A THESIS

entitled

INHIBITION OF REACTIONS
IN HYDROGEN–CHLORINE FLAMES

submitted by

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2. ABSTRACT.

This thesis describes studies of the inhibition and promotion of the chemical reactions taking place in hydrogen-chlorine flames. The effects of twelve additives are compared by measuring an increase or decrease in the burning velocity when a particular additive is introduced.

The Introduction reviews all the previous work done on both the slow and explosive reaction of hydrogen with chlorine. Possible mechanisms are discussed, and inhibition and promotion studies are described.

The Experimental section describes the apparatus, the photographic arrangement and the method of calculation of the burning velocity.

The method of presentation of the results of burning velocity measurements for hydrogen-chlorine-additive flames, burning with either an air surround or a nitrogen surround, is described at the beginning of the Results section. For flames burning with a nitrogen surround, methane, deuteromethane-$d_4$, acetylene, methyl chloride and methyl bromide promote the reaction, whilst ethane, n-butane, isobutane and ethylene inhibit the reaction. Dimethyl ether and oxygen show both promoting and inhibiting effects.
In the Discussion it is shown that application of several theories of flame propagation cannot discriminate between the two possible mechanisms, viz. normal chain propagation and energy-branching, in operation in hydrogen-chlorine flames.

It is found that an increase in the flame temperature can account for only part of the observed effect when an additive is introduced. Diffusion of the surrounding atmosphere into the flame also apparently affects the results.

A normal chain propagation scheme is preferred to an energy-branching scheme. The production and subsequent decomposition of chloro derivatives of the additives explains many of the experimental observations. In general, those additives giving free radicals and atoms on decomposition of the chloro derivative are good promoters, and those giving reasonably stable products are relatively poor promoters.
ACKNOWLEDGMENTS

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Department of Chemical Engineering and Chemical Technology,
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INTRODUCTION.
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## Section 1. Introduction

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1.1. General.

Although the explosive reaction of hydrogen with chlorine has been extensively studied by many workers, the mechanism still remains in some doubt. On the other hand, the kinetics of the slow hydrogen-chlorine reaction are now fairly well established. The initiation and termination steps vary according to the experimental conditions but the reaction is believed to be propagated by a non-branching chain cycle involving hydrogen and chlorine atoms, as originally suggested by Nernst 1

\[
\begin{align*}
(1) \quad & \text{Cl} + \text{H}_2 \xrightarrow{k_1} \text{HCl} + \text{H} \\
(1') \quad & \text{H} + \text{HCl} \xrightarrow{k_1'} \text{H}_2 + \text{Cl} \\
(2) \quad & \text{H} + \text{Cl}_2 \xrightarrow{k_2} \text{HCl} + \text{Cl}
\end{align*}
\]

Reaction (1) is almost thermoneutral, and the reverse reaction (1') which will have a similar activation energy, is also included. Furthermore, reaction (2) has a much lower activation energy than reaction (1) and is considered to be the most facile propagation step 2,3.

The applicability of the Nernst scheme to the explosive reaction is rather less conclusive, particularly
when a third body is present in the reactant mixture. In this section, however, an attempt will be made to see how far the mechanism believed to operate during the slow reaction can be used to explain the experimental features of the explosive reaction. Thus, in the first instance, a brief account is given of the slow reaction and then, later on, the possible relevance of the proposed mechanism to flame reactions is discussed.

1.2. The slow reaction between hydrogen and chlorine.

1.2.1. The photochemical reaction.

The interaction of hydrogen and chlorine under the influence of light was first observed by Cruickshank. It has since been shown that reaction can be brought about by absorption of light of any wavelength less than 478 millimicrons, and in the region of weak banded absorption (mercury green line) as far as 546 millimicrons. Numerous studies have now been made of the photochemical reaction and it is now widely accepted that the Nernst chain satisfactorily accounts for most of the kinetic features.

According to this, initiation takes place by the photodissociation of chlorine molecules,

\[(3) \text{Cl}_2 + h\nu \xrightarrow{k_3} \text{Cl} + \text{Cl}\]
followed by the propagation steps (1), (1') and (2); the most likely termination steps are:

(4) \[ \text{Cl} + \text{Cl} + M \xrightarrow{k_4} \text{Cl}_2 + M \]

(5) \[ \text{H} + \text{H} + M \xrightarrow{k_5} \text{H}_2 + M \]

(6) \[ \text{H} + \text{Cl} + M \xrightarrow{k_6} \text{HCl} + M \]

where \( M \) is the third body. It has been shown that removal of chlorine atoms by reaction (4) is the main termination step.

The rate of initiation equals \( \Phi I_{\text{abs}} \), where \( \Phi \) is the quantum efficiency of the primary reaction, expressed as the number of chlorine atoms produced per quantum absorbed, and \( I_{\text{abs}} \) is the number of quanta absorbed per second per unit volume. If reactions (5) and (6) are neglected, a steady state analysis gives the rate of formation of hydrogen chloride as:

\[
\frac{d[H\text{Cl}]}{dt} = \frac{2k_1 k_2 [H_2][\text{Cl}_2]}{k_3[\text{Cl}_2] + k_1' [H\text{Cl}]} \left[ \frac{\Phi I_{\text{abs}}}{k_4 M} \right]^{\frac{1}{2}}
\]

1.2.1.1.

and the chain length as:

\[
\frac{\lambda}{\Phi} = \frac{2k_1 k_2 [H_2][\text{Cl}_2]}{k_3[\text{Cl}_2] + k_1' [H\text{Cl}]} \left[ \frac{\Phi k_4 [M] I_{\text{abs}}}{k_4 M} \right]^{\frac{1}{2}}
\]

1.2.1.2.
\[ \gamma \] is the quantum yield, defined as the number of molecules of hydrogen chloride formed per quantum of light energy absorbed.

If reaction (1') is neglected, the rate equation takes the form:

\[
\frac{d [HCl]}{dt} = 2k_1 [H_2] \left( \frac{\Phi_{\text{labs}}}{k_2 [H]} \right)^{\frac{1}{2}} \quad \ldots \ldots \quad 1.2.1.3.
\]

According to the above analysis the rate of reaction would be expected to be proportional to the square root of the light intensity for termination occurring only in the gas phase, and a similar analysis shows that the rate of reaction is proportional to the first power of the light intensity when termination takes place only at the walls of the vessel. Depending on the experimental conditions, the rate of reaction is found to be proportional to a power of the light intensity between 0.5 and 1.0 \(^6\).\(^{10}\)

A study of the effect of temperature showed that the rate of reaction increased by a factor of 1.37 for every 10°C rise in temperature \(^11\).

The rate of reaction is found to depend on other experimental conditions and in particular the total pressure. Three distinct pressure effects have been observed. At very low pressures (0.2 - 3 mm. Hg) wall
termination is efficient \(^{12-14}\) and reaction (4) is probably important. Removal of chain centres takes place by the reactions:

\[
\begin{align*}
(7) \quad & \text{Cl} + \text{wall} \xrightarrow{k_7} \text{destruction} \\
(8) \quad & \text{H} + \text{wall} \xrightarrow{k_8} \text{destruction}
\end{align*}
\]

At intermediate and higher pressures where termination takes place both in the gas phase and at the walls of the vessel, further termination reactions, including the formation and removal of \(\text{Cl}_3\) radicals, have been proposed \(^{5-7,15,16}\).

\[
\begin{align*}
(9) \quad & \text{Cl} + \text{Cl}_2 \xrightarrow{k_9} \text{Cl}_3 \\
(10) \quad & \text{Cl}_3 \xrightarrow{k_{10}} \text{Cl} + \text{Cl}_2 \\
(11) \quad & 2\text{Cl}_3 \xrightarrow{k_{11}} 3\text{Cl}_2 \\
(12) \quad & \text{Cl} + \text{Cl}_3 \xrightarrow{k_{12}} 2\text{Cl}_2
\end{align*}
\]

Reaction (9) has been suggested to occur when chlorine atoms of sufficiently high energy content react with chlorine molecules \(^5\) and \(\text{Cl}_3\) may subsequently be removed by a three-body collision at the vessel walls \(^7\), or by further dissociation.
Reactions (9) to (12) have been included to explain the experimental findings in the pressure range (3-200 mm.Hg.) where the rate of reaction has been found to be directly proportional to the chlorine pressure 17.

At pressures greater than 200 mm.Hg. reactions (9) to (12) are again believed to occur and the general findings may be summarised as a rate expression of the type 5,9,17,18:

\[
\text{rate} = \frac{k \left[ \text{Cl}_2 \right]^0 \left[ \text{H}_2 \right]}{[\text{HCl}]} \quad \ldots \ldots \quad 1.2.1.4.
\]

Finally Chapman and Grigg 14 showed the relationship between the rate of reaction and total pressure to be:

\[
\text{rate} \propto (\text{total pressure})^{2.5} \quad \ldots \ldots \quad 1.2.1.5.
\]

1.2.2. The thermal reaction.

The thermal reaction between hydrogen and chlorine is believed to take place by a mechanism generally similar to that of the photochemical reaction. The chief difference is that in the thermal reaction both chain initiation and chain termination take place mainly at the walls 19-22. Initiation occurs by the thermal reaction:

\[
(13) \quad \text{Cl}_2 + \text{wall} \xrightarrow{k_{13}} \text{Cl} + \text{Cl} + \text{wall}
\]
The propagation steps are described by reactions (1), (1') and (2) and termination takes place principally as a result of the heterogeneous recombination of chlorine atoms:

\[ (14) \quad \text{Cl} + \text{Cl} + \text{wall} \xrightarrow{k_{14}} \text{Cl}_2 + \text{wall} \]

Application of the steady state method gives the following expression for the rate of reaction:

\[
\frac{d[HCl]}{dt} = \frac{2k_1 k_2 [\text{Cl}_2] [\text{H}_2]}{k_s [\text{Cl}_2] + k_1 [\text{HCl}]} \left( \frac{k_{13}}{k_{14}} \right)^{\frac{1}{2}} [\text{Cl}_2]^{\frac{1}{2}} \quad 1.2.2.2.
\]

and, if, as before, reaction (1') is neglected, this becomes:

\[
\frac{d[HCl]}{dt} = 2k_1 \sqrt{\frac{k_{13}}{k_{14}}} [\text{H}_2] [\text{Cl}_2]^{\frac{1}{2}} \quad 1.2.2.2.
\]

For a vessel coated with potassium chloride experimental results have confirmed a rate expression very similar to equation 1.2.2.2.\textsuperscript{19}, but the experimental evidence with other surfaces has shown the rate to be either independent of \textsuperscript{23,24}, or directly proportional to \textsuperscript{19,20} or proportional to the square of the hydrogen pressure. The rate has also been found to be proportional to the first power of the chlorine pressure \textsuperscript{19,20} and to be either dependent on \textsuperscript{19,24} or independent of \textsuperscript{20,23} the hydrogen chloride pressure, according to the experimental conditions used. The nature of the surface of the reaction vessel
was again found to affect the kinetics, and the rather conflicting results were explained by a mechanism involving chain-initiation by dissociation of hydrogen molecules and chain termination as a result of the heterogeneous recombination of hydrogen and chlorine atoms:

\[
\begin{align*}
(15) \quad H_2 + \text{wall} & \xrightarrow{k_{15}} H + H + \text{wall} \\
(16) \quad H + Cl + \text{wall} & \xrightarrow{k_{16}} HCl + \text{wall}
\end{align*}
\]

The reaction has also been investigated in the presence of other added initiators, including hydrogen atoms, chlorine atoms, ionised nitrogen, alpha particles, and X-rays. These experiments confirmed that absorbed light was involved in the initiation step only, the reaction then following the Nernst scheme.

1.2.3. Catalysis of the slow reaction.

The slow reaction is liable to inhibition by diluents whose effect may be purely physical (e.g. cooling), or to catalysis by substances which become chemically involved in the reaction. It is often quite difficult to differentiate between physical and chemical mechanisms, and indeed in many cases both effects are clearly involved.
1.2.3.1. **Physical additives**.

Reactions at the walls of the containing vessel have been shown to influence the kinetics by production of chlorine atoms (reaction (13)) and by removal of chlorine atoms (reactions (14) and (16)) and of hydrogen atoms (reaction (16)) \(^{12,13,22,30}\); these effects have already been discussed.

Although the experimental results are not quite definite, it appears that hydrogen chloride exerts some inhibiting effect in the gas phase \(^{7,9,23,24,30}\). Water vapour also has been found both to promote and to retard the reaction under various conditions \(^{3,31-33}\).

1.2.3.2. **Chemical additives**.

Studies have been made of the influence of nitrogen compounds and of oxygen only, and the behaviour of these additives is therefore discussed in detail.

**Nitrogen compounds.**

A study of the effects of nitrogen compounds on the temperature and pressure ignition limits has been made by Ashmore and his co-workers \(^{34-38}\). These results are discussed here in order to distinguish them from the flame reactions which are considered later.
Small amounts of nitrosyl chloride were added to equimolar mixtures of hydrogen and chlorine at 300°C and at total pressures less than 150 mm Hg. An induction period was observed which increased with the concentration of nitrosyl chloride, but was followed by a reaction proceeding at a constant rate. The replacement of nitrosyl chloride by nitric oxide reduced the induction period.

During the induction period nitrosyl chloride is assumed to decompose to give chlorine atoms:

\[
(17) \quad \text{NOCl} + M \xrightarrow{k_{17}} \text{NO} + \text{Cl} + M
\]

and this reaction is followed by a further initiation step:

\[
(18) \quad \text{NO} + \text{Cl}_2 \xrightarrow{k_{18}} \text{NOCl} + \text{Cl}
\]

and by the propagation steps (1) and (2). The termination reaction is:

\[
(19) \quad \text{Cl} + \text{NOCl} \xrightarrow{k_{19}} \text{NO} + \text{Cl}_2
\]

This mechanism gives rise to a rate equation of the form:

\[
\frac{d[\text{HCl}]}{dt} = \frac{k[H_2] [\text{Cl}_2] [\text{NO}]}{[\text{NOCl}]} \quad \ldots \ldots \quad 1.2.3.2.1.
\]

At ignition temperatures above 390°C small amounts of nitrosyl chloride sensitised explosion and lowered the ignition boundary, presumably due to the formation of nitric oxide by reaction (17).
At the same total pressure and at low temperatures (250°C), as little as 1 mm Hg of chloropicrin considerably lowered the ignition boundary. At higher temperatures the formation of nitrosyl chloride by decomposition tended to inhibit the reaction, but at still higher temperatures (above 400°C), the sensitising effect, described above, was observed.

At atmospheric pressure nitrogen trichloride has an inhibiting effect on the photochemical reaction:

\[(20) \ NCl_3 + Cl + M \xrightarrow{k_{20}} NCl_4 + M\]

whilst at low pressures it may sensitise the reaction in the dark, causing explosion. Initial decomposition of nitrogen trichloride appears to take place by the reaction

\[(21) \ NCl_3 \xrightarrow{k_{21}} NCl_2 + Cl\]

**Oxygen.**

Oxygen is generally accepted to be an inhibitor of the slow reaction, the most important terminating steps being:

\[(22) \ H + O_2 + M \xrightarrow{k_{22}} HO_2 + M\]

\[(23) \ Cl + O_2 + M \xrightarrow{k_{23}} ClO_2 + M\]
Experimental results for the photochemical reaction have led to the rate expressions

\[
\frac{d[HCl]}{dt} = k \frac{I_{abs}[Cl_2]}{[O_2]} \quad \ldots \ldots \ldots \quad 1.2.3.2.2.
\]

and

\[
\frac{d[HCl]}{dt} = k \frac{[Cl_2]^2}{[O_2]} \quad \ldots \ldots \ldots \quad 1.2.3.2.3.
\]

provided that the hydrogen pressure is not too low. A general equation has been proposed which holds over quite a wide range of partial pressures of hydrogen:

\[
\frac{d[HCl]}{dt} = \frac{k [H_2][Cl_2]^2}{k'[H_2]^{(2-x)}[O_2] + [Cl_2]} \quad 1.2.3.2.4.
\]

where \(x < \frac{1}{2}\). The latter equation indicates that inhibition is appreciable only when hydrogen is present in large amounts. This suggests that reaction (22) is the most important chain-terminating step.

