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A T H E S I S

entitled

THE INFLUENCE OF HALOGEN COMPOUNDS

ON GASEOUS OXIDATION PROCESSES

submitted by

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ABSTRACT

This thesis describes an investigation of the effects of four bromomethanes and hydrogen bromide on the gaseous oxidation of several fuels. In the Introduction the relevant basic theory of chain reactions is first outlined and then the general oxidation mechanisms are considered with particular reference to the compounds studied in this work. Finally the modes of action of various additives in gaseous oxidation reactions are described.

In the Experimental Section a full account is given of the vacuum system used and the methods employed for the preparation and purification of the reactants are outlined. The procedures employed for obtaining pressure-time curves and the methods of chemical and gas-liquid chromatographic analysis used are also fully described.

The Results Section consists largely of rate measurements for the various fuel-oxygen-additive systems studied. Graphs derived from this basic data are also included showing the effects of the various additives relative to one another.

Hydrogen bromide exerts a marked, usually promoting, influence on the oxidation of all the fuels studied while the bromomethanes have a well-defined effect only on oxidation reactions occurring at above 400°C. When the halomethanes do exert an appreciable influence on combustion reactions their effect is qualitatively similar to that of hydrogen bromide. This latter additive retards only the oxidations of formaldehyde and methane while the bromomethanes retard only the oxidation of methane. These retarding effects are confined to the later stages of reaction and to small amounts of additive.

In the Discussion an attempt is made to explain these results in terms of the reaction mechanisms involved. Promotion by hydrogen bromide is ascribed either to its direct reaction with oxygen providing an extra mode of chain-initiation, or to its interaction with intermediate peroxides giving rise to enhanced chain-branching. Hydrogen bromide exerts its retarding influence on the oxidation of formaldehyde largely by reacting readily with hydroxyl radicals, thereby significantly reducing the concentration of these important chain-carriers. In the methane oxidation system hydrogen bromide also effectively removes methyl radicals, thereby interrupting the normal chain cycle. The bromomethanes themselves do not appreciably affect the combustion of the fuels studied and it is only their oxidation or pyrolysis products, bromine and hydrogen bromide, which have a pronounced influence as additives.

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INTRODUCTION   Page

A. THE MECHANISM OF THE GASEOUS OXIDATION OF ORGANIC COMPOUNDS

1. General

When the vapour of any organic compound is mixed with air or oxygen under sufficiently energetic conditions of temperature and pressure, a chemical reaction will occur which will eventually cause the complete destruction of the compound. Depending upon the experimental conditions employed, the reaction will either take place slowly and more or less isothermally, or the mixture will ignite spontaneously with the passage of a flame and the emission of light and heat. The final products generally include oxides of carbon and steam, but if the conditions are carefully controlled, high yields of intermediate products such as aldehydes, ketones, and peroxides can frequently be isolated. The manner in which these compounds are produced during the reaction has been the subject of much work since the beginning of this century but the detailed reaction mechanisms have been elucidated in only a few systems. This is not surprising in view of the extremely complex state of affairs which exists during a gaseous oxidation reaction. It is found that the reaction route followed is very dependent on the experimental conditions used. For example, the oxidation of paraffin hydrocarbons gives mainly oxygenated organic products at fairly low temperatures, (1-3) but at rather higher temperatures the principal product is the olefin with the same carbon skeleton as the starting material. If the reaction temperature is further increased, lower olefins and paraffins appear in increasing amounts, while the quantities of oxygenated products and undegraded olefins steadily decrease. In the same way, the amounts of the various

products formed are affected by the proportion of oxygen in the
reacting gases, by the total pressure in the system, by the presence of
additives, and by the nature and extent of the surface of the reaction
vessel.   Nevertheless a stage has been reached where it is possible to
outline a general reaction mechanism for the gaseous oxidation of
organic compounds.   This mechanism, as applied to hydrocarbons and
their simple derivatives, will now be discussed in some detail in the
following sections.

2. The theory of chain reactions

a) Linear and branched chain reactions

It is now firmly established that the gaseous oxidation of
most fuels occurs through a free radical chain mechanism.   This is
clearly shown by many characteristic features such as great sensitivity
to the surface conditions and to the presence of additives.

