyst was generally renewed after approximately 48 litres of acetylene had passed over it, at a rate of 2.5 cc. per second. Pressures were about atmospheric.



Results

From each 48 litres of acetylene, approximately 3-5 cc. of a yellow oil were obtained, the amount depending on the temperature of the reaction. Over the range examined, the amount of product from each run increased with rise in temperature. The liquid product contained a small amount of low boiling constituents and about half a cubic centimeter of a dark brown gum. This was similar to the homogeneous reaction between acetylene and hydrogen sulfide. The catalyst was completely blackened throughout every lump and the reaction vessel itself was coated with a slight deposit of carbon. The odor was of the highly aromatic coal tar type.

The liquid products were distilled in vacuo at 20°C. into a trap maintained at -183°C. A clear yellow oil resulted. A fractionation of this liquid was made. Liquid came over continuously from 50°C. to 110°C., the main fraction, of about 40%, was taken from 84-86°C.

A test for thiophene was made on this 84-86°C. fraction using isatin dissolved in concentrated sulfuric acid (15). No blue color was noticed, indicating the absence of any thiophene.

About 2 ccs. of this same fraction was added to a 10% aqueous solution of chloramine T, and heated to 30°C. No precipitate was found, but it was later discovered that the available chloramine T had deteriorated and would no longer react as such. It is planned to repeat this test.

The action of halogens on this oil was studied. Chlorine (6) gas, passed through the liquid resulted in a colorless solution. Absorption occurred readily and without appreciable evolution of heat. Bromine (6) also added readily, resulting in a fuming oil. The fumes identified as hydrogen bromide persisted even after a month. Both of these point to divinyl sulfide as the product.

Hydriodic acid was added to an alcoholic solution of the 84-86°C. fraction (6). It added readily at 50°C., the material darkening and finally yielded a layer of dark green oily liquid, the nature of which was not determined.

Discussion.

A reaction does occur when acetylene is passed over an alumina gel catalyst containing sulfates, at 350-490°C. The rate, as indicated by the amount of product obtained for every 48 litres of acetylene, increases with temperature over this range, but here again polymerization of the acetylene occurs. The yield of products is small and even more complex than in the case of the homogeneous acetylene - hydrogen sulfide reaction.

The liquid products were not positively identified. Thiophene is not present, and although the 84-86° fraction possessed a number of reactions similar to divinyl sulfide, the addition product with hydriodic acid, in alcohol solution, is not $\beta\beta'$ di-iodo diethyl sulfide. However, a test using chloramine T solution will positively confirm the presence or absence of divinyl sulfide.

The catalyst is very quickly used up. The amount of liquid products formed is greatest for the first 12 litres of acetylene passed over it. Practically none is obtained after 48 litres of acetylene have been passed over the catalyst. No attempt was made to reactivate the catalyst.

The method would seem to have little industrial promise. As in the case of the homogeneous acetylene hydrogen-sulfide reaction, temperatures required are probably in excess of those practical for large scale operation. The yield is small and the products complex. In addition to these objections, the catalyst is quickly destroyed and the connecting tubing between the furnace and the traps gels quickly coated with a dark sludge which would likely lead to trouble after operation for any considerable time.

The only further work planned on this reaction is a positive identification, with chloramine T solution, of the 84-86° fraction of the liquid products.

REACTION BETWEEN ETHYLENE CHLORIDE AND HYDROGEN SULFIDE

Experimental and Procedure.

The apparatus used for this experiment was similar to that used in the homogeneous gas phase reaction between acetylene and hydrogen sulfide. The ethylene chloride was stored in a small bulb, attached by one of the ground joints. The tubing between this bulb and the reaction vessel was electrically heated by a helix of nichrome wire. The ethylene chloride was admitted to the evacuated reaction vessel by heating with a small flame. The hydrogen sulfide was then admitted. The ratio of ethylene chloride to hydrogen sulfide was 2:1 by volume; the total pressure was atmospheric. The reaction vessel was maintained at 200°C. Reaction was allowed to proceed for ten hours.

Results and discussion.

No pressure change was expected nor did any occur. When the products were condensed out in a trap in liquid air, there appeared to be two layers of liquid in the trap, one of which was the unreacted ethylene chloride. This liquid was vapourized into a 1% solution of selenious acid in concentrated sulfuric acid. If more than 0.005 milligrams of mustard gas were present, a red precipitate of selenium would be detected. No such precipitate or coloration occurred, so that is very doubtful if mustard gas were present. The residual gases were drawn through a solution of silver nitrate, to test for the presence of hydrogen chloride. No precipitate of silver chloride was obtained, also indicating that no reaction occured.

The above method was attempted in an effort to avoid the difficulty encountered in chlorinating divinyl sulfide to mustard gas. However it must be concluded that no mustard gas is obtained under the above conditions from ethylene chloride and hydrogen sulfide.

DISCUSSION

The possibilities of synthesising mustard gas from acetylene have been investigated, particularly through divinyl sulfide as an intermediate product. No definite conclusions may be reached from a consideration of the work done to date. It seems still possible, though remotely so, that, divinyl sulfide might be obtained from the homogeneous gas phase reaction between hydrogen sulfide and acetylene or from, the catalytic reaction of acetylene with solid sulfides or sulfates. However, on account of the high temperatures required, poor yields, and complexity of the products it seems very unlikely that it is commercially possible to prepare divinyl sulfide from acetylene, and especially so, when the low cost of the present manufacture of mustard gas from ethylene and sulfur chloride is taken into account. From a theoretical point of view, the reaction might well be further investigated to determine the products of the reaction and to estimate the yields obtainable. This would take considerable time due to the very low yields which are obtained.

In addition to the difficulty of preparing divinyl sulfide from acetylene, there is the problem of obtaining mustard gas from it. The work of Bales and Nickelson (1) has shown that hydrogen chloride adds to divinyl sulfide to give $\alpha\alpha'$dichloro diethyl sulfide, a harmless, non vesicoant isomer of mustard gas. Hydrogen bromide adds similarly. Thus some method of chlorinating must be sought which would result in the $\beta\beta'$dichloro diethyl sulfide. It seems that it would be well to investigate this aspect of the problem before a too lengthy investigation of the synthesis of divinyl sulfide from acetylene.

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