Due to the probable instability of \(HO_2\) and \(ClO_2\) at high temperatures, inhibition of the thermal reaction is less effective than for the photochemical reaction. For the thermal reaction, where initiation occurs at the walls of the vessel and termination either at the walls or in the gas phase \(22,24,41,42\), a rate equation has been obtained which satisfactorily describes the experimental results \(24\):
A comparison between nitrogen trichloride and oxygen suggests that the former is the more effective inhibitor. Nitrogen trichloride removes chlorine atoms by reaction (20), whereas the inhibiting effect of oxygen probably involves reaction (22). On the basis of the propagation steps (1) and (2), already outlined, it would appear that chlorine atoms are the principal species involved in chain termination.

1.2.4. General mathematical analysis.

Ashmore has proposed a general expression for the rate of production of hydrogen chloride, which is valid for both the photochemical and thermal reactions. If \( \theta \) is the rate of generation of chain centres and \( \alpha \) is the probability that a given centre, as a result of undergoing reactions (1) and (2), will create a new centre, then:

\[
\text{Rate of reaction} = \theta \left( \frac{\alpha}{1-\alpha} \right) \quad \text{............ 1.2.4.1.}
\]

By considering two chain centres, e.g. a hydrogen atom and a chlorine atom, whose probabilities of reacting to produce a new centre are \( \alpha \) and \( \beta \) respectively, the rate of reaction is given by the expression:

\[
\frac{d[HCl]}{dt} = \frac{k[Cl_2]}{[HCl] + k'[O_2]} \quad \text{........ 1.2.3.2.5.}
\]
Rate = θ \left[ \frac{(1 + \beta)}{1 - \alpha \beta} \right] \quad \ldots \ldots \quad 1.2.4.2.

This expression may be modified, using the same principles, for the case where a known additive is present in the system.

1.3. The explosive reaction between hydrogen and chlorine.

As in the photochemical reaction, dissociation of chlorine molecules results from absorption of light, so in the flame reaction an initial source of energy, such as a pilot flame, is usually necessary to start reaction, by providing the energy required to effect dissociation of chlorine molecules. The hydrogen-chlorine flame, once ignited, burns with the evolution of light and a large amount of heat. Indeed, flame temperatures may be as high as 2500°K \textsuperscript{44,45}. The heat from the flame front may be transferred back towards the cold, unburnt mixture and may thus provide sufficient energy for further dissociation of chlorine molecules.

1.3.1. Physical measurements on flames.

As with slow combustion, certain physical measurements provide a description of stationary and explosive flame propagation, and these are now considered.
1.3.1.1. **Flammability limits.**

A flammable mixture may be defined as one in which a flame will propagate after an initial source of ignition is removed. With a non-flammable mixture the flame will die away. The limit of flammability is the boundary composition which separates mixtures capable of propagating flame from those which are not. With fuel-rich mixtures an upper limit is reached, and with oxidant-rich mixtures, a lower limit. Between these limits a flame will propagate at any mixture composition.

Several experimental limit values for hydrogen-chlorine mixtures have been determined, but the conflicting results indicate that the influence of external factors such as vessel diameter, method of ignition and direction of flame propagation (upward, downward) have not been entirely eliminated. A comparison of results is given in Table I, from which it may be seen that flame propagation may be possible for mixtures with a hydrogen content of between 3.9 and 89.0%. 
<table>
<thead>
<tr>
<th>Lower Limit %H₂</th>
<th>Upper Limit %H₂</th>
<th>Method of Ignition</th>
<th>Direction of Propagation</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.8</td>
<td>88.5</td>
<td>Spark</td>
<td>Upward</td>
<td></td>
<td>46</td>
</tr>
<tr>
<td>5.0</td>
<td>89.0</td>
<td>Spark</td>
<td>Upward</td>
<td>Temp. 50°C.</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pressure 380 mm.Hg.</td>
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</tr>
<tr>
<td>3.9</td>
<td></td>
<td>Spark</td>
<td>-</td>
<td>Pressure increases lower limit.</td>
<td>48</td>
</tr>
<tr>
<td>10.4</td>
<td>83.9</td>
<td>Spark</td>
<td>Downward</td>
<td>Small Explosion Vessel.</td>
<td>49</td>
</tr>
<tr>
<td>7.0</td>
<td>83.0</td>
<td>Spark</td>
<td>-</td>
<td>Small Glass Sphere 14 cm³.</td>
<td>50</td>
</tr>
<tr>
<td>6.0</td>
<td>84.5</td>
<td>Spark</td>
<td>-</td>
<td>Steel Bomb. 810 cm³.</td>
<td>50</td>
</tr>
<tr>
<td>5.5</td>
<td>87.0</td>
<td>Spark</td>
<td>Centre</td>
<td>Compares two types of ignition</td>
<td>51</td>
</tr>
<tr>
<td>7.0</td>
<td>89.0</td>
<td>Hot wire</td>
<td>Centre</td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>8.1</td>
<td>85.7</td>
<td>Spark</td>
<td>Downward</td>
<td>Also compares ignition.</td>
<td>52</td>
</tr>
<tr>
<td>9.8</td>
<td>52.5</td>
<td>Light</td>
<td>Downward</td>
<td>Burning Magnesium wire.</td>
<td>52</td>
</tr>
<tr>
<td>10.0</td>
<td>84.0</td>
<td>-</td>
<td>-</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>11.0</td>
<td>86.0</td>
<td>Spark</td>
<td>Upward</td>
<td>Atmospheric Pressure.</td>
<td>54</td>
</tr>
<tr>
<td>19.0</td>
<td>82.0</td>
<td>Spark</td>
<td>Upward</td>
<td>Pressure 100 mm.Hg.</td>
<td>54</td>
</tr>
</tbody>
</table>

N.B. Unless stated, all results refer to atmospheric temperature and pressure.
1.3.1.2. Flame temperature.

The temperature of a hydrogen-chlorine flame cannot be measured by the normal sodium line reversal method. Reasonably accurate estimates have resulted only from theoretical calculations based on the thermal properties of the mixture, and these suggest a maximum value of approximately 2500°K, for a mixture containing approximately 52% hydrogen, 48% chlorine.

The only experimental determinations give a maximum flame temperature of 1173°K using a platinum-rhodium thermocouple, and 1730°K using an infra-red spectrometer and radiation measurements. Both these values are accepted as being rather low, possibly due to heat losses.

1.3.1.3. Flame structure and radiation.

Flame structure and radiation studies have often been used to help obtain an understanding of the mechanism of flame reactions. Light emission is accepted as being caused by the recombination of normal and excited chlorine atoms, and the resulting continuum is reported to extend into the visible or near ultra-violet region 47,56 and perhaps as far as 2760 Å 58. The flame is pale greyish-green with a reddish border and a
non-visible inner cone \(^55,59\) which is luminous only with chlorine-rich mixtures \(^60\).

1.3.1.4. **Burning velocity.**

The burning velocity is usually defined as the velocity of the flame front relative to the unburnt gas, and in a direction normal to the flame front; this quantity can be shown to be directly proportional to the square root of the rate of reaction \(^61\). It may be measured, for example, by the means of the flat-flame burner \(^61\), the bunsen tube \(^62\) and the soap bubble method \(^62\), and the relative merits of these methods have been discussed in some detail \(^61-64\).

The co-ordination of experimental values of burning velocity with theories based on various suggested mechanisms of reaction provides a convenient means of testing the suitability of these mechanisms. Furthermore, burning velocity determinations may be used to compare relative rates of reaction of different mixtures.

At atmospheric pressure the maximum burning velocity of a hydrogen-chlorine flame has been determined experimentally as 410 cm.sec\(^{-1}\) \(^59\) and 480 cm.sec\(^{-1}\), for mixtures containing 64% and 60% hydrogen respectively. At lower pressures (35-260 mm.Hg) the corresponding value
is 225 cm\textsec^{-1} for a mixture containing 50\% hydrogen. The results are rather contradictory and generally suggest a maximum value between 400 cm\textsec^{-1} and 500 cm\textsec^{-1} for mixtures containing between 50\% and 64\% hydrogen.

1.3.2. Flame kinetics.

For convenience the chain propagation involved in the flame may be classified as:

1.3.2.1. Normal chain propagation.
1.3.2.2. Energetic chain propagation.

The first type of propagation includes non-branching reactions, whereas the second type is used to cover chain-branching reactions. The application of each of these concepts to the experimental results is now considered.

1.3.2.1. Normal chain propagation.

The experimental features of the hydrogen-chlorine reaction have been explained on the basis of a typical Nernst mechanism as shown in sections 1.1 and 1.2. An initial source of energy provides chlorine atoms in a much greater quantity than for slow combustion, and these are available for the propagation steps (1), (1') and (2). The heat associated with the flame is largely provided by the highly exothermic reaction (2) (+45 kcal.mole\textsuperscript{-1})
For stationary flames, termination of the reaction occurs in the gas phase and equilibrium conditions are suitable for the maintenance of a flame.

Rozlovskii 66 has calculated, from experimental data on burning velocity, the effective activation energy for the flame reaction under conditions where excess chlorine is present. The value found (34.7 kcal.mole\(^{-1}\)) was similar to that for the preflame reaction, suggesting that the Nernst scheme is again involved.

Theoretical values of burning velocity predicted from theories based on the Nernst scheme have been compared with experimental data, and whereas some have provided similar absolute values of burning velocity 67,68, others have been more successful in describing the variation of burning velocity with mixture composition 44,69,70. No single theory predicts both quantities accurately, but this may be due, in part, to unreliable experimental results.

1.3.2.2. Energetic chain propagation.

The presence of excited chlorine and hydrogen chloride molecules has been suggested 31 as an alternative means of explaining the kinetics of the
explosive reaction between hydrogen and chlorine. The existence of these high energy molecules has been used to explain the apparent occurrence of chain-branching.\textsuperscript{65,66}

The basic assumption made in mechanisms involving energised molecules is that the energy liberated in reaction (2) may be stored in the product molecule, hydrogen chloride, as vibrational energy:

\[ \text{(24)} \quad \text{H} + \text{Cl}_2 \xrightarrow{k_{24}} \text{HCl}^* + \text{Cl} \]

where HCl\(^*\) is an excited molecule.

Since the system may contain a number of chlorine molecules which, by Maxwell's distribution law, have a rather high energy, then if, on collision of chlorine molecules with excited hydrogen chloride molecules, the combined energies of the two species exceed the dissociation energy of chlorine, the chlorine molecules will dissociate into atoms:

\[ \text{(25)} \quad \text{HCl}^* + \text{Cl}_2 \xrightarrow{k_{25}} \text{HCl} + 2\text{Cl} \]

The probability of a collision leading to the above chain-branching reaction is rather small\textsuperscript{31}, and hence a large number of excited hydrogen chloride and chlorine molecules must be available. Subject to the same energy requirements for dissociation of chlorine molecules, an alternative step involving two excited hydrogen chloride
molecules is:

\[(26) \quad 2\text{HCl}^* + \text{Cl}_2 \xrightarrow{k_{26}} 2\text{HCl} + 2\text{Cl}\]

Although such a termolecular reaction will also result in dissociation of a chlorine molecule, it is less likely to take place than the bimolecular process. Experimental evidence is available for the existence of excited hydrogen chloride molecules, the presence of which has been suggested to explain other experimental features of the hydrogen-chlorine reaction.

A further chain-branching reaction may take place which does not involve excited hydrogen chloride molecules. This is:

\[(27) \quad \text{H} + 2\text{Cl}_2 \xrightarrow{k_{27}} \text{HCl} + 3\text{Cl}\]

which is endothermic to the extent of 12.0 kcal.mole\(^{-1}\).

As flame kinetics are usually studied by comparison of theoretical and experimental values of burning velocity, a brief review is now given of theories applicable to the hydrogen-chlorine flame reaction.

1.3.3. Flame propagation theories of burning velocity.

A general review of some of these theories is given elsewhere, and they may be classified as:
1.3.3.1. Diffusion theories.
1.3.3.2. Thermal theories.
1.3.3.3. Comprehensive and other theories.

1.3.3.1. Diffusion theories.

Models based on the transmission of reaction by the diffusion of active species, particularly hydrogen atoms \(^67,74\), from one gas layer to the next, give predictions which are not in good agreement with the experimental results \(^74\).

1.3.3.2. Thermal theories.

Models based on heat transfer by thermal conduction from one gas layer to the next, to initiate reaction in the newly-heated layer, have also not been successful in predicting accurate values of burning velocities \(^74\).

1.3.3.3. Comprehensive and other theories.

The nomenclature used in this section is as follows:

- \(S_u\) = burning velocity (cm/sec\(^{-1}\)).
- \(i\) = order of the branching reaction.
- \(T_f\) = final flame temperature (°K).
- \(T_o\) = initial temperature of the mixture (°K).
\[ T_m = \text{mean temperature of the flame front (°K)}. \]
\[ E = \text{energy of activation (kcal.mole}^{-1}). \]
\[ K = \text{constant}. \]
\[ R = \text{gas constant}. \]

Most recent theories have been based on the suggestion that reaction is created both by the transfer of heat and active species, and, although many of the derivations are unsuitable for application to hydrogen-chlorine flames, two theoretical sets of equations have met with limited success. Both theories assume an unbranched chain reaction and show good agreement with some experimental results.

For hydrogen-chlorine flames containing nitrogen as a diluent an equation has been proposed for \( i \) and \( E \):

\[ \log Su + \frac{1}{2} \log T_m - \frac{1}{2} \log Y = K - \frac{0.4343 E}{2RT_m} \quad 1.3.3.3.1. \]

where \( Y = \frac{100 - \% \text{ nitrogen}}{100} \quad 1.3.3.3.2. \)

and \( T_m \) is given by

\[ T_m = T_o + 0.74 (T_f - T_o) \quad 1.3.3.3.3. \]

For \( i = 2 \) this equation explains some of the experimental results if an energy branching scheme, including reactions (24) and (25), is assumed.
The above and similar expressions based on the Nernst scheme have been applied to other experimental measurements. Although, however, the experimental results are often unreliable, no single equation has been completely successful in predicting burning velocities, or even providing conclusive evidence for preferring one reaction mechanism to another. As is already shown here, the introduction of an additive to the flame may help to clarify the reaction mechanism, and the effects of other additives are now considered.

1.3.4. Catalysis of the explosive reaction.

As with the slow reaction it is often difficult to differentiate between physical and chemical mechanisms, but, for convenience, a chemical mechanism is considered as one in which an appreciable effect is observed for concentrations of additive as low as 5%.

1.3.4.1. Physical additives.

Inhibition of the reaction by thermal loss or dilution effects is most probable when additives are present in relatively large amounts. Flammability limits, burning velocity and flame temperature form the most important criteria for measurement.
Gaseous additives have little effect on the lower flammability limit. Nitrogen, hydrogen chloride, carbon dioxide and carbon monoxide all have similar inhibiting effects, approximately 70% being necessary to render a hydrogen-chlorine mixture totally non-flammable. Air has a less powerful inhibiting effect, 73% being necessary to prevent combustion, presumably due to reduction of the normal inhibiting effect by the oxygen present in the air.

Furthermore, 30-56% nitrogen is necessary for a 60% reduction in the maximum burning velocity, whilst theoretical calculations have shown that approximately 46% nitrogen is necessary to reduce the flame temperature by 1000°K.

Nitric oxide normally exerts an inhibiting effect by narrowing the flammability limits but may promote reaction in hydrogen-rich mixtures. This last effect may be due to hydrogen burning in nitric oxide.

In contrast to the slow reaction, the limits are little affected by increasing the water content of the gas mixture to 87% relative humidity.

The explosive reaction has been extensively studied in the presence of a large number of additives, and it is found that a high concentration of any "physical
diluent" is needed to produce significant effects. Apart from being very wasteful, combustion under these conditions may warrant the use of large and clumsy apparatus. From this point of view it is desirable to investigate the effects of additives present only in small concentrations.