A typical example of a free radical chain reaction is
provided by the hydrogen-oxygen reaction (4).   In this reaction,
free radicals are first produced by some initiating reaction.   Here,
this reaction is now thought to be:

$$H_2 + O_2 \longrightarrow H_2O_2 \longrightarrow 2\ \dot{O}H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

This reaction occurs only very infrequently on account of its high
activation energy.   The $\dot{O}H$ radical produced is very reactive and can,
for example, readily react with hydrogen:

$$\dot{O}H + H_2 \longrightarrow H_2O + \dot{H} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2$$
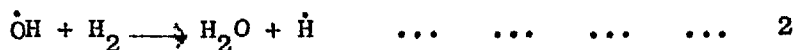
as in reaction 2, producing a hydrogen atom which is more or less
equally reactive.   This process of constant regeneration of active
species is known as chain propagation.   The above reaction involves
the interaction of a free radical with a molecule and in general this

type of process requires little or no activation energy.   The reaction

chain may then be continued as follows:

$$\dot{H} + O_2 \longrightarrow \dot{O}H + \dot{\underset{\bullet}{O}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 3$$

$$\underset{\bullet}{\dot{O}} + H_2 \longrightarrow \dot{O}H + \dot{H} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 4$$
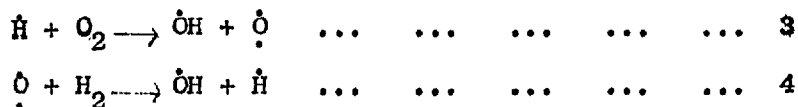
In these reactions, one chain carrier produces two chain carriers, both

of which can continue the chain, and these reactions are therefore

termed chain-branching reactions.   In this reaction, then, a very slow

chain-initiating reaction is followed by a rapid chain-branching process.

When two chain carriers combine, either at the wall, or in the

gas phase, a stable molecule of product normally results.   This process

is called chain termination.   For the hydrogen-oxygen reaction, the

process may be shown simply as:

$$\left. \begin{array}{l} OH \longrightarrow wall \\ H \longrightarrow wall \\ O \longrightarrow wall \end{array} \right\} \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 5$$

Alternatively, termination may occur in the gas phase in which case the

presence of a third body is usually required to remove the excess

energy present at the moment of collision.

It is possible to give a detailed explanation of the

experimental phenomena observed in the hydrogen-oxygen system in terms

of a free-radical chain mechanism of the type outlined above.   Thus it

can be considered satisfactorily proven that the hydrogen-oxygen

reaction is in fact a free-radical chain process.   However, another

possible concept is that of a purely molecular reaction.   Here, it is

necessary to postulate the collision of two hydrogen molecules with one

oxygen molecule, the product, water, being formed at the moment of

collision by the simultaneous rupture and formation of several bonds. This may be represented:

$$2H_2 + O_2 \longrightarrow \begin{matrix} H \\ | \\ H \end{matrix} + \begin{matrix} O \\ \vdots \\ O \end{matrix} + \begin{matrix} H \\ | \\ H \end{matrix} \longrightarrow \begin{matrix} H - O - H \\ H - O - H \end{matrix}$$
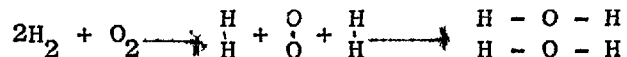
However it can be shown from kinetic theory that the probability of the correct conditions occurring for such a termolecular collision to take place and to lead to chemical reaction is very low and this molecular reaction does not occur in practice.

In a chain reaction, the chain length is defined as the average number of molecules of the initial reactant(s) transformed for each chain carrier produced by the initiating reaction (5). If there is no branching, the chain carriers produced can only react in two ways. They can either propagate the chain or suffer termination. As a result of propagation, one molecule of product and another chain centre are formed in each reaction cycle. Then if:

α = probability of propagation

β = probability of termination

$$\alpha + \beta = 1$$

The probability, P_s, that a chain will recur S times before termination occurs is then the product of the probability that propagation will recur S-1 times i.e. α^{S-1} and the termination probability β. Thus

$$P_s = \alpha^{s-1}\beta = \alpha^{s-1}(1-\alpha)$$

Now as P_s is a probability,

$$\sum_{s=1}^{\infty} P_s = 1$$

Also, by definition, the chain length, ν, is the mean value of s, so that

$$\nu = \bar{s} = \sum_1^{\infty} P_s S = \sum_1^{\infty} S \alpha^{s-1}(1-\alpha) = (1-\alpha)^{-1} = \beta^{-1}$$