1.3.4.2. **Chemical additives.**

Propane has been reported as the only successful chemical inhibitor of the hydrogen-chlorine explosive reaction, a 10% addition lowering the upper flammability limit from 87% to 60% hydrogen 79. On the other hand oxygen has a promoting effect, as little as 6% raising the upper flammability limit to 95% hydrogen 48,49,51.

However, Corbeels and Scheller 65 observed surprisingly large promoting effects when small amounts of methane, methylene dichloride, chloroform, carbon tetrachloride and stannic chloride were added separately to a hydrogen-chlorine flame of maximum burning velocity composition, and containing 30% nitrogen. Promoting effects reached a maximum at additive concentrations less than 1%, followed by a decrease in burning velocity. However, the results could not be explained on a kinetic basis as described above.
It is clear that catalysis of the explosive hydrogen-chlorine reaction has been studied only to a limited extent, and that little is known regarding the reaction mechanism.

However, this type of inhibition or catalysis, as applied to these, and, by inference, other reactions, may be seen to be extremely interesting, both academically and from an industrial viewpoint. It would appear to be desirable to extend the study of a range of chemical additives to obtain basic information not only on the catalysed process, but also on the underlying mechanism of the flame reaction.
SECTION 2.

EXPERIMENTAL.
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Section 2.

2.1. Apparatus.

2.1.1. General design.

The apparatus is illustrated in Plate 1 and shown diagrammatically in figs. 1 and 2.

Fig. 1 shows the general flow system. Gases are obtained under pressure from cylinders and are purified where necessary (see section 2.2); they then pass through control valves $V_1$, $V_2$, $V_3$ and $V_4$, flow-meters $F_1$, $F_2$, $F_3$ and $F_4$ and hence to the mixing chambers $M_1$ and $M_2$. The resulting mixture of gases flows through the flame trap, $T$, to the tube $B$ where it is burnt. In later experiments a nitrogen jacket, $N$, was placed round the burner.

After the gas has passed from the mixing chambers, light is excluded from the apparatus to prevent any pre-reaction before the gases leave the burner.

Fig. 2 shows the optical arrangement. The light beam originating at $M_e$ is condensed by a lens, $C$, to a point source, $P$, set at the focus of the first schlieren lens, $S_1$, which provides parallel light across the schlieren field. An identical schlieren lens, $S_2$, brings the light to a focus at the knife edge, $K$. $L_1$ is merely a magnifying lens and $L_2$ is the camera lens which throws an image onto the photographic plate, $Ph$, whilst $F_i$ filters out ultra-violet light.
General apparatus for burning velocity determinations
Line Diagram of Apparatus.
Optical Arrangement.
2.1.2. The flow system.

2.1.2.1. Control valves.

Initial coarse control was obtained by pressure-reducing valves supplied by the British Oxygen Company Ltd.; these valves were attached to the cylinder, except in the case of chlorine, where, due to the corrosive properties of this gas, a corrosion-resistant regulator, model 15C-660, supplied by the Matheson Company Inc., was used. In addition, in this case, a Monel check valve was incorporated to prevent suck-back of foreign materials.

Fine-control needle valves $V_1$, $V_3$, $V_4$ (type LB2B) were supplied by Edwards High Vacuum Ltd., and modified by replacing the brass outlets with stainless steel fittings, to avoid corrosion. These valves were used with all gases except nitrogen where a control valve, $V_2$, as supplied by the Rotameter Manufacturing Company Ltd., was found to be satisfactory.

2.1.2.2. Flow-meters.

All flow rates, with the exception of those of nitrogen and monomethylamine, were measured by capillary flow-meters of general construction as shown in fig. 3. The capillary tubes were interchangeable according to the flow range to be determined, and could be used to measure flow rates up to $500 \text{ cm}^3 \text{ min}^{-1}$. 
Capillary Flow Meter Construction

FIGURE 3

Capillary

Manometer

Manometer liquid
Nitrogen flow rates were measured by a series 825 Rotameter, supplied by the Rotameter Manufacturing Company Ltd and calibrated for a flow range of 50 to 500 cm$^3$ min$^{-1}$ at N.T.P. A smaller Rotameter of flow range 5 to 50 cm$^3$ min$^{-1}$ was used to measure the flow rates of monomethylamine.

2.1.2.3. **Mixing chambers.**

The construction of the mixing chambers is shown in fig.4. Each chamber is composed of two arms, one containing glass wool and the other glass beads of diameter 3-4 mm., in order to give turbulent mixing with a minimal free volume.

2.1.2.4. **Flame trap.**

With the higher burning-velocity mixtures the probability of flash-back is high and a flame trap is used to quench the flames before they reach the mixing vessels. This consists essentially of a stainless steel sintered disc of diameter 1.25 inches, cut from material of porosity 1, and fitted between two stainless steel flanges, with a rubber seal to maintain airtight conditions (fig.5).

The flame trap also served the additional purpose of filtering out any particles entrained in the gas mixture. These discs were replaced after approximately 12 hours' use, when the pores became blocked.
Mixing Chamber Construction.

Glass Beads

Glass Wool
One flange of the flame trap
2.1.2.5. **Nitrogen jacket.**

A diagram of the nitrogen jacket is shown in fig. 6. The jacket is constructed from 1/8" thick perspex, which is sealed to maintain airtight conditions. Windows of selected plate glass are set in the sides of the jacket, in line with the optical system. These may be removed for cleaning, and an airtight seal with the jacket is obtained with paraffin wax. The burner projects through the base and is held in position with an airtight rubber cork. A small hole in the front of the case allows facilities for lighting and this is sealed with plasticine during all experimental observations. Nitrogen inlet tubes are set in the base, and there is an exit hole for waste gases in the top.

2.1.2.6. **Burner tubes.**

Stainless steel burner tubes of external diameter 3.175 mm. and internal diameters 1.35, 1.73 and 2.159 mm. were employed for the major part of the initial work. For high burning-velocity estimations, use was made of stainless steel capillary tubes (internal diameter $\frac{1}{8}$ mm.), and for very low burning velocities, tubes of internal diameters up to 4.5 mm. were used. In the later stages of the work, silica tubes of similar internal
Nitrogen jacket
and external diameters were used. All burner tubes were approximately 30 cm. long.

Although the Monel tubes are supposedly resistant to chlorine corrosion, deposits were nevertheless left inside them, and they were therefore eventually replaced by stainless steel tubes which remained comparatively clean. When a nitrogen jacket was used, flames were found to be more stable on silica tubes than on stainless steel tubes. Silica tubes remained completely free of deposits.

All experimental observations were carried out in a fume cupboard.

2.1.3. The optical system.

2.1.3.1. Component parts.

The light source was a mercury vapour discharge lamp supplied by A.E.I., type ME/D, and with a rating of 200-250 v./250 w. The condenser lens had a focal length of approximately 35 cm. Both schlieren lenses were of focal length 70 cm., but replacement of any of these by a lens of smaller focal length did not affect the results. The enlarging lens had a focal length of 20 cm., and a Taylor Hobson 'Ental' lens of 5 cm. focal length served as the camera lens. All lenses and other component parts were set in stands and
aligned by means of an optical bench, which was 3 metres long, and had levelling screws attached to it. A 'box' type camera was constructed with a variable speed shutter set in one end and a photographic plate holder in the other.

2.1.3.2. Photographic materials.

Ilford H.P.S. photographic plates, size $3\frac{1}{4}$ inches by $4\frac{1}{4}$ inches, were developed in Ilford contrast FF developer, diluted nine times with water.

2.2. Materials.

2.2.1. Primary reactants.

Hydrogen was the 'high purity' grade, supplied by the British Oxygen Company Ltd., and quoted to contain a minimum of 99.95% hydrogen. The main impurities were nitrogen ($\leq 0.05\%$) and traces of oxygen, carbon monoxide and carbon dioxide.

Chlorine was supplied by Imperial Chemical Industries Ltd., with a quoted minimum purity of 99.9%; the gas contained a maximum of 0.02% water vapour.

Nitrogen ('white spot' grade) was supplied by the British Oxygen Company Ltd. The minimum purity was quoted as 99.9%, and the impurities were water vapour ($\leq 0.002\%$), neon ($\leq 0.0006\%$), helium ($\leq 0.0001\%$) and trace quantities of
oxygen, carbon dioxide, hydrogen, argon and carbon compounds.

2.2.2. Gaseous additives.

The minimum purity in most cases was 99%. If account is taken of the total concentration (<5% in most experiments) of additive in the total gas mixture, an impurity content of as much as 0.1% in the additive would constitute only 0.005% of the total gas mixture; the effect of such a small concentration of impurity would not be detectable under the conditions of these experiments.

Methane was supplied by Air Liquide and the minimum purity was quoted as 99.5%.

Deuteromethane - $d_4$ was supplied by Merck, Sharp and Dohme Ltd., and had a quoted minimum purity of 99%. The only likely impurity was air (<1%).

Ethane was supplied by the British Oxygen Company Ltd., and contained approximately 99.5% ethane. The main impurity was methane (<0.5%).

n-Butane and isobutane were "commercially pure" samples of minimum purity 99.0% supplied by the Matheson Company Inc.

Ethylene was supplied by the British Oxygen Company Ltd., who quote a typical analysis of 98.23%. The main impurity
was nitrogen (1.17%), and other impurities were carbon dioxide (0.27%), oxygen (0.14%), methane (0.03%), hydrogen (0.1%) and carbon monoxide (0.06%).

Acetylene was also supplied by the British Oxygen Company Ltd., and the minimum impurity was quoted as 99.0%. The main impurities were oxygen and nitrogen (combined concentration <1%) and water vapour (<0.02%) with trace quantities of hydrogen sulphide and phosphine. The gas also contained a small quantity of acetone. Removal of acetone, oxygen and water vapour was effected by passage through a purification train containing (in order), (a) concentrated sodium bisulphite solution, (b) 30% sodium hydrosulphite + 2% indigo carmine in 10% potassium hydroxide solution, (c) water, and (d) silica gel.

Dimethyl ether was supplied by May and Baker Ltd., who quoted its minimum purity as 99.0%.

Methyl chloride was supplied by Imperial Chemical Industries Ltd., and was quoted as almost 100% pure. The main impurity was water vapour (<0.01%).

Methyl bromide was supplied by May and Baker Ltd., and its minimum purity was quoted as 99.9%. The main impurities were hydrogen bromide (0.02%) and traces of sulphuric acid and methyl alcohol.
Monochloroamine was again supplied by May and Baker Ltd., with a quoted minimum purity of 98.0%. The main impurities were dimethylamine (0.8%), trimethylamine (0.2%), water vapour (0.5%) and ammonia (<0.2%).

Oxygen was supplied by the British Oxygen Company Ltd., with a minimum purity of 99.5%, the remainder being mainly argon (<0.5%). Other impurities present in trace amounts only were water vapour, nitrogen, carbon dioxide, hydrogen and hydrocarbons of low molecular weight.

2.3. Experimental procedure.

2.3.1. The flow system.

Slight corrosion of the fine-control valve was apparent when chlorine was used, but this effect was small since the gas was almost dry. Replacement of the valve was necessary after approximately 4 months' use.

With methyl bromide some condensation took place as the gas issued from the valve, and a liquid trap—a cooled glass tube immersed in water at room temperature—was used to collect any condensing methyl bromide.

Self-ignition was sometimes observed when acetylene came into contact with chlorine in the mixing system, and this process was catalysed by the presence of
traces of oxygen. This phenomenon was largely avoided by flushing the system beforehand with nitrogen to remove any oxygen present, and by flushing again with nitrogen, after an experiment, to avoid reaction caused by diffusing oxygen.

The addition of monomethylamine eventually proved impracticable due to the formation of ammonium chloride in the mixing chambers, producing a white deposit which soon blocked the flow lines.

All flow—meters were calibrated using the bubble meter method. For slightly soluble gases the soap solution was saturated with the gas concerned before calibration, and the error involved was found to be negligible compared with other experimental errors. Monomethylamine was found to be exceedingly soluble in all liquids available, particularly water, and its calibration curve was assumed to be the same as for a gas of similar density and viscosity, which are the principal variables affecting the calibration.

The capillary flow—meters were found to give a readily reproducible flow but were nevertheless checked before each run. Dibutyl phthalate was a suitable manometric liquid for all gases (see fig.3) except chlorine. Liquid paraffin was used for chlorine and this was found to be
Line pressures were measured by a mercury manometer, topped with dibutyl phthalate for most gases, but with liquid paraffin for chlorine.

Taps and joints were greased with paraffin wax supplied by May and Baker Ltd., but taps were excluded from the apparatus from the point where chlorine entered the system, in order to avoid chemical attack on the paraffin wax.

In the later experiments with a nitrogen jacket, the jacket was flushed with a continuous stream of nitrogen to remove any oxygen initially present and to remove waste gases during the experiments.

2.3.2. Lighting of the flame.

A coal gas pilot flame was used to light flames burning with an air surround. However, in order to prevent air from entering the nitrogen jacket when lighting, an alternative procedure was needed which did not involve the exposure of any part of the flame to atmospheric oxygen. For this purpose two copper wires were positioned in the side of the jacket so that their ends were just above the burner tube. One wire was earthed and the other was exposed to a high tension, high frequency
discharge; the resulting spark across the burner was sufficient to light the flame in most cases. Some difficulty was experienced in lighting a hydrogen-rich flame by this method. A chlorine-rich mixture was established for lighting purposes only, and the chlorine concentration was then reduced until a hydrogen-rich mixture was obtained.

2.3.3. Handling of the optical system.

The knife edge was set horizontally in all cases, and the light intensity falling on the plates could be controlled by raising or lowering the knife edge.

For a given mixture, a steady flame was established on top of the burner and could be observed from the back of the camera. When steady-state conditions were established, a photograph was taken with an exposure time of approximately half a second.

A roughly six-fold enlargement was obtained with the above optical arrangement.

2.3.4. Handling of the photographs.

The photographic plates were developed for a period of ca. 4 minutes, allowed to remain in the fixer for ca. 10 minutes, washed, and allowed to dry, a typical photograph being shown in fig.7. The negative was
Typical Schlieren Photograph
projected onto drawing paper to give a sixty-fold to hundred-fold enlargement. The image was traced onto the paper and an accurate estimate of the enlargement was made from a knowledge of the dimensions of the original burner and the burner image.

2.4. Method of estimation of the burning velocity.

2.4.1. Cone area.

From the image tracings the cone area (curved surface) is calculated as follows. The cone is divided into some ten or twelve equal segments, each of slope length, $s$. The radii of the base of each segment from top to bottom are respectively $r_1$, $r_2$, $r_3$ ..... $r_{n-1}$, $r_n$. This is shown in fig.8. The cone is thus divided in such a way that each segment forms a frustum of a cone, and the areas are $\pi s (0+r_1)$, $\pi s (r_1+r_2)$ ..... $\pi s (r_{n-2}+r_{n-1})$, and for the final segment of slope height $s_1$, the area is $\pi s_1 (r_{n-1} + r_n)$. Summation of these gives the total surface area as:

$$A = 2\pi s (r_1 + r_2 + r_3 + ..... r_{n-1}) + \pi s_1 (r_{n-1} + r_n)$$

An alternative method of calculation, namely that using the cone angle $\theta$ was considered, but this proved to be no better and was, indeed, often less accurate.
Estimation of Cone Area
2.4.2. Deduction of the burning velocity.

The burning velocity is defined here as the total volume flow of the unburnt gases divided by the area of the flame front (cone area).

\[ Su = \frac{V_f}{A} \]  \hspace{1cm} \text{2.4.2.1.}

where \( Su \) = burning velocity (cm.\,sec\(^{-1}\))

\( V_f \) = volume flow rate (cm\(^3\) sec\(^{-1}\))

\( A \) = cone area (cm\(^2\)).

The volume flow-rate is the sum of the volume flow-rates for each gas.

2.5. Experimental conditions and observations.

Experiments were conducted for the following flames under various conditions.

(a) A hydrogen-chlorine flame, burning with an air surround.

(b) A hydrogen-chlorine flame with additives, burning with an air surround.

(c) A hydrogen-chlorine flame with a constant quantity of nitrogen (usually 30\%), containing additives, and burning with an air surround.