If, now, branching occurs, the expression for ν must incorporate the branching probability δ since branching must act in such a way as to reduce the effect of termination. It follows that under these conditions:

$$\nu = (\beta - \delta)^{-1}$$

The reaction rate, w, in any chain process is equal to the product of the initial rate of chain generation, n_o, and the chain length. Thus

$$w = \frac{n_o}{\beta - \delta}$$

When $\beta \gg \delta$, w is fairly small and slow reaction occurs. As $\delta \rightarrow \beta$, $w \rightarrow \infty$. Thus a very high rate of reaction is obtained and this leads to a chain-branching explosion. The cause of this type of explosion is basically different from that of a thermal explosion which is considered later. The condition:

$$\beta = \delta$$

thus defines the boundary between slow combustion and chain explosion. Explosion does not, of course, imply an infinite rate but merely a very high one so that all the reactant is transformed in a finite but very short time. Physically, α , β, and δ are the ratios of the numbers of reactions of the various types to the total number of reactions.

The effect of the various types of elementary reaction on the overall reaction may be considered from another viewpoint as follows:

The rate of change of concentration of a given chain carrier with time in a reacting system is given by the equation:

$$\frac{dn}{dt} = n_o - (g-f)n \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 6$$

where g and f are kinetic termination and branching coefficients respectively. A term for propagation does not appear in this equation

as the number of chain carriers is unchanged by this process. If $g > f$, a steady state is soon set up in the reacting mixture with a fixed concentration of chain carriers and the reaction takes place slowly. This may be shown by integrating equation 6 and putting $n = 0$ at $t = 0$. Then:

$$n = \frac{n_o \left[1 - \exp. \left\{ -(g-f)t \right\} \right]}{g-f}$$

If $g \gg f$, the exponential term soon becomes negligible so that

$$n = \frac{n_o}{g-f}$$

Now the reaction rate, w, is the product of a kinetic factor, a, and the concentration of chain carriers, n.

Thus, $w = an = \dfrac{an_o}{g-f}$

Therefore, when $g > f$, w soon reaches a constant value and slow combustion occurs as previously stated. In practice the rate of reaction gradually diminishes due to the consumption of reactants.

On the other hand, when $f > g$

$$n = \frac{n_o}{f-g} \left[\exp. \ (f-g)t - 1 \right]$$

and thus the rate, w, increases exponentially with time. When $g \ll f$, the rapid increase in rate obtained leads to a chain-branching explosion.

When $f = g$, $\qquad n = n_o t$

and so the rate increases linearly with time. With f equal to or just greater than g, the reaction rate increases steadily with time and explosion will eventually occur if the rate of initiation is high enough to enable a very high rate to be attained before all the reactants are consumed.

Equation 6 relates to one given chain carrier involved in the development of the chain and the values of n_o, g, and f will be characteristic of this particular species. However, in any real system several different chain carriers are usually present. Thus in the hydrogen-oxygen reaction H, O, and OH radicals all play a part. The system is then described by three differential equations of type 6 which makes the mathematical treatment rather complex although the basic concept is unchanged.

Furthermore, in this treatment the chain termination and branching rates have been assumed to be proportional to the concentration of the radicals present. This is equivalent to assuming that the chains operate independently of one another. However, termination and branching can involve radical-radical interactions or secondary reactions of radicals with intermediate products. If these reactions are allowed for, the basic equation must be modified to:

$$\frac{dn}{dt} = n_o + (f-g)n - g_o n^2$$

where the term $g_o n^2$ allows for the loss of radicals through recombination reactions. This equation can also be treated mathematically to give the relationship between n and t for various values of f, g, and g_o. Explosion limits are obtained as in the simpler treatment.

It is thus seen that in a chain reaction, the overall change occurring is a summation of the effects of initiation, propagation, branching, and termination. The relative frequencies of these steps depends both on the nature of the reactants and the experimental parameters of the system.

b) Degenerately branched chain reactions

Most reactions between hydrocarbons and oxygen show autocatalysis under suitable experimental conditions. The rate expression takes the form:

$$w = a \exp. (\phi t)$$

However, the rate increases far more slowly than in reactions involving completely branched chains which lead to explosion. It might, at first sight, seem possible to explain this very slow rate of increase by assuming that the radical responsible for the chain branching reacts very slowly because the branching reaction is very endothermic. However any radical is eventually lost to the wall and it can be estimated that the maximum lifetime of a radical in the gas phase is about 100 seconds. Since autocatalysis can only occur if the branching rate is greater than the termination rate, it will be observed only if the time required to generate a radical by branching is less than 100 seconds. However in the slow oxidation reactions under consideration, the characteristic time ϕ^{-1} is appreciably greater than 100 seconds. In fact, the actual lifetimes of the free radicals of interest in hydrocarbon oxidations are less than 1 second and so ordinary radical branching schemes do not apply when $\phi^{-1} > 1$ sec.

The phenomena observed in hydrocarbon combustion at low temperatures are, however, satisfactorily explained in terms of Semenov's theory of delayed or 'degenerate' chain branching. This theory postulates the build up during the induction period of a moderately stable intermediate by a chain cycle. This intermediate then breaks down slowly in a chain branching reaction and thus extra radicals are introduced steadily into the reacting system, leading to

autocatalysis. The reaction velocity thus increases considerably as a result of the slow development of these branching chains, but at fairly low temperatures ignition does not occur because the effects produced by the consumption of reactants cause the reaction to slow down before it has reached a sufficiently high rate.

The following simple treatment may be considered:
The rate of change with time of the concentration of a given chain carrier is given by:

$$\frac{dn}{dt} = n_o + \alpha\,n - fn - gn$$

where n = Concentration of chain carriers

          α = Coefficient of linear chain branching

          f = Coefficient of linear chain breaking in the gas phase

          g = Coefficient of linear chain breaking at the walls

Then $\dfrac{dn}{dt} = n_o + (\alpha - f - g)n = n_o + \phi n$

where ϕ is termed the net branching factor. From this equation, it follows that:

$$n = \frac{n_o}{\phi}\,(e^{\phi t} - 1) \approx Ae^{\phi t}$$

The rate of reaction, w, at any instant is proportional to the number of chain centres present at that time.

Thus $w\ \alpha\ n\ \alpha\ e^{\phi t}$ or:

       $w = A'\,e^{\phi t}$

This relationship is found to be obeyed experimentally under suitable conditions and thus the treatment is essentially valid. However, this treatment does assume that no temperature change occurs in the system and also that no appreciable amount of reactants are consumed.

Thus the relationship will only hold experimentally for the early stages of a slow reaction. The validity of the relationship can be tested by plotting log (rate) against time when a straight line of slope ϕ should be obtained. The parameter normally used for rate is $\frac{d}{dt}$ ($\triangle$P) where $\triangle$ p = pressure change observed. Semenov has shown that this relationship is observed in many of the cases of slow combustion investigated. If the initial reaction temperature is sufficiently high, then a hydrocarbon-oxygen mixture will eventually explode through this chain-branching mechanism. If explosion occurs at the time when a critical rate is reached, then:

$$W_c = Ae^{\phi t}{}_c$$

where t_c = time preceding explosion.

It has been assumed here that the temperature remains constant until the instant at which explosion occurs as A and ϕ are functions of temperature. This will not be strictly true in practice and so the explosion observed will be due to self-heating as well as to chain branching.

c) Thermal explosion

An explosion in a mixture of oxygen and the vapour of an organic compound may be caused by the rapid development and growth of chain centres under essentially isothermal conditions. This chain-branching type of explosion has been fully dealt with in the previous sections. Alternatively the explosion of such a mixture may be due simply to the heat liberated in the underlying chemical reactions, in which case it is said to be thermal in nature. It is thought that below the explosion temperature, a slow reaction proceeds. Under suitable

conditions, the heat evolved in this reaction cannot be conducted away through the walls of the vessel and thus it raises the temperature of the reacting gases. Since the reaction rate almost always increases exponentially with temperature, the overall reaction is accelerated; and this in turn increases the rate of heating. Thus both a progressive self-heating of the combustible mixture and self-acceleration of the reaction rate lead to the occurrence of explosion.