(d) A hydrogen-chlorine flame as in (c) but with a nitrogen jacket instead of the air surround.
SECTION 3.

RESULTS.
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Section 3. Results.

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   3.2.4. Burning velocities of hydrogen-chlorine-nitrogen flames.
      3.2.4.1. Burning with an air surround.
      3.2.4.2. Burning with a nitrogen surround.
   3.2.5. Burning velocities of hydrogen-chlorine mixtures with additives and burning with an air surround.
      3.2.5.1. n-Butane.
      3.2.5.2. Methane and methyl chloride.
   3.2.6. Burning velocities of hydrogen-chlorine-nitrogen flames with additives and burning with an air surround.
   3.2.7. Burning velocities of hydrogen-chlorine-nitrogen flames with additives and burning with a nitrogen surround.

3.3. Observations on the flames.

3.4. Burning velocities of other fuel-chlorine flames burning with an air surround.
3.1. Effects of variables.

3.1.1. The flow system.

Burning velocity measurements of the type discussed here are affected by various external factors, and it is necessary to consider the relative importance of such factors prior to detailed discussion of the results.

3.1.1.1. The mixing chambers.

The gas mixture leaving the mixing chambers was analysed by gas chromatography, and the results were compared with those expected from the flow meter readings. The maximum error was found to be 1.5% with an average error of 1.1%, and these values were considered to be within the normal limits of accuracy of the experimental method used.

3.1.1.2. The length of the burner tube.

For correct flame shape it is essential that the unburnt gas mixture in the burner tube has laminar flow. In the first instance the Reynolds number, Re, which is given by

\[ Re = \frac{\rho d v}{\mu} \]
where $\rho = \text{density of the gas (gm.cm}^{-3}\text{)}$

$d = \text{diameter of the burner tube (cm.)}$

$v = \text{velocity of the gas in the pipe (cm.sec}^{-1}\text{)}$

$\mu = \text{viscosity of the gas (gm.cm}^{-1}\text{sec}^{-1}\text{)}$

should have a value such that laminar conditions are established. In this work a value $Re < 1000$ was selected.

Furthermore, Coulson and Richardson state that the minimum length of tube to establish such conditions, known as the entry length, $l_e$, is given by

$$l_e = 0.0288 \text{Re.d} \quad \ldots \ldots \text{3.1.1.2.2.}$$

For tubes of the dimensions used in most of this work (diameter = 0.2 cm.) the minimum length necessary from equation 3.1.1.2.2. is 6 cm. However, to ensure completely laminar conditions, burner tubes of approximately 10 times the minimum entry length were used. Where comparative studies were carried out, burner tube lengths were kept substantially constant.

**3.1.1.3. The diameter of the burner tube.**

The burning velocity of a given mixture was found to increase slightly as the burner tube diameter decreased, probably due to the greater importance of wall
effects. However, these effects were important only with very small tube diameters ($< 0.1 \text{ cm}$). As the majority of this work was carried out with burner tubes of approximately 0.2 cm. diameter, these effects could be neglected. To eliminate even the slightest error the burner tube diameter was, however, kept substantially constant for most determinations.

3.1.1.4. The material of the burner tube.

A stainless steel burner tube was found to be suitable for the initial experiments. However, in the later work (using a nitrogen jacket) the flame tended to be unstable and a silica burner was used instead. In this way, too, any corrosion of the burner material by the waste gases was avoided. The value of the burning velocity was considerably influenced by the burner material, being much higher for the insulating material (silica). Comparison of fig.33(a) (stainless steel burner) with fig.33(c) (silica burner) indicated that the burner material had little effect on the characteristics of the curve but merely altered the burning velocity values. 4.0% methyl chloride reduced the burning velocity by 43% in the former case and by 41% in the latter. Figs.33(b) and 33(d) added further support to these conclusions. However, for a given set of comparative studies the burner material was kept the same.
3.1.1.5. Other side effects.

Burning velocity determinations with and without a water condenser round the burner tube showed that cooling had negligible effect.

Determinations with and without an extraction fan above the burner showed that any additional disturbances due to air currents also have a negligible effect on the burning velocity.

The rate of flow of the nitrogen used as a purging gas was varied over the range 0-4 litres min\(^{-1}\) (purging rates used in these experiments), but this had a negligible effect on the value of the burning velocity.

3.1.2. The photographic arrangement.

3.1.2.1. The light source.

It has been shown that the hydrogen-chlorine reaction can be photochemical and experiments were carried out to determine the relative importance of irradiation necessary for photographic recording. The burning velocity remained constant for a given mixture, when an ultra-violet filter was introduced between the light source and the flame, and when the laboratory lights were dimmed. Thus it could be concluded that effects of
light are negligible, or at least remain constant under these conditions. However, in order to eliminate any possible source of error, a constant permanent light source was used for all experiments.

3.1.2.2. The photographic materials.

The effects of differing density of print, and shrinkage of the printing paper were found to be small. However, to avoid any error due to these variables, and also to allow for greater enlargement of the images, all images were traced on to drawing paper.

3.1.2.3. Flame shape.

Experiments with a constant mixture composition, but with cones of varying shape resulted in almost constant burning velocity determinations, and any slight error due to this cause was neglected.

3.2. Burning velocity measurements.

3.2.1. Experimental conditions selected for the burning velocity estimations.

Experiments have been carried out for various hydrogen-chlorine-additive mixtures, burning both in the open atmosphere (an air surround) and in a nitrogen jacket (nitrogen surround). The observed values, which show an
appreciable difference from one another under otherwise similar conditions, are reported in the form of graphs.

When the burning velocities for various mixtures are compared with that for a selected standard (usually a mixture without any additives), other experimental conditions are kept substantially constant.

3.2.2. Method of presentation of the results.

The effects of chemical additives on the burning velocity of a given mixture have been generally observed as a result of measurements involving the introduction of an additive to a mixture of constant fuel:oxidant ratio \(^65\). This ratio has often been selected as that giving the maximum burning velocity for the mixture without additives and effects of changes in stoichiometry have been ignored \(^65\). However, it has been shown for methane-hydrogen-air mixtures \(^81\) that the observed effects depend on the fuel:oxidant ratio selected. Fig.9 suggests similar conclusions for the addition of methane to hydrogen-chlorine mixtures burning with an air surround. A constant quantity of nitrogen (30%) is present in all mixtures, but this acts merely as a diluent (see sections 3.2.4.1 and 3.2.7), and lowers the burning velocity to
Effects of methane addition to a hydrogen-chlorine mixture containing 30% nitrogen for various hydrogen:chlorine ratios.

Stainless Steel burner
Air surround

$H_2:Cl_2$ at Maximum Burning Velocity = 1.78
Over the range of mixtures studied (hydrogen 40%-70%) four entirely different results are observed; with stoichiometric and fuel-lean mixtures promoting effects tend to be in evidence, whereas with fuel-rich mixtures inhibition is generally favoured. Fig.10, which shows the results of experiments for similar mixtures burning with a nitrogen surround, indicates that the relative effect of methane as a promoter of the burning velocity depends on the hydrogen:chlorine ratio selected.

In particular the position of the maximum burning velocity for a hydrogen-chlorine mixture without additives (expressed as the percentage of hydrogen in the mixture) has been shown to be as low as 50% in one case and as high as 64% in another. Indeed, results presented later in this study show two entirely different positions of maximum burning velocity (see figs.14 and 15(b)), depending on the conditions of the experiment, and selection of either of these mixture compositions as the true position may show differing effects for the introduction of an additive (see fig.9).

In the major part of this work results have been presented in a manner which is independent of the hydrogen:chlorine ratio selected. A small amount of
Effects of methane addition to a hydrogen-chlorine mixture containing 30% nitrogen for various hydrogen:chlorine ratios.

FIGURE 10

Silica Burner
Nitrogen surround

$H_2:Cl_2$ at Maximum Burning Velocity = 1.18
additive has been introduced into the hydrogen-chlorine mixture (which in many cases contained a constant quantity of nitrogen) and the maximum burning velocity, together with the position of the maximum, has been determined for the given mixture. The results obtained in this way are typified by curves obtained for hydrogen-chlorine mixtures containing constant quantities of n-butane and burning with an air surround. Fig.11 shows that as little as 1.85% n-butane is sufficient to lower the maximum burning velocity from 540 cm·sec$^{-1}$ (see fig.14 later) to 221 cm·sec$^{-1}$, and to move the position of the maximum from 64% hydrogen (see fig.14 later) to 54.8% hydrogen. Fig.12 shows that further small additions of n-butane lower the maximum burning velocity by an even greater amount, and, at the same time, the position of the maximum shifts even further towards a fuel-lean composition. Fig.13 shows a rather extreme case where 14.75% n-butane has lowered the maximum burning velocity to 14.6 cm·sec$^{-1}$ and has shifted the position of the maximum to 19.4% hydrogen.

The above method of presentation provides a more standard means of comparing the effects of different chemical additives, an allowance being made at the same time for possible changes in stoichiometry.
FIGURE 11
Maximum burning velocity for a hydrogen-chlorine mixture containing 1.85% n-butane.

Stainless steel burner
Air surround

Maximum burning velocity = 221 cm sec\(^{-1}\)
Maximum at 55.0% Hydrogen

%H_2 = \frac{H_2}{H_2 + Cl_2} \times 100
FIGURE 12

Maximum burning velocities for hydrogen-chlorine mixtures containing 2.39% and 3.19% n-butane.

\[ \%H_2 = \frac{H_2}{H_2 + Cl_2} \times 100 \]

- ○ n-butane = 2.39%
- ⊗ n-butane = 3.19%
Maximum burning velocity for a hydrogen-chlorine mixture containing 14.75% n-butane.

Stainless steel burner
Air surround

Maximum burning velocity 14.6 cm. sec⁻¹
Maximum at 19.4% Hydrogen

}%H₂ = \frac{H_2}{H_2 + CI_2} \times 100
3.2.3. **Burning velocities of hydrogen-chlorine flames.**

As a means of comparing the initial results with additives it is of interest to determine the maximum burning velocity and position of the maximum for hydrogen-chlorine mixtures. Fig. 14 shows results for a mixture burning with an air surround; the maximum burning velocity is 540 cm sec\(^{-1}\) and the position of the maximum is at 64% hydrogen. The results are somewhat higher than those of Bartholomé\(^59\), but the curves show the same general shape. At very high flow rates, when the gas flow is no longer laminar, even higher burning velocities are obtained. However, burning velocities of such magnitude are difficult to determine accurately and should provide only a rough guide towards an absolute value. It may be noted that all determinations have been made with a stainless steel burner.

For a hydrogen-chlorine mixture burning with a nitrogen surround the results indicate that the maximum burning velocity is around 650 cm sec\(^{-1}\) (fig. 15(a)), and that the position of the maximum is at approximately 59% hydrogen (fig. 15(b)). These determinations were made with a silica burner tube.
FIGURE 14

Maximum burning velocity of a hydrogen-chlorine mixture burning with an air surround.

Stainless steel burner

- Tube diameter = 0.8 mm
- Tube diameter = 1.10 mm
- Tube diameter = 1.10 mm (high flow rates)

Results of Bartholome
Addition of nitrogen to a hydrogen-chlorine mixture burning with a nitrogen surround.

(a) Silica burner

(b) Silica burner
3.2.4. Burning velocities of hydrogen-chlorine-nitrogen flames.

3.2.4.1. Burning with an air surround.

The determination of the maximum burning velocity for a mixture containing 30% nitrogen, using a stainless steel burner, is shown in fig. 16. The maximum burning velocity is approximately 201 cm/sec. and the position of maximum is at 67% hydrogen. A similar determination with a silica burner instead of a stainless steel burner gives a maximum burning velocity of approximately 271 cm/sec., again at 67% hydrogen. The general characteristics of the curves are, however, the same.

Nitrogen has been added in increasing quantities to two hydrogen-chlorine mixtures of constant hydrogen:chlorine ratios (fig. 17), and burning with an air surround; the curve for a mixture of the maximum burning velocity composition always lies above that for a stoichiometric mixture, and, indeed, the two curves are almost parallel. Thus the maximum burning velocity for a hydrogen-chlorine-nitrogen mixture under these conditions always lies well on the fuel-rich side of stoichiometric, and the addition of nitrogen does not upset the stoichiometry to any measurable extent.
FIGURE 16
Burning velocities of hydrogen-chlorine mixtures containing 30% nitrogen and burning with an air surround.

\[ \gamma N_2 = \frac{N_2}{N_2 + H_2 + Cl_2} \times 100 \]

- Silica burner
- Stainless steel burner

Burning Velocity (cm/sec.)

% Hydrogen
Addition of nitrogen to hydrogen-chlorine mixtures of constant hydrogen:chlorine ratios and burning with an air surround.

Stainless steel burner

- $\text{H}_2:\text{Cl}_2 = 1.78$
- $\text{H}_2:\text{Cl}_2 = 1.00$

Burning Velocity (cm/sec.) vs. % Nitrogen
3.2.4.2. **Burning with a nitrogen surround.**

Maximum burning velocity determinations for hydrogen-chlorine mixtures containing a constant quantity of nitrogen and burning with a nitrogen surround are presented in fig.18. It should be noted that the positions of the maxima are generally better defined than for mixtures burning with an air surround. An increase in the quantity of nitrogen added appears to shift the position of maximum towards more fuel-lean mixtures. The change in the value of the maximum burning velocity and the shift of the position of the maximum, as a result of an increase in nitrogen content, are shown in figs.15(a) and 15(b) respectively.

Furthermore, it can be seen that for a flame having a nitrogen surround the maximum burning velocity occurs nearer the stoichiometric composition than for the corresponding determination with an air surround (fig.14).

3.2.5. **Burning velocities of hydrogen-chlorine mixtures with additives and burning with an air surround.**

Much of the initial experimental work was carried out with n-butane and this is therefore selected as a typical fuel. In the case of the results of the three additives reported in this section, small additions could not be considered, as burning velocities were too high to be measured accurately. However, these results covered a wide
Burning velocities of hydrogen-chlorine mixtures containing constant proportions of nitrogen and burning with a nitrogen surround.

![Graph showing burning velocities](image)

\[
D = \frac{N_2}{N_2 + H_2 + Cl_2}
\]

Silica burner:
- D = 0.10
- D = 0.15
- D = 0.20
- D = 0.25
- D = 0.30
- D = 0.35
range of concentrations of additive in each case, from which selection of the more important regions, for investigations in later work, could be considered. All determinations involved the use of stainless steel burners.

3.2.5.1. n-Butane.

n-Butane was studied over the range of concentrations 2-15% and maximum burning velocity determinations are presented in fig.19 (see also figs.11-13). The maximum burning velocity of a n-butane-chlorine mixture has also been determined as 10.8 cm.sec\(^{-1}\), at a n-butane composition of 14.8% (see fig.50 later). As little as 2.2% n-butane reduces the maximum burning velocity by the same amount as 30% nitrogen under the same conditions. It appears likely that considerable inhibition is present even with amounts of n-butane less than 2.0%, and that the greatest effect is apparent for concentrations less than 5.0%.

Fig.20 shows the maximum burning velocity plotted against the fraction of n-butane in the fuel mixture. If burning velocities were merely weighted averages then the points should lie on the straight line shown. The deviations observed may be due to the interplay of possible inhibiting effects.
FIGURE 19
Addition of n-butane to a hydrogen-chlorine mixture burning with an air surround.

Stainless steel burner

\[
\% n-C_4H_{10} = \frac{n-C_4H_{10} \times 100}{n-C_4H_{10} + H_2 + Cl_2}
\]

Maximum burning velocity (cm, sec\(^{-1}\))

% n-Butane
Maximum burning velocity as a function of fuel ratio for a hydrogen-chlorine-n-butane mixture burning with an air surround.

Stainless steel burner

\[ \phi = \frac{n-C_4H_{10}}{n-C_4H_{10} + H_2} \]
The movement of the position of the maximum burning velocity is apparent from figs. 11-13. It has previously been shown (fig. 14) that the position of maximum burning velocity for a hydrogen-chlorine mixture burning with an air surround occurs around 64% hydrogen. However, from fig. 21 it may be seen that for n-butane concentrations above 3.0% a higher burning velocity is obtained for a stoichiometric mixture than for a 'maximum-burning-velocity' mixture, indicating the shift of the maximum towards the fuel-rich side of stoichiometric composition. At very small n-butane concentrations the curves in fig. 21 may even cross.

The shift of the position of the maximum with increase in n-butane concentration is shown in fig. 22. Here the percentage of hydrogen is corrected for the amount of n-butane present in the mixture. The movement of the maximum may be expected to follow the straight line joining the extreme points.

3.2.5.2. Methane and methyl chloride.

Methane and methyl chloride have been studied over a wider range of concentrations (0-35%) and show similar inhibiting effects to each other (fig. 23), although neither are as effective as n-butane; as much as
Addition of n-butane to hydrogen-chlorine mixtures at constant hydrogen:chlorine ratios and burning with an air surround.

Stainless steel burner

- $\text{H}_2: \text{Cl}_2 = 1.78$
- $\text{H}_2: \text{Cl}_2 = 1.00$

**Figure 21**

Burning Velocity (cm sec$^{-1}$)

<table>
<thead>
<tr>
<th>% n-Butane</th>
<th>Burning Velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>150</td>
</tr>
<tr>
<td>4.0</td>
<td>120</td>
</tr>
<tr>
<td>5.0</td>
<td>90</td>
</tr>
<tr>
<td>6.0</td>
<td>60</td>
</tr>
</tbody>
</table>
Shift of position of maximum (\% hydrogen) with increase in n-butane concentration for a hydrogen-chlorine-n-butane mixture burning with an air surround.

Stainless steel burner.
Addition of methane and methyl chloride to a hydrogen-chlorine mixture burning with an air surround.

**Stainless steel burner**

- ○ methyl chloride
- ✗ methane

**FIGURE 23**

Maximum burning velocity (cm/sec.)

% Additive
11.0% and 9.0% respectively are necessary to give the same effect as 30% nitrogen. Similar effects to n-butane, if somewhat less pronounced, are suggested in figs. 24 and 25. At concentrations greater than 7.0% methyl chloride is a better inhibitor than methane, but at concentrations less than 7.0% methane is a better inhibitor than methyl chloride. Indeed, at very low concentrations (around 2.0%) methyl chloride may even promote the reaction (fig. 25).

3.2.6. Burning velocities of hydrogen-chlorine-nitrogen flames with additives and burning with an air surround.

From the work with methane, methyl chloride and n-butane reported in the previous section, the region of small concentrations of additive (0-5%) was selected for further study, as this was expected to be the region showing rather distinguishing features for a particular additive. In addition, those additives having significant effects in small concentrations are of particular interest in this work. The study of additives in high concentrations (≥ 5.0%) is difficult due to a large amount of carbon formation.

In order to reduce the burning velocity to a value which could be measured with some accuracy, a
Maximum burning velocity as a function of fuel ratio for a hydrogen-chlorine-methane mixture burning with an air surround.

Stainless steel burner.

\[ \phi = \frac{\text{CH}_4}{\text{CH}_4 + \text{H}_2} \]
Maximum burning velocity as a function of fuel ratio for a hydrogen-chlorine-methyl chloride mixture burning with an air surround.

\[ \phi = \frac{\text{CH}_3\text{Cl}}{\text{CH}_3\text{Cl} + \text{H}_2} \]

Stainless steel burner
constant quantity of nitrogen (30%) has been added to all mixtures. It has been indicated (fig. 17) that nitrogen merely has a diluting effect and does not enter into any chemical reaction.

As in previous work the maximum burning velocity was measured for various concentrations of additive. The position of the maximum (% hydrogen) for each concentration, the change in maximum burning velocity, and the shift of the maximum with increase in additive concentration were all recorded.

With the exception of methyl bromide (which showed initial promotion) all additives showed inhibiting effects even in small concentrations. A common feature for each additive was the rapid shift of the position of the maximum towards stoichiometric composition when concentrations were as low as 0.5%; a decrease in burning velocity in most cases was followed by a corresponding movement of the maximum towards the fuel-lean mixture. Positions of the maxima were rather difficult to determine accurately and were meant to give a general indication only.

The characteristics for the introduction of each particular additive are shown in figs. 26-34. Scales are kept constant when plotting burning velocity trends for each additive so that the effects may be easily compared.
Addition of methane to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(a) Stainless steel burner.

(b) Stainless steel burner.
Addition of ethane to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(a) Stainless steel burner

(b) Stainless steel burner
Addition of n-butane to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(a) Stainless steel burner

(b) Stainless steel burner
Addition of isobutane to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(a) Stainless steel burner

(b) Stainless steel burner
Addition of ethylene to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(a) Stainless steel burner

(b) Stainless steel burner
Addition of acetylene to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(a) Stainless steel burner

(b) Stainless steel burner
Addition of dimethyl ether to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(a) Stainless steel burner

(b) Stainless steel burner
Addition of methyl chloride to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(a) Stainless steel burner

(b) Stainless steel burner
Addition of methyl chloride to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(c) Silica burner

(d) Silica burner
Addition of methyl bromide to a hydrogen-chlorine mixture containing 30% nitrogen and burning with an air surround.

(a) Stainless steel burner

(b) Stainless steel burner
The shift of the maximum is also shown on similar scales for most of the additives, except where there is an unusually large movement (e.g. for isobutane).

The paraffin hydrocarbons were found to be the most effective inhibitors. The apparent order of effectiveness of all inhibitors was $n$-butane $>$ isobutane $>$ ethane $>$ methane $>$ ethylene $>$ acetylene $>$ methyl chloride $>$ dimethyl ether $>$ methyl bromide. However, this was meant as a general indication only as the accuracy of the experiments did not allow a definite distinction between the effectiveness of some inhibitors (e.g. ethane and isobutane).

3.2.7. Burning velocities of hydrogen-chlorine-nitrogen flames with additives and burning with a nitrogen surround.

Experiments as in section 3.2.6. were repeated with a nitrogen atmosphere surrounding the flame, so that any effects due to the diffusion of oxygen into the flame could be determined. Observations on all the previous additives were repeated and further studies were carried out with deuteromethane-d$_4$ and oxygen. All concentrations of additives used were between 0 and 2%, as smoke formation in many cases made observations at higher concentrations rather difficult. The maximum burning velocity was again
expressed as a function of the concentration of additive, and the approximate shift of maximum was noted. The exact position of the maximum was again rather difficult to determine.

Under these conditions the effects of each additive were rather more readily distinguishable but it was rather difficult to deduce their relative inhibiting powers. However, additives are compared wherever possible, and simple results for nitrogen are first shown in fig.35, for comparison purposes only. It may be noted that 2% nitrogen reduces the maximum burning velocity from 186.5 cm.sec\(^{-1}\) (see fig.13) to 174 cm.sec\(^{-1}\).

The effect of nitrogen as a diluent was studied for mixtures containing methane (figs.36 and 37) and the relative extent of promotion was found to be approximately the same in each case. Thus nitrogen was assumed to have negligible effects on the chemical mechanism involved.

Methane (fig.36(a)), deuteromethane-\(^{d_4}\) (fig.38(a)), acetylene (fig.43(a)), methyl chloride (fig.45(a)) and methyl bromide (fig.46(a)) all showed surprisingly large promotional effects, even in very small amounts, and their relative order of effectiveness as promoters was methyl bromide\(\rightarrow\)deuteromethane-\(^{d_4}\)\(\rightarrow\)methyl
Addition of further nitrogen to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

Silica burner

% Nitrogen

Maximum burning velocity (cm. sec⁻¹)
Addition of methane to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

(b) Silica burner

FIGURE 36

Position of maximum ($\% H_2$)

Maximum burning velocity (cm/sec.)

$\%$ Methane
Addition of methane to a hydrogen-chlorine mixture containing 20% nitrogen and burning with a nitrogen surround.

**FIGURE 37**

(a) Silica burner

(b) Silica burner
Addition of deuteromethane-d₄ to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

(b) Silica burner

% Deuteromethane-d₄

Position of maximum (%H₂)

Maximum burning velocity (cm. sec⁻¹)
Addition of ethane to a hydrogen–chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

Maximum burning velocity (cm. sec⁻¹)

(b) Silica burner

Position of maximum (%H₂)

% Ethane
FIGURE 40

Addition of n-butane to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

Maximum burning velocity (cm. sec⁻¹)

(b) Silica burner

Position of maximum (cH₂)

% n-Butane
Addition of isobutane to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

(b) Silica burner
Addition of ethylene to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

(b) Silica burner
Addition of acetylene to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

(b) Silica burner
Addition of dimethyl ether to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.
Addition of methyl chloride to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

(b) Silica burner

Position of maximum (%F₂) vs. % Methyl chloride

Maximum burning velocity (cm. sec⁻¹) vs. % Methyl chloride
Addition of methyl bromide to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

(b) Silica burner
Addition of oxygen to a hydrogen-chlorine mixture containing 30% nitrogen and burning with a nitrogen surround.

(a) Silica burner

(b) Silica burner

Maximum burning velocity (cm/sec.)

Position of maximum (%H₂)

% Oxygen
chloride > methane > acetylene. As the maximum burning velocity increased, the position of the maximum generally tended towards fuel-rich mixtures. However, when a maximum was reached and subsequently started to decrease, the position of the maximum started to show a shift towards fuel-lean mixtures (figs. 36(b), 38(b), 43(b), 45(b), 46(b)).

Ethane (fig. 39(a)), n-butane (fig. 40(a)), isobutane (fig. 41(a)) and ethylene (fig. 42(a)) all showed inhibiting effects, and all except ethylene indicated a slight promotion in very small concentrations (<0.3%). However, inaccuracies in the experiments may account for part or all of the promoting effects observed. In all cases the shift of the position of the maximum was towards fuel-lean mixtures (figs. 39(b), 40(b), 41(b), 42(b)). Ethane, n-butane and isobutane all showed similar behaviour, and all were more effective as inhibitors than ethylene, for additive concentrations less than 0.6%.

Initial inhibition followed by rapid promotion was indicated by oxygen (fig. 47(a)), and the position of the maximum, after a possible shift towards fuel-lean mixtures, later showed a surprisingly large shift towards a fuel-rich composition (fig. 47(b)).

The most surprising results of all were found with dimethyl ether (fig. 44) which first showed behaviour
similar to that of oxygen (slight inhibition) and then a rapid promotion characteristic of methane. Although the maximum burning velocity fell to a value similar to that found with oxygen the subsequent increase was much greater than for methane (32% increase compared with a 14% increase). The shift of the maximum was towards fuel-rich mixtures.

Methyl chloride, dimethyl ether and oxygen showed the greatest movement of the maximum towards a fuel-rich composition.

3.3. Observations on the flames.

The flames studied varied somewhat in appearance, according to the experimental conditions and the mixture under investigation. Details of all flames are given in Tables II, III and IV. It may be observed that smoke formation for flames burning with a nitrogen surround occurred at a lower concentration of additive than for flames burning with an air surround.

At the higher additive concentrations the cones of flames burning with an air surround had a thick, pale-yellow tip, and those with a nitrogen surround had a red tip. These were sometimes followed by smoke formation.
Table II.

Hydrogen-chlorine flames.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td>Inner Cone Boundary</td>
</tr>
<tr>
<td>-</td>
<td>Air</td>
<td>Steel</td>
<td>Luminous pale green</td>
</tr>
<tr>
<td>-</td>
<td>Air</td>
<td>Steel</td>
<td>White</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Air</td>
<td>Steel</td>
<td>Luminous pale green</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Air</td>
<td>Steel</td>
<td>Thin white</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Nitrogen</td>
<td>Silica</td>
<td>Luminous pale green</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Nitrogen</td>
<td>Silica</td>
<td>Thin white</td>
</tr>
</tbody>
</table>

Notes The pale-green flames are for fuel-lean mixtures, and are less well defined than the white cones of flames on the hydrogen-rich side of the 'maximum burning velocity' mixture. Flames between stoichiometric and 'maximum burning velocity' mixtures showed similar appearance to fuel-lean flames. The white diffusion mantle was present only for flames burning with an air surround. The inside of the inner cone boundary was transparent.
### Table III.

**A. Hydrogen-chlorine flames with additives.**

**B. Hydrogen-chlorine-nitrogen flames with additives.**

<table>
<thead>
<tr>
<th>Type of flame</th>
<th>Additive</th>
<th>Flame Characteristics</th>
<th>Additive Concentrations for</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inner Cone Boundary</td>
<td>Outer Cone Boundary</td>
</tr>
<tr>
<td>A</td>
<td>methane</td>
<td>white</td>
<td>pale blue</td>
</tr>
<tr>
<td>A</td>
<td>n-butane</td>
<td>white</td>
<td>pale green</td>
</tr>
<tr>
<td>A</td>
<td>methyl chloride</td>
<td>white</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>methane</td>
<td>pale blue</td>
<td>blue</td>
</tr>
<tr>
<td>B</td>
<td>ethane</td>
<td>white</td>
<td>blue</td>
</tr>
<tr>
<td>B</td>
<td>n-butane</td>
<td>white</td>
<td>blue-green</td>
</tr>
<tr>
<td>B</td>
<td>isobutane</td>
<td>white</td>
<td>blue-green</td>
</tr>
<tr>
<td>B</td>
<td>ethylene</td>
<td>white</td>
<td>blue</td>
</tr>
<tr>
<td>B</td>
<td>acetylene</td>
<td>pale pink</td>
<td>blue</td>
</tr>
<tr>
<td>B</td>
<td>dimethyl ether</td>
<td>white</td>
<td>blue</td>
</tr>
<tr>
<td>B</td>
<td>methyl chloride</td>
<td>white</td>
<td>blue</td>
</tr>
<tr>
<td>B</td>
<td>methyl bromide</td>
<td>white</td>
<td>blue</td>
</tr>
</tbody>
</table>

**Notes.** All observations were for flames on stainless steel burners, and burning with an air surround. A white
diffusion mantle was present in all cases. All flames exhibited a double cone. The inner cone was the sharper of the two. Pale yellow tips and smoke formation were less likely with fuel-lean mixtures than with fuel-rich mixtures. For flames burning without nitrogen (type A), the outer diffusion mantle blew off at very high concentrations of additive. Flames for compositions between stoichiometric and 'maximum burning velocity' mixtures were similar to fuel-lean flames.
Table IV.

Hydrogen - chlorine - nitrogen flames with additives and burning with a nitrogen surround.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Flame Characteristics</th>
<th>Additive Concentration for</th>
<th>Red tip</th>
<th>Smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inner Cone Boundary</td>
<td>Outer Cone Boundary</td>
<td>Diffusion Mantle</td>
<td></td>
</tr>
<tr>
<td>methane</td>
<td>pale green</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>deuteromethane-d₄</td>
<td>pale green</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ethane</td>
<td>white</td>
<td>-</td>
<td>-</td>
<td>0.9%  1.5%</td>
</tr>
<tr>
<td>n-butane</td>
<td>white</td>
<td>-</td>
<td>-</td>
<td>0.3%  1.1%</td>
</tr>
<tr>
<td>isobutane</td>
<td>white</td>
<td>-</td>
<td>-</td>
<td>0.3%  1.0%</td>
</tr>
<tr>
<td>ethylene</td>
<td>white</td>
<td>-</td>
<td>-</td>
<td>0.6%  1.5%</td>
</tr>
<tr>
<td>acetylene</td>
<td>white</td>
<td>-</td>
<td>-</td>
<td>0.3%  2.0%</td>
</tr>
<tr>
<td>dimethyl ether</td>
<td>white</td>
<td>-</td>
<td>-</td>
<td>1.5%  -</td>
</tr>
<tr>
<td>methyl chloride</td>
<td>pale green</td>
<td>-</td>
<td>-</td>
<td>0.8%  -</td>
</tr>
<tr>
<td>methyl bromide</td>
<td>pale green</td>
<td>-</td>
<td>-</td>
<td>0.6%  -</td>
</tr>
<tr>
<td>oxygen</td>
<td>pale green</td>
<td>-</td>
<td>white</td>
<td>-</td>
</tr>
</tbody>
</table>

Notes. All observations were on silica burners. A diffusion mantle was present only for flames containing oxygen. One cone only was observed and the inner section was transparent. A red tip and smoke formation were more
likely with fuel-lean than with fuel-rich mixtures. The occurrence of a red tip generally coincided with a fall in burning velocity after initial promotion had taken place. Flames between stoichiometric and 'maximum burning velocity' mixtures showed similar characteristics to fuel-lean flames.
3.4. Burning velocities of other fuel-chlorine flames burning with an air surround.