Thermal explosions can be considered theoretically as follows:

The rate at which heat is evolved during a reaction is given by the quantity QVw where

Q = Heat of reaction per mole

V = Volume of reaction vessel

w = Number of moles reacting per unit time and volume

On the other hand, the rate at which heat is absorbed by the walls of the vessel is given by $ak(T-T_o)$ where

a = Total surface area of the walls

k = Coefficient of thermal conductivity

T = Average temperature in the reaction vessel

T_o = Temperature of the walls

Then the rate of accumulation of heat in the reaction vessel is given by the equation:

$$\frac{dq}{dt} = QVw - ak(T-T_o)$$

The reaction rate, w, for any elementary reaction is given by:

$$w = k_n b^n \exp. \left[-E/_{RT} \right]$$

where k_n = Rate constant for the reaction

b = Number of reactant molecules present

$$n = \text{Molecularity of the reaction}$$

$$E = \text{Activation energy}$$

$$T = \text{Absolute temperature}$$

$$R = \text{Gas constant}$$

Now the region of slow combustion in the system is defined by the equation:

$$\frac{dq}{dt} = 0 = QVw - ak(T-T_o)$$

If this equation has a real root in T, then the system will reach equilibrium at this temperature subject, of course, to the consumption of reactants, and slow combustion will result.   If, however, T_o is sufficiently large, the equation has no real root in T and $\frac{dq}{dt}$ is always positive.   Thus the temperature increases steadily leading to explosion. The critical or 'ignition' temperature depends on various parameters. Thus increase in pressure, insofar as it increases the reaction rate, decreases the ignition temperature.   The ignition temperature is also decreased by increasing the vessel diameter as this increases V far more than a.   If w is dependent on the nth power of the pressure, as given in a previous equation, then it can be shown that the relationship between ignition temperature and ignition pressure assumes the form:

$$\log \frac{P}{T^{(1 + \frac{2}{n})}} = \frac{A}{T} + B$$

where A and B are constants for a given system.   Over small ranges of temperature, the equation:

$$\log \frac{P}{T} = \frac{A}{T} + B$$

is quite adequate.   In this treatment the parameter, time, is not considered in detail.   No equation can thus be given for the time

elapsing prior to explosion.

The pressure-temperature relationships at the explosion boundaries of many experimental systems have been found to obey equations of the type given above but in themselves such relationships are not very informative.   In particular they do not serve to distinguish between thermal and branched-chain explosion limits as the temperature-pressure relationships of the latter are generally governed by similar equations.   Other methods must therefore be used to diagnose whether the explosion occurring in a given system is mainly thermal or of the chain-branching type.

3.   The chemical steps involved

a)   The initiating reaction

In a mixture of hydrocarbon and oxygen at a given temperature and pressure, it is first necessary to consider which process is the most likely to lead to the initiation of the reaction.   Now the rate at which a given elementary reaction occurs depends both on the activation energy required and on the steric factor for the reaction. On considering the data at present available on these factors, it seems probable that the initial interaction of a hydrocarbon RH with oxygen simply involves the transfer of a hydrogen atom during a bimolecular collision according to the equation:

$$RH + O_2 \longrightarrow \dot{R} + H\dot{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

Some independent evidence is available for the existence of the $H\dot{O}_2$ radical (6,7) and its heat of formation is believed to be +47 K. cal. per mole.   As the bond dissociation energy of R-H lies in the range 70-100 K. cal. per mole depending upon the nature of R, the

initiating reaction will be endothermic to the extent of 20-50 K. cal. per mole. Consequently the activation energy for the initiation reaction will also lie broadly in this range which is quite acceptable, on the basis of the independent evidence available, for this type of reaction. Furthermore, there is no reason to suspect an abnormally low steric factor in this reaction and thus it is a satisfactory initiating step.

However, unless RH is any but the simplest of hydrocarbons, the various hydrogen atoms will not all be equivalent and a number of different isomeric radicals will result from the initial attack. It is thus necessary to know how the different hydrogen atoms differ in their tendency to be abstracted.

Most of the early conclusions as to the preferred point of attack in the oxidation of hydrocarbons were based on the composition and sequence of formation of intermediate products.(8). In general, however, such results do not give reliable quantitative information about the relative probabilities of initial attack at the various positions, for the different intermediates formed in the early stages vary considerably in their vulnerability to further oxidation, so that analytical data always tends to be weighted in favour of the more stable compounds irrespective of the proportions in which the products appear initially.