To complete the studies with hydrogen-chlorine-additive mixtures, burning velocities of methane-chlorine, ethane-chlorine, n-butane-chlorine and methyl chloride-chlorine flames were determined. All flames exhibited a bluish-green inner cone which was masked by a yellow outer flame and by smoke formation. The maximum burning velocities for each mixture are shown in figs. 48-51, where it may be observed that the maximum burning velocity for a n-butane-chlorine flame lies between that for a methane-chlorine flame and an ethane-chlorine flame. Methyl chloride flames did not show a definite maximum but the burning velocity gradually decreased with increase in chlorine content above 25%.
FIGURE 48

Burning velocities of methane-chlorine mixtures burning with an air surround.

Stainless steel burner

Maximum burning velocity = 51.0 cm/sec.

\[
\frac{\text{methane (max)}}{\text{methane (stoich)}} = 1.15
\]
Burning velocities of ethane-chlorine mixtures burning with an air surround.

Stainless steel burner

Maximum burning velocity = 8.5 cm. sec.\(^{-1}\)

\[
\frac{\text{ethane (max.)}}{\text{ethane (stoich.)}} = 1.44
\]
FIGURE 50

Burning velocities of n-butane-chlorine mixtures burning with an air surround.

Stainless steel burner

Maximum burning velocity = 10.8 cm/sec.

\[
\frac{n\text{-butane (max.)}}{n\text{-butane (stoich.)}} = 1.74
\]
FIGURE 51
Burning velocities of methyl chloride-chlorine mixtures burning with an air surround.

Stainless steel burner

Burning velocity (cm. sec⁻¹)

% Methyl chloride
SECTION 4.

DISCUSSION.
CONTENTS.

Section 4. Discussion.

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Section 4.

4.1. Chemical kinetic theories applied to hydrogen-chlorine flames.

Burning velocities of hydrogen-chlorine flames, in conjunction with adiabatic flame temperatures calculated accurately from recent data, may be used to identify the prevailing reaction mechanism. Equations may be derived on the assumption that this particular mechanism operates in the flame. In this work the theories of Van Tiggelen, Zeldovich, Istratov and Librovich and Rozlovskii have been specially considered. Insertion in such equations of the values of the burning velocity and of the corresponding flame temperature, for mixtures of constant fuel:oxidant ratio should then result - if the theory concerned is applicable - in a straight line from which the activation energies of a particular step or series of steps may be calculated.

The Van Tiggelen theory assumes a branching reaction between either the fuel or oxidant and a chain carrier in the flame front, and may be applied to mixtures containing an increasing amount of inert gas (in this case nitrogen). The theory has been considered previously (section 1.3.3.3) but for convenience the derived equation is repeated here:
\[ \log S_u + \frac{1}{2} \log T_m - \frac{1}{2} \log Y = K - \frac{0.4343E}{2RT_m} \] 1.3.3.3.1.

where the symbols are defined as previously.

The nature of the first order branching reaction \((i = 1)\) may be open to various interpretations (here \(E = E_v\)), but the second order branching reaction involves the following steps:

\[
\begin{align*}
(24) \quad & H + Cl_2 \rightarrow HCl^* + Cl \quad \ldots \quad E_A \\
(25) \quad & HCl^* + Cl_2 \rightarrow HCl + 2Cl \quad \ldots \quad E_B
\end{align*}
\]

and here \(E = E_A + E_B\). (\(E_A\) may be assumed to have a value of 2 kcal.mole\(^{-1}\) 2,37). In figs. 52 and 53 the equation is applied to the results for two hydrogen-chlorine-nitrogen mixtures of constant fuel:oxidant ratio, and in fig.54 it is applied to the results for maximum burning velocity mixtures. Straight line relationships are obtained in all cases, even when the assumption of constant mixture composition is ignored (fig.54).

The second theory, that of Zeldovich, assumes that for flames in which a chain mechanism is in operation, all significant reaction takes place in a narrow zone, the temperature of which is close to the final flame temperature.

For a reaction where initiation involves a third body \(M\):
Application of the equations of Van Tiggelen for a mixture containing 52% hydrogen, 48% chlorine.
Application of the equations of Van Tiggelen for a mixture containing 58% hydrogen, 42% chlorine.
Application of the equations of Van Tiggelen for mixtures of variable hydrogen:chlorine ratio.
(3') \[ Cl_2 + M \rightarrow 2Cl + M \] \[ E_C \]

and is followed by the propagation steps:

(1) \[ Cl + H_2 \rightarrow HCl + H \] \[ E_D \]

(2) \[ H + Cl_2 \rightarrow HCl + Cl \]

this theory leads to the following equation for a mixture containing excess hydrogen:

\[
\log Su + \log \frac{T_f - T_o}{T_f^2} = K_1 \frac{0.4343 (E_C + E_D)}{4RT_f} \tag{4.1.1}
\]

where \( K_1 \) is approximately constant for a given mixture, \( E_C \) is the activation energy for reaction (3'), \( E_D \) is the activation energy for reaction (1), and other constants are defined as previously.

For an energy chain involving reactions (24) and (25), followed by reaction (1), if steady state conditions in the flame are assumed, analysis leads to the equation 65:

\[
\log Su + \log \left( \frac{T_f - T_o}{T_f^2} \right)^{3/2} = K_2 - \frac{0.4343 \left( E_B + E_D \right)}{2RT_f} \tag{4.1.2}
\]

where \( K_2 \) is approximately constant for a given mixture.

The application of equations 4.1.1 and 4.1.2 to mixtures of the previously selected constant fuel:oxidant ratios (figs. 55 and 56) and to mixtures of variable fuel:oxidant ratios (fig. 57), result in straight line relationships in all cases.
Applications of the equations of Zeldovich for a mixture containing 52% hydrogen, 48% chlorine.
Application of the equations of Zeldovich for a mixture containing 58% hydrogen, 42% chlorine.
Application of the equations of Zeldovich for mixtures of variable hydrogen:chlorine ratio.

\[ \log Su + \frac{1}{2} \log \left( \frac{T_f - T_0}{T_f^2} \right) \]

\[ \frac{1}{T_f} \times 10^4 \ \text{K}^{-1} \]
Istratov and Librovich \(^{44}\) assume that the flame reaction takes place by a 'normal chain propagation' scheme involving reaction (3') followed by reactions (1) and (2). If the effect of temperature on such physical properties as specific heat, density, etc. is neglected, the equation may be expressed in a similar manner to previous equations:

\[
\log Su - \frac{3}{2} \log T_f = K_3 - 0.4343 \left( E_0 + E_D \right) 4.1.3.
\]

where \(K_3\) is approximately constant for a given mixture.

Application of equation 4.1.3. to the experimental results provides a straight line relationship in all cases (figs. 58 and 59) and, surprisingly the best fit to a straight line is obtained for mixtures of variable composition (fig. 59).

Rozlovskii \(^{77}\) has derived an equation which may be used to predict the overall activation energy for the flame reaction, \(E_R\). A refined equation yields activation energies which are almost the same as those values predicted by the simpler equation:

\[
\log Su = K_4 - \frac{0.4343 E_R}{2RT_f} 4.1.4.
\]

where \(K_4\) is approximately constant for a given mixture.
Application of the equation of Istratov and Librovich for mixtures containing 52% hydrogen and 58% hydrogen.

- 52% Hydrogen/48% chlorine
- 58% Hydrogen/42% chlorine

\[ \log S + \frac{3}{2} \log T \]

\[ \frac{1}{T} \times 10^4 (\text{K}^{-1}) \]
Application of the equations from Rozlovskii and Istratov and Librovich for mixtures of variable hydrogen:chlorine ratio.

\[ \log S_u = \frac{1}{T_f} \times 10^4 \, (^0K^{-1}) \]
When equation 4.1.4. is applied to the present experimental results, straight-line plots are again obtained for mixtures of constant fuel:oxidant ratio (fig. 60) and an even closer approximation is obtained for mixtures of variable fuel:oxidant ratio (fig. 59).

In view of the fact that the Van Tiggelen equation is unable to distinguish between a first order and second order reaction, that the Zeldovich equation is capable of predicting both an 'energy branching' scheme and a 'normal chain propagation' scheme, and that all equations are capable of correlating results not strictly applicable (mixtures of variable composition), the theories must be somewhat doubtful. This is hardly surprising in view of the rigid assumptions and approximations used in the derivation of the equations.

However, values of activation energy predicted by all the equations are presented in Table V, and these values are compared with expected values so that at least tentative conclusions may be drawn regarding the particular mechanism in operation.

In general the activation energies predicted by all the foregoing equations increase with increasing concentration of hydrogen in the mixture, but for mixtures
Application of the approximate equation derived from Rozlovskii for mixtures containing 52% hydrogen and 58% hydrogen.

- ○ 52% Hydrogen / 48% Chlorine
- ☒ 58% Hydrogen / 42% Chlorine
### Table V.

Activation energies predicted from the theories applied to the hydrogen-chlorine flame reaction.

<table>
<thead>
<tr>
<th>Mixture composition</th>
<th>Equation applied</th>
<th>$E_A + E_B$</th>
<th>$E_C + E_D$</th>
<th>$E_B + E_D$</th>
<th>$E_B$</th>
<th>$E_V$</th>
<th>$E_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%H$_2$</td>
<td>%Cl$_2$</td>
<td></td>
<td>kcal.mole$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>48</td>
<td>Van Tiggelen, $i=1$</td>
<td></td>
<td></td>
<td>20.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>48</td>
<td>Van Tiggelen, $i=2$</td>
<td>19.0</td>
<td></td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>48</td>
<td>Zeldovich</td>
<td>48.9</td>
<td>22.1</td>
<td>16.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>48</td>
<td>Istratov and Librovich</td>
<td></td>
<td></td>
<td>38.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>48</td>
<td>Rozlovskii</td>
<td></td>
<td></td>
<td></td>
<td>31.0</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>42</td>
<td>Van Tiggelen, $i=1$</td>
<td></td>
<td></td>
<td>27.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>42</td>
<td>Van Tiggelen, $i=2$</td>
<td>25.1</td>
<td></td>
<td>23.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>42</td>
<td>Zeldovich</td>
<td>57.5</td>
<td>26.8</td>
<td>20.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>42</td>
<td>Istratov and Librovich</td>
<td></td>
<td></td>
<td>48.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>42</td>
<td>Rozlovskii</td>
<td></td>
<td></td>
<td>35.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>variable</td>
<td>Van Tiggelen, $i=1$</td>
<td></td>
<td></td>
<td></td>
<td>44.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>variable</td>
<td>Van Tiggelen, $i=2$</td>
<td></td>
<td></td>
<td></td>
<td>38.3</td>
<td>36.3</td>
<td></td>
</tr>
<tr>
<td>variable</td>
<td>Zeldovich</td>
<td></td>
<td></td>
<td></td>
<td>92.0</td>
<td>47.2</td>
<td>41.2</td>
</tr>
<tr>
<td>variable</td>
<td>Istratov and Librovich</td>
<td></td>
<td></td>
<td></td>
<td>85.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>variable</td>
<td>Rozlovskii</td>
<td></td>
<td></td>
<td></td>
<td>54.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of constant fuel:oxidant ratio the values are rather lower than the expected values. For mixtures of variable composition predicted values of activation energy are higher than the expected values, but the significance of these predictions is uncertain and will not be considered further.

The theories dealing with the activation energy for the 'normal chain propagation' scheme (Zeldovich 76 and Istratov and Librovich 44) predict values of \((E_C + E_D)\) between 38.7 and 57.5 kcal.mole\(^{-1}\) (Table V) compared with the expected value of 63 kcal.mole\(^{-1}\) \(^2\). In view of the likely errors in the theories already discussed, a predicted activation energy which is within 10% of the theoretical value is as good agreement as can reasonably be expected. Indeed, the value of 57.5 kcal.mole\(^{-1}\) is surprisingly close to the expected value. Furthermore, Rozlovskii 77 has proposed an activation energy of 34.7 kcal.mole\(^{-1}\) for the preflame reaction, based on a normal chain propagation scheme, and his 77 values in Table V are close to this value.

Finally it is of interest to note that, if the temperature corrections on the left hand side of the equations 4.1.1 and 4.1.3 (i.e. those predicting a 'normal chain propagation' scheme) are ignored, the two equations both become:

\[
\log Su = K_5 - \frac{0.4343 (E_C + E_D)}{4 \frac{RT_f}{p}} \tag{4.1.5}
\]

where \(K_5 = K_1 = K_3\).
Here, when several assumptions already discussed are ignored, it is possible to obtain values of activation energy, $(E_C + E_D)$, for mixtures of constant fuel:oxidant ratio, of $62.0 \text{ kcal.mole}^{-1}$ (52% hydrogen) and $71.2 \text{ kcal.mole}^{-1}$ (58% hydrogen). These values are much nearer to the expected value than those predicted by equations 4.1.1. and 4.1.3.

Reaction (2) is highly exothermic ($45 \text{ kcal.mole}^{-1}$) and in the application of the 'energy-branching' scheme (reactions (24) and (25)), if all this energy were to be stored in the excited hydrogen chloride molecule, then consideration of reaction (25) suggests that the minimum value of $E_B$ is $12 \text{ kcal.mole}^{-1}$. However, transfer to the hydrogen chloride molecule of all the energy liberated in reaction (2) is unlikely, and $30 \text{ kcal.mole}^{-1}$ is a more likely amount to be transferred; $E_B$ would thus take on a minimum value of $27 \text{ kcal.mole}^{-1}$. The values of the activation energy predicted by the Van Tiggelen 82 and Zeldovich 76 equations are in surprisingly good agreement (Table V). The values are generally low, and even the higher predicted value ($23.1 \text{ kcal.mole}^{-1}$) would require approximately $34 \text{ kcal.mole}^{-1}$ of the total energy liberated in reaction (2) ($45.0 \text{ kcal.mole}^{-1}$) to be stored in the excited hydrogen chloride molecule. In view of the foregoing discussion this is rather doubtful, and thus the lower values
of $E_B$, too, are hardly possible. As with other equations the prediction of activation energies to within better than 10% of the expected value is unlikely.

If any functions other than burning velocity on the left hand side of equations 1.3.3.1 and 4.1.2 are neglected, values of the predicted activation energy are obtained which perhaps add more support to the possibility of an 'energy-branching' scheme.

The doubtful predicted values of activation energy obtained for all the equations considered may be due in the main to the rather doubtful assumptions on which the equations are derived. However, the influence of physical factors such as diffusion should be emphasised. In addition, adiabatic flame temperatures (which have already been shown to be an important variable on which the predicted values of activation energy may depend) calculated for these equations, depend on the source of information for such functions as heat contents and equilibrium constants.

Although considerable doubt has been thrown on the validity of the theoretical equations, some general conclusions may be drawn from the applications already considered. No definite proof has been obtained that a particular mechanism operates in the hydrogen-chlorine flame, although values of activation energy predicted for the
'normal chain propagation' scheme are rather more likely than predictions based on an 'energy-branching' scheme. However, the assumption of a Maxwell distribution in the flame, upon which the 'energy-branching' scheme is essentially based, may not be legitimate, and a mechanism of more solid foundation (the normal chain propagation scheme) may be preferred, a fact borne out by Rozlovskii's results 77. There is no doubt, however, that further evidence is necessary to prove that any particular mechanism is in operation.

4.2. The influence of additives.

4.2.1. Significance of the method of presentation of the results.

The effects of additives on the burning velocity of fuel-oxidant mixtures have generally been measured by :-

(a) Introduction of increasing amounts of a given additive (e.g. 0 to 5%) to mixtures of constant fuel:oxidant ratio.
(b) Introduction of a constant quantity (e.g. 2%) of different additives separately to mixtures of constant fuel:oxidant ratio.

The basic assumption has been made in previous work that the stoichiometry remains more or less constant. However, in practice even small quantities of an additive have a considerable effect on the stoichiometry of a
fuel-oxidant reaction.

In the present work, therefore, the maximum burning velocity has been estimated for a fuel-oxidant mixture to which a given amount of additive has been introduced. This procedure avoids the effect of an additive being dependent on a given fuel:oxidant ratio. However, the use of one particular concentration of several different additives cannot in itself give an accurate picture of the relative effectiveness of these additives. For example, from fig.61, the relative effects of various additives at concentrations of 0.2, 0.8 and 1.6% are quite different, and it is therefore necessary to complete the investigation over the entire range of concentrations where measurements can be made. By a similar argument the values of the burning velocity to the right of the curves in fig.61 cannot justifiably be extrapolated to higher concentrations. Measurements are not, however, made with larger amounts of additive since it is principally small concentrations that are of interest in chemical inhibition. Furthermore, above the concentrations used here radiation losses considerably affect the shape of the burning velocity curve, and carbon formation makes experimental determinations difficult.

Thus the effects of additives can be legitimately compared only by plotting the maximum burning velocities
Comparison of selected additives.
obtained for given additive concentrations against the amounts of additive in the mixture, for as wide as possible a range of additive concentrations. This method of presentation has been used throughout this work.

Furthermore, the movement of the position of the maximum burning velocity with increase in additive concentration gives some guide as to possible reactions in the flame (see section 4.2.4 later). The movement of the position of the maximum is thus shown in the appropriate figures, but serves only as an approximate guide as to the nature of the chemical reactions in which the additive is involved.

4.2.2. Flames burning with an air surround.

The effect of additives on flames burning with an air surround is to produce inhibition in almost all cases (except methyl bromide). However, comparison of the results reported in sections 3.2.6 and 3.2.7 shows that to a close approximation the best inhibitor in section 3.2.6 corresponds to the best inhibitor (n-butane) in section 3.2.7, and the worst inhibitor in section 3.2.6 corresponds to the best promoter (methyl bromide) in section 3.2.7. It may thus be supposed that the action of the additives is essentially the same in both cases, but the small amount of oxygen present in those flames burning with an air
surround affects the kinetics, at least in the initial stages of the reaction. After initial inhibition, oxygen raises the burning velocity by a considerable amount (fig.47), and an additive-free mixture containing a little oxygen has been selected as a standard for comparison of the results reported in figs.26-34. It appears that the action of an additive is to lower the burning velocity by reaction with, and subsequent removal of, the oxygen available, and at the same time to react with chlorine or hydrogen, as though no oxygen was present, to raise the burning velocity. The final burning velocity depends on the relative magnitudes of the above effects. For example, in the case of methyl bromide, the promotion exhibited in fig.46 appears to be more or less balanced by the lowering of the burning velocity due to the removal of oxygen which has diffused into the flame (fig.34).

Finally it should be particularly noted that in figs.26-34 the movement of the maximum, for the introduction of very small amounts of an additive to a flame burning with an air surround, is rapid and in the opposite direction to the movement of the maximum for introduction of oxygen (fig.47). This supports the suggestion that the removal of oxygen in the initial stages of reaction is probably the predominant reaction.
Thus, the introduction of oxygen into the flame, by diffusion of air into the flame, is expected to have a considerable effect on the kinetics. An attempt is made, therefore, to estimate the amount of air diffusing into the flames, by comparison of flames, with and without added oxygen, burning in an inert surround, with the corresponding flames burning with an air surround.

When a silica burner was used the maximum burning velocity for a hydrogen–chlorine mixture containing 30% nitrogen and burning with an air surround was found to be 271 cm. sec.\(^{-1}\) at a hydrogen concentration of approximately 67%. In order to set up these conditions (both as regards the value of the burning velocity and the position of the maximum) it was necessary to introduce approximately 1.7% oxygen into a flame burning with a nitrogen surround (fig. 47). If this amount of oxygen was diffusing in from the air surround, it would be accompanied by approximately four times the amount of nitrogen. This result is only approximate as it should be noted that in one instance an oxygen–nitrogen mixture diffuses into the flame and in the second case only nitrogen diffuses into the flame and oxygen is introduced in the premixed gases. It has also been assumed that the rate of diffusion of air is the same as the rate of diffusion of nitrogen.
As nitrogen has been shown to exert merely a cooling effect and is not expected to react chemically, the effect on the flame has been assumed to be small and constant under otherwise identical conditions. However, the amount of nitrogen calculated to diffuse into the flame would result in a lowering of the burning velocity by only ca. 35 cm sec⁻¹. Application of corrected values of the burning velocity from fig.18 to the equations of section 4.1 results in a decrease of approximately 5% in the calculated activation energy values reported in Table V.

4.2.3. The effect of an increase in the adiabatic flame temperature.

Adiabatic flame temperatures have been calculated by an accurate method 61 using recent data 83, and a plot of the results for a hydrogen-chlorine mixture containing 30% nitrogen is shown in fig.62. Two curves are presented. The approximate calculation assumes no dissociation of the molecules, and flame temperatures have been calculated using the specific heats of the gases. The accurate calculation is of particular interest here, and dissociation of the molecules into atoms results in a lowering of the flame temperature, to give the results shown. The shape of the curve is explained by the large difference in the dissociation constants for hydrogen and chlorine at
Adiabatic flame temperature calculations for a hydrogen-chlorine mixture containing 30% nitrogen.

Approximate (no dissociation)

Accurate (assuming dissociation)

\[%H_2 = \frac{H_2}{H_2 + Cl_2} \times 100\]
the particular temperatures considered. As the extent of dissociation of chlorine is greater than that of hydrogen at these temperatures, the greatest effect is observed for chlorine-rich mixtures. Indeed, for hydrogen-rich mixtures the curves eventually coincide.

It is well known that an increase in the flame temperature is associated with an increase in the burning velocity. For example, introduction of 1% methane into the mixture leads to an increase of approximately $140^\circ C$ in the calculated adiabatic flame temperature, assuming that all the methane reacts to give carbon tetrachloride, i.e. that the maximum possible heat release takes place. In view of the foregoing discussion complete chlorination of the methane, although hardly likely, would result in an increase of approximately 7% in the flame temperature, whereas the burning velocity increases by at least 13% (see fig. 36). Furthermore, additives such as methyl chloride and methyl bromide are even more effective than methane in amounts as low as 0.5%. For example, 0.5% methyl chloride, burning to carbon tetrachloride in the flame, raises the calculated adiabatic flame temperature by 1.5% and yet the burning velocity increases by at least 19%.

Thus, although the slight increase in the flame temperature, due to the introduction of a small amount of additive, makes a small but definite contribution towards an
increase in the burning velocity, the magnitude cannot be explained solely on this basis and other possibilities must be considered.

4.2.4. The general features of the burning velocity curves.

From the results reported in section 3.2.7 it can be seen that the addition of organic compounds has an unexpected and individual effect on both the position of the maximum burning velocity, and on the actual value of the burning velocity. These results are primarily treated in a semiquantitative manner to investigate what information may be obtained. In particular oxygen is seen to have a definite influence, and it is expected that the effect of this additive will be present for flames burning with an air surround.

Of the additives showing large promotional effects, methane, deuteromethane-d₄, acetylene, methyl chloride and methyl bromide all show a rapid increase of burning velocity to a maximum and then a subsequent regular fall in value. It is observed experimentally that the maximum value of the burning velocity coincides roughly with the appearance of a red tip in the flame, due to carbon formation, and heat losses by carbon radiation may then become very significant, resulting in a decrease in the
burning velocity. Smoke formation is not observed for the concentrations employed here, except for acetylene which, incidentally, shows the largest rate of fall after reaching a maximum.

Ethane, n-butane and isobutane act as inhibitors and the burning velocity gradually decreases. All exhibit considerable smoke formation even in very small concentrations, and it may well be suggested that, if heat losses by radiation could be avoided, these additives, too, would show a small promoting effect, as is indicated for very small amounts of additive.

In the case of ethylene, the picture is not so clear, but again the decrease in burning velocity may well be largely a thermal effect, and without this even ethylene could promote the reaction.

Heat losses by radiation when oxygen is used as an additive are likely to be much smaller, and after initial inhibition the ensuing increase may be due to a chain-branching reaction between hydrogen and oxygen.

The similarity between the initial inhibiting and the subsequent promoting effects of both oxygen and dimethyl ether (fig.44) tends to suggest that some sort of common mechanism exists. In particular the initial inhibition seems to be associated with some oxygen-
containing species and the promoting effect of dimethyl ether may be due to oxygen promotion associated with promotion due to methyl radicals derived from the ether (see fig.36). The ultimate decrease in burning velocity coincides with carbon formation and simultaneously larger heat losses.

The results above, indicating the probable formation of methyl radicals, and the formation of carbon in the flame, suggest that the additive may rapidly break down at such high temperatures. This breakdown would probably be negligibly slow under non-flame conditions.

In the accompanying curves showing the movement of the position of maximum burning velocity, a movement of the maximum towards a fuel-rich mixture composition indicates a reaction between hydrogen and the additive or its intermediates. A movement in the opposite direction indicates that chlorine may be reacting with the additive or its intermediates. The shift towards a chlorine-rich mixture composition is often accompanied by carbon formation. It has been shown (fig.18) that nitrogen in increasing amounts tends to shift the position of maximum towards a chlorine-rich composition, and thermal losses, both for nitrogen and when carbon formation takes place, may have some effect in causing this movement.
4.2.5. **Application of the 'energy-branching' scheme.**

The 'energy-branching' scheme for hydrogen-chlorine flames implies that a large proportion of the total energy (45 kcal.mole⁻¹) for the reaction:

\[ \text{(24)} \ H + \text{Cl}_2 \rightarrow \text{HCl}^* + \text{Cl} \]

is stored in the excited hydrogen chloride molecule, HCl*. This energy may be used in the dissociation of chlorine molecules to give a branching reaction:

\[ \text{(25)} \ \text{HCl}^* + \text{Cl}_2 \rightarrow \text{HCl} + 2\text{Cl} \]

If this scheme is applied to account for the promotional effects observed with some additives, two methods of producing further free atoms or radicals may be visualised:
(a) A reaction may take place which is more exothermic than reaction (24), and hence the excited product of the reaction may have a greater chance of obtaining sufficient energy to cause dissociation, on reaction with chlorine molecules.
(b) The additive may require less energy for dissociation than a chlorine molecule (57 kcal.mole⁻¹), and thus any excited products of reactions similar to reaction (24) will also require less energy to cause dissociation.

Of the additives exhibiting greater promotion (methane, methyl chloride, methyl bromide and oxygen, for example), reaction of their derivatives in a
similar manner to the non-branching reaction (24), results in a step much less exothermic than 45 kcal.mole\(^{-1}\). Hence, it is unlikely that a reaction species will contain energy in excess of that for an excited hydrogen chloride molecule.

Furthermore, all additives used have a bond dissociation energy for removal of an atom or radical which is greater than that for chlorine molecules. The additive having the lowest bond dissociation energy for the removal of an atom is methyl bromide (66 kcal.mole\(^{-1}\)), but even this is rather larger than that necessary to dissociate a chlorine molecule.

Assuming, furthermore, that free atom production can take place by the breakdown of an excited hydrogen chloride molecule, HCl\(^*\), containing, for example, 30 kcal.mole\(^{-1}\) of the total energy, then a further 72 kcal.mole\(^{-1}\) is necessary to dissociate the molecule\(^2\). The energy to dissociate methyl chloride (see later), for example, is 82 kcal.mole\(^{-1}\)\(^2\), and it is hardly likely that an additive requiring a greater activation energy for dissociation than the excited hydrogen chloride molecule will promote the reaction.

Hence, an 'energy-branching' scheme appears unable to account for the experimental observations.
4.2.6. Application of the normal chain propagation scheme.

The large effects observed, even for small amounts of an additive, suggest a chemical mechanism similar to the 'normal chain propagation' scheme but involving also the additive concerned.

It has already been suggested 61 that the relationship between the burning velocity and the rate of reaction is of the form:

\[ Su^2 \propto e^{-E_N/RT_f} \] 4.2.6.1.

where \( E_N \) is the activation energy for the reaction and other symbols are as defined previously. This may be written:

\[ Su^2 = F e^{-E_N/RT_f} \] 4.2.6.2.

where \( F \) is a factor which takes into account all other variables. Taking logarithms:

\[ 2 \log Su = \log F - \frac{0.4343 E_N}{RT_f} \] 4.2.6.3.

If the activation energy for the removal of a particular atom or radical from the molecule introduced is the controlling factor for the reaction, then a plot of \( \log Su \) against \( E_N \) could, in fact, produce a straight line relationship. However, for the reactions considered, this could hardly be realised as reaction (3') has been shown to be most important,
but if the initial removal of an atom or radical from the molecule considered is an important step in the reaction, one would expect the maximum burning velocity to be greater for the more easily removed atom or radical. Fig. 63 shows the application of such reasoning to most of the additives exhibiting promotional effects.

The peak value of the burning velocity, taken from figs. 35-47 is plotted against the activation energy for the removal of the most easily removed atom or radical. This is a bromine atom for methyl bromide, a chlorine atom for methyl chloride, hydrogen atoms for methane and acetylene and a methyl radical for dimethyl ether. The correlation is surprisingly good, except for dimethyl ether, and it is interesting to note that the better promoters may perhaps provide a methyl radical in the initial stage. Dimethyl ether shows a much higher burning velocity than is to be expected from the activation energy of the initial reaction and it is possible that the remaining radical, \( \text{CH}_3\text{O} \), may exert some considerable promoting influence, or, in fact, provide further radicals, \( \text{CH}_3 \) and \( \text{O} \), which may themselves enhance reaction. However, the reactions of all these additives are discussed later.

In fig. 64 the rate of increase of burning velocity for the gradual introduction of the additive in very
Application of equation 4.2.6.3 for some additives exhibiting promotion.

- dimethyl ether
- methyl bromide
- methyl chloride
- methane
- acetylene
small amounts (i.e. the slope of the burning velocity-additive curve for initial introduction of the additive) is again compared with the activation energy for the step involving the easiest removal of an atom or radical, for the same additives as previously. Here, all points fall near or on a simple curve, and it should be particularly noted that the result for dimethyl ether, in contrast to the preceding graph, falls in with those of other promoters. However, the general shape of the curve (fig. 44) indicates that reactions other than the splitting of a CH$_3$ radical are involved. Indeed the shift of the position of the maximum indicates that a reaction between hydrogen and derivatives of the additive may be important, and this could well be a hydrogen-oxygen reaction. Other additives (except deuteromethane-d$_4$ and oxygen) show some considerable inhibition which may in the main be due to heat losses. Indeed, even those additives exhibiting promotion may also be influenced by such losses, and hence the general shape of the curve may not always suggest the true operating mechanism. In the first instance mechanisms are suggested for each additive used. It should be noted, however, that many of the experimental results are to some extent unexpected, and these mechanisms should provide only a first insight into those reactions taking place in the particular flame under consideration.
Rate of increase of burning velocity for additives showing promotion.

![Graph showing rate of increase of burning velocity vs. activation energy](image)
The normal chain propagation scheme for the hydrogen-chlorine reaction has already been extensively discussed, but the possible initiating, propagating and terminating steps are repeated here for convenience.

**Initiation**

(3') \( \text{Cl}_2 + M \rightarrow 2\text{Cl} + M \)

(15') \( \text{H}_2 + M \rightarrow 2\text{H} + M \)

**Propagation**

(1) \( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \)

(2) \( \text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \)

**Termination**

(4) \( \text{Cl} + \text{Cl} + M \rightarrow \text{Cl}_2 + M \)

(5) \( \text{H} + \text{H} + M \rightarrow \text{H}_2 + M \)

(6) \( \text{H} + \text{Cl} + M \rightarrow \text{HCl} + M \)

Thus the reaction will be promoted if there is an increase in the number of active centres, and if these centres are made available for propagation steps. It may well be that the action of an additive causes promotion by a branching reaction of the additive, or, on the other hand, by reacting with \( \text{Cl} \) or \( \text{H} \) which would otherwise be lost in some immediate termination step. Also, as hydrogen chloride is likely to be formed in large amounts by the propagation
steps (1) and (2) and possibly the terminating reaction (6), atoms may be produced by the decomposition of hydrogen chloride at the very high temperatures encountered in the flame.

\[(6') \text{HCl} + M \rightarrow H + Cl + M\]

On the other hand, the additive itself may be a source of atoms or free radicals either by a chain propagating step or as a result of its decomposition in the flame.

Termination of the reaction may take place as a result of the enhanced steps (4) - (6), or by the reaction of any available free atom or radical with the additive or its derivative. Furthermore, as will be seen later, products derived from reactions of the additive with chlorine may themselves break down to produce relatively stable molecules.

The additives used may now be considered in more detail, and reference will be made to the above chain propagation steps. Heats of reaction for a particular step are derived from values given by Semenov 2 and will be included where known.

Methane (fig. 36), although having a maximum burning velocity with chlorine which is lower than that for the hydrogen-chlorine flame (fig. 48), exerts a
strong promotional effect. The foregoing discussion in relation to figs. 63 and 64 suggests that a likely decomposition step is:

\[(32) \quad \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} -101\]

or alternatively

\[(33) \quad \text{CH}_4 + \text{Cl} \rightarrow \text{CH}_3 + \text{HCl} + 1\]

\[(33') \quad \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 + 2\]

Reactions (33) and (33'), having much lower activation energies than reaction (32), are more likely. Reaction (33) has a lower activation energy than reaction (33') \(^2\) and is probably the main propagating step, but reaction (33') should not be excluded. Both reactions (33) and (33') lead to the production of \(\text{CH}_3\) radicals. Reaction (33) may be followed by the propagating step: \(^8\)

\[(34) \quad \text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl} + 25\]

Fig. 36(b) shows little or no movement of the maximum which suggests that hydrogen atoms or molecules may play some part in these reactions.

If it is assumed that decomposition of the product, \((\text{CH}_3\text{Cl})\), of propagation steps similar to reaction (34) is a source of atoms which may act as further chain centres by:
then a chain-branching reaction has in fact taken place. The $\text{CH}_3$ radical is available for steps similar to (34) whilst the $\text{Cl}$ atom is available for propagation steps similar to (1) and (33). Under these conditions, decomposition of hydrogen chloride molecules by reaction (6') is less likely due to a much higher bond dissociation energy (102 kcal.mole$^{-1}$) than for methyl chloride.

The gradual rise of the burning velocity curve may thus be explained by a reaction involving chlorination of the methane by the propagation steps (33) and (34), and subsequent branching by reaction (35).

Methyl chloride and methyl bromide (figs. 45 and 46) show surprisingly rapid promotion of the reaction, methyl bromide being the better promoter. At the same time, for methyl chloride the position of maximum moves towards a fuel-rich mixture composition, indicating a reaction involving hydrogen in particular. Decomposition of both additives takes place by reactions (35) and (36):

\[
(35) \quad \text{CH}_3\text{Cl} \, \rightarrow \, \text{CH}_3 + \text{Cl} \quad -82
\]

\[
(36) \quad \text{CH}_3\text{Br} \, \rightarrow \, \text{CH}_3 + \text{Br} \quad -66
\]

Both reactions are far more likely than dissociation of hydrogen chloride by reaction (6'). Reaction (36) has a lower activation energy (or bond dissociation energy) than
reaction (35) and leads to the production of a larger number of CH₂ radicals. The CH₂ radicals propagate the chain by reaction (34) followed by reaction (35). Hence, methyl bromide is the better promoter, and this is confirmed by figs. 45 and 46. The shift of maximum shown in fig. 45(b) may be due to the production of chlorine molecules by the termination reaction (4), resulting from an upset of normal equilibrium conditions in the flame by the introduction of Cl atoms derived from reaction (35). The removal of hydrogen by the propagation step (1) involving Cl atoms produced by reaction (35) is hardly likely as Br atoms would have the same effect as a result of the reaction:

(37) Br + H₂ → HBr + H

and the expected movement towards a fuel-rich mixture composition in this case is not realised (fig. 46(b)). However, it should be noted, that Br atoms may be removed by propagation steps involving both hydrogen and chlorine molecules:

(38) Br + Cl₂ → BrCl + Cl
(38') Br + H₂ → HBr + H

Here, production of Cl atoms and H atoms simultaneously may account for the stationary position of the maximum observed in fig. 46(b). If this is the case, then removal of hydrogen
molecules by reaction (1), involving Cl atoms derived from reaction (35), is likely to occur.

In particular the relatively slow rise to a maximum shown by methane, when compared with methyl bromide and methyl chloride, may be explained by the need to chlorinate the methane by reactions (33) and (34) before a branching reaction (35) can take place. Hence a greater number of steps is necessary.

Deuteromethane-d₄ (fig.38) exerts a surprisingly large promotional effect which is approximately twice that for methane. Due to the higher activation energy for the removal of D atoms from CD₄ than for the removal of H atoms from CH₄ it would be expected that promotion by methane would be greater than by deuteromethane-d₄. However, it is suggested ⁸⁵ that, if the main controlling steps for the reaction of deuterium or hydrogen with chlorine are (2) and a similar reaction:

\[(39) \quad D + Cl₂ \rightarrow DCl + Cl\]

then the rate of reaction with deuterium is greater than the rate of reaction with hydrogen.

In a similar manner it is suggested that, if the reaction of CH₃ or CD₃ radicals with chlorine molecules is a necessary and important chain propagation step, then the greater promoting effects of deuteromethane-d₄ might appear
possible. Reaction (34), involving \( \text{CH}_3 \) radicals and chlorine molecules, has already been suggested as one of the propagating steps which explains the influence of methane; results with deuteromethane-\( d_4 \) confirm this.

The initial reaction probably involves \( \text{Cl} \) or \( \text{H} \) atoms, otherwise lost by termination, in a similar manner to previous reactions:

\[
(40) \quad \text{CD}_4 + \text{Cl} \rightarrow \text{CD}_3 + \text{DCl}
\]

\[
(40') \quad \text{CD}_4 + \text{H} \rightarrow \text{CD}_3 + \text{HD}
\]

giving rise to the necessary \( \text{CD}_3 \) radicals.

Acetylene (fig.43) is a less effective promoter than the additives already discussed, but, in a similar manner, the initiating steps involved may be \( ^8 \)4:

\[
(41) \quad \text{C}_2\text{H}_2 + \text{Cl} \rightarrow \text{C}_2\text{H} + \text{HCl} \quad -19
\]

\[
(41') \quad \text{C}_2\text{H}_2 + \text{H} \rightarrow \text{C}_2\text{H} + \text{H}_2 \quad -18
\]

The fact that the activation energies for these reactions are high compared with those for reactions (33) and (33') shows why acetylene is a less good promoter than methane. The stationary position of the maximum (fig.43(b)) indicates that both reactions (41) and (41') may be important, as is suggested by their similar heats of reaction.

The \( \text{C}_2\text{H} \) radicals produced above may enter into further reaction by the propagation step:
\[(42) \text{C}_2\text{H} + \text{Cl}_2 \rightarrow \text{C}_2\text{HCl} + \text{Cl}\]

Comparison of the bond dissociation energies for the removal of H atoms from acetylene and methane indicates that the activation energy for the reaction:

\[(43) \text{C}_2\text{HCl} \rightarrow \text{C}_2\text{H} + \text{Cl}\]

is probably around 100 kcal.mole\(^{-1}\). Hence, reaction (43), although more probable than reaction (6'), is far less likely to produce chain initiators than is reaction (35) and the promoting effects of acetylene will be correspondingly less than those of methane.

Oxygen (fig.47) exerts initial inhibiting effects which may involve the removal of free H atoms or Cl atoms:

\[(44) \text{Cl} + \text{O}_2 \rightarrow \text{ClO}_2\]
\[(44') \text{H} + \text{O}_2 \rightarrow \text{H}_2\text{O}_2\]

Reactions (44) and (44') are probably the main terminating steps but further reactions should be considered:

\[(45) \text{Cl} + \text{O}_2 \rightarrow \text{ClO} + \text{O}\]
\[(45') \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \quad -15\]

which may be followed by:

\[(46) 2\text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2\]
\[(46') 2\text{OH} \rightarrow \text{H}_2 + \text{O}_2\]
The more or less stationary position of the maximum (fig. 47(b)) suggests termination by removal of both Cl and H.

After initial inhibition the burning velocity increases rapidly and the rate of increase rises with increasing oxygen concentration. Furthermore, there is a rapid movement of the maximum towards a fuel-rich mixture composition. These trends suggest a chain branching reaction between hydrogen and oxygen, including the steps (45') and (47):

\[(47) \quad H_2 + O \rightarrow OH + H + O\]

Reaction (47) takes place as a result of the accumulation of O atoms by reactions (45) and (45').

Termination may continue to take place by reaction (45), and if, in the later stages, reaction (47) becomes more important (this is shown by the linear disappearance of hydrogen (fig. 47(b)) and the non-linear dependence on oxygen concentration in later stages) then the propagation step (2) may become more important than (1) due to the subsequent increase in the proportion of H in the mixture.

Dimethyl ether (fig. 44) exhibits initial inhibition and the reactions here are rather difficult to explain due to the relative complexity of the molecule. However a reaction with hydrogen atoms has been suggested
and it is likely that the main propagation steps are:

\[
(48) \quad \text{CH}_3\text{OCH}_2 + \text{Cl} \rightarrow \text{CH}_3\text{OCH}_2 + \text{HCl}
\]

and

\[
(48') \quad \text{CH}_3\text{OCH}_2 + \text{H} \rightarrow \text{CH}_3\text{OCH}_2 + \text{H}_2
\]

followed by:

\[
(49) \quad \text{CH}_3\text{OCH}_2 + \text{H} \rightarrow \text{CH}_3 + \text{OCH}_3
\]

\[
(50) \quad \text{CH}_3\text{O} \rightarrow \text{CH}_3 + \text{O}
\]

and reaction (34) to produce methyl chloride.

The initial inhibition is followed by rapid promotion of the reaction and at the same time the position of maximum moves towards a fuel-rich composition (fig. 44). Apart from the likely reaction involving methyl chloride to produce free radicals (reaction (35)), there is also a reaction involving hydrogen and the O atoms produced in reaction (50). This is probably a branching reaction similar to reaction (47). Hence, the two sources of free radicals give a surprisingly large promotion, leading to a higher maximum burning velocity than expected.

The initial inhibition may in fact be due to the relative stability of the products of reactions (48) and (48'), and the number of steps involved before radicals or atoms instrumental in causing promotion are produced.
Ethylene (fig. 42) appears to exert an inhibiting effect even in the initial stages. At high temperatures substitution is the likely process \(^8\), and the main initial reaction probably involves chlorine atoms:

\[
(51) \quad C_2H_4 + Cl \rightarrow C_2H_3 + HCl -1
\]

This is followed by \(^8\):

\[
(52) \quad C_2H_3 + Cl_2 \rightarrow C_2H_2Cl + Cl +29
\]

the resulting vinyl chloride being much less likely than methyl chloride to undergo homolytic fission to give reactive free radicals.

Ethane, \(n\)-butane and isobutane (figs. 39-41) all show very similar inhibiting effects. As with other hydrocarbons, the initial reactions probably involve free Cl atoms or H atoms, and the main steps involve a Cl atom. The reactions have been discussed elsewhere \(^8\) and presumably take place by:

\[
(53) \quad C_2H_6 + Cl \rightarrow C_2H_5 + HCl + 4
\]

\[
(54) \quad n-C_4H_{10} + Cl \rightarrow n-C_4H_9 + HCl + 8
\]

\[
(55) \quad iso-C_4H_{10} + Cl \rightarrow iso-C_4H_9 + HCl + 17
\]

all of which have similar activation energies. Reaction with chlorine of the free radicals produced above takes place by:
Free atom and radical production in the flame has been explained previously by the breakdown of the products. However, dissociation of the products of reactions (56) - (58) has been shown to produce relatively stable molecules 87-89:

\[
(59) \quad \text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl} \\
(60) \quad \text{n-C}_4\text{H}_9\text{Cl} \rightarrow \text{n-C}_4\text{H}_8 + \text{HCl} \\
(61) \quad \text{iso-C}_4\text{H}_9\text{Cl} \rightarrow \text{iso-C}_4\text{H}_8 + \text{HCl}
\]

Hydrogen chloride has been suggested as a rather ineffective producer of free atoms (due to the large activation energy for its breakdown) and, indeed, ethylene has been shown to inhibit the reaction. Hence, n-butene and isobutene may be expected to inhibit the reaction also. Thus, the breakdown of the chloro-derivatives of these three additives suggests little possibility of producing the free atoms or radicals necessary for promoting effects (cf. reaction (35)), and inhibition is to be expected (see figs. 39 - 41).
4.3. **Conclusions.**

Burning velocities of hydrogen-chlorine flames, with and without additives, depend on such external factors as burner diameter. It is expected that the maximum burning velocity of a hydrogen-chlorine flame, on a silica burner, is between 600 and 700 cm sec⁻¹ at a hydrogen concentration of approximately 58%, although the effects of burner diameter at high burning velocities may make the burning velocity value higher than the true value.

An increase in the nitrogen content of the mixture in hydrogen-chlorine-nitrogen flames moves the position of the maximum towards a stoichiometric mixture composition. Diffusional effects are probably quite important. Nitrogen reduces the burning velocity, probably as a result of thermal effects.

It is important that the dependence of the effect of an additive on the fuel:oxidant ratio be eliminated, and a new method of study has been proposed here. The effects of additives have been studied over as wide a range of concentrations as possible.

The results for flames with additives and burning with an air surround are influenced by the diffusion of oxygen into the flame, and the initial reaction may take
place between oxygen and the additive. It is important to eliminate the effects due to the diffusion of the surrounding air into the flame.

For hydrogen-chlorine-nitrogen flames, with additives, and burning with a nitrogen surround, the results are unexpected. Strong promotional effects are observed in many cases, and an increase in the flame temperature cannot account for the magnitude of the observed effects. Any reduction in burning velocity is probably due to a fall in the flame temperature as a result of carbon radiation heat losses. The better inhibitors exhibit considerable smoke formation.

The observed effects are probably due to a production of free atoms or radicals in the flame. However, application of several theories of flame propagation for hydrogen-chlorine flames cannot distinguish between the different mechanisms in the flame, but merely shows the limited application of such theories.

No evidence is found to support the 'energy-branching' scheme, and, indeed, the observed effects of additives tend to oppose this scheme.

The 'normal-chain-propagation' scheme may be used to interpret the reactions taking place in the flame.
Initial reaction of the hydrocarbons may be with atoms normally lost by recombination in the flame. Free radicals are produced and these are available for further reaction with chlorine molecules to give the chloro-derivative of the hydrocarbon, by a chain propagating step. New chain centres may be produced by breakdown of this chlorinated product in the flame. Methyl derivatives break down to give methyl radicals and chlorine atoms which are available for further chain propagating steps and hence explain the promoting effects observed. The chloro-derivatives of ethane, n-butane and isobutane, on the other hand, break down to give the relatively stable olefins and hydrogen chloride, thus explaining the lack of promoting effects.

The rapid promoting effects of methyl chloride and methyl bromide are due to immediate breakdown of the additives on entering the flame. The strong promoting effects observed with oxygen and dimethyl ether are probably due mainly to a reaction between hydrogen and oxygen. Chloro derivatives of ethylene and acetylene are relatively stable compared with methyl chloride, and are thus less effective as promoters.

A wide range of additives has been studied and suitable conditions for their comparison have been established. It is suggested that the study of further
methyl derivatives and of oxygenated compounds may be of interest, and provide additional evidence for a particular mechanism. Chemical analysis of the flames may indicate the presence of certain free radicals or atoms and hence help in explaining the kinetics of the reaction.

Additional evidence for the action of these inhibitors may be found by measurement of the flammability limits of the various hydrogen-chlorine-additive mixtures considered here.
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