Recently, however, some direct evidence has been obtained regarding the point of attack in the oxidation of hydrocarbons. One such approach has involved 'labelling' different parts of the hydrocarbon molecule with suitable isotopes-generally either deuterium, carbon-13 or carbon-14, and then tracing the labelled part

of the molecule on oxidation. In one study (9,10) involving some deuterated propanes and butanes, conditions for oxidation were chosen under which fission of C-C bonds was largely avoided so that the principal products were the corresponding olefin and water. The deuterium content of the water formed from various deuterated starting compounds was determined by infra-red spectroscopy and the results obtained showed that the removal of hydrogen from a secondary C-H group took place roughly twice as fast as the corresponding removal from a primary C-H group. Another similar but rather more detailed investigation (11) involved an analysis of the combustion products of ^{14}-C-labelled 2-methylpentanes. This hydrocarbon contains primary, secondary, and tertiary C-H groups and compounds were synthesised in which the isotopic carbon was present in each of the five skeletal positions. These compounds were oxidised with a deficit of oxygen and determinations were made of the activities of the principal products formed from the different labelled hydrocarbons under these conditions. From the results obtained, it is clear that, in common with other reactions involving attack by free radicals, (12,13) the tertiary C-H groups are by far the most vulnerable positions and the primary C-H groups are the least readily oxidised.

Other workers (14,15) have used the method of competitive oxidation in which direct measurements are made of the relative rates of disappearance of two hydrocarbons from a mixture of these with oxygen. In this way, too, it has been shown that the ease of initial attack by oxygen on the C-H bonds in paraffin hydrocarbons decreases in the order: tertiary > secondary > primary.

It is not possible to give universally applicable quantitative values for the differences in the ease of attack at the three types of C-H bonds, for these will vary considerably with the precise environment of the groups concerned. In general, however, it appears that in paraffin hydrocarbons at temperatures from 250-450°C., the relative rates of oxidative attack at primary, secondary, and tertiary centres are in the approximate ratio 1:3:15, the difference becoming more marked the lower the temperature.
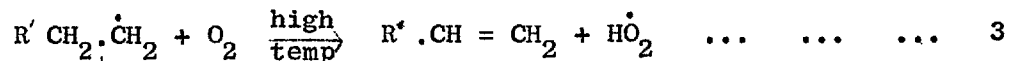
b) The behaviour of $\overset{\bullet}{R}$

The next stage in the reaction will now depend on the behaviour of the radical $\overset{\bullet}{R}$. This species may either decompose in some way, isomerize, dimerize, or combine with oxygen. However, it seems unlikely that the first three processes can effectively compete with the reaction of the radical with oxygen, except perhaps at high temperatures. These reactions all require an appreciable activation energy, whereas alkyl radicals at any rate are known to add rapidly to oxygen in a process apparently requiring little or no activation energy (1,16,17). On the other hand, there is little doubt that the interaction with oxygen can take place in more than one way. At low temperatures the predominant reaction is association to give an $R\overset{\bullet}{O}_2$ radical:

$$\overset{\bullet}{R} + O_2 \longrightarrow R\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \ 2$$

With simple alkyl radicals such as methyl, a third body is required (18), but with larger radicals this may not be necessary as it is possible for the energy liberated on collision to be shared over several modes of vibration of the resultant radical. However, it is generally agreed that this process is exothermic to an extent such that at the instant of its formation, the $R\overset{\bullet}{O}_2$ radical is in a **vibrationally**

excited state (19). At higher temperatures, another reaction apparently also takes place resulting in the formation of an unsaturated compound and an $H\dot{O}_2$ radical:

$$R'CH_2.\dot{C}H_2 + O_2 \xrightarrow{\text{high temp}} R^*.CH = CH_2 + H\dot{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad 3$$

Competition between these two reactions undoubtedly accounts in the main for the progressive change from oxygenated to olefinic products which is observed as the reaction temperature is increased (2,3).

c) The behaviour of $R\dot{O}_2$

Even if the $R\dot{O}_2$ radical formed at low temperatures has an appreciable lifetime, there are various fates which it can undergo. Thus it has been frequently suggested (20-22) that these radicals react with the initial organic compound to form a hydroperoxide:

$$R\dot{O}_2 + RH \longrightarrow ROOH + \dot{R} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 4$$

However, a critical examination of the evidence for such a process reveals direct support in only relatively few cases. Other possible fates for the $R\dot{O}_2$ radical include unimolecular decomposition to give a carbonyl compound and an alkoxy radical (4,23).

$$R.\underset{\underset{O.\dot{O}}{|}}{C}H.R \longrightarrow R.CHO + R\dot{O} \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 5$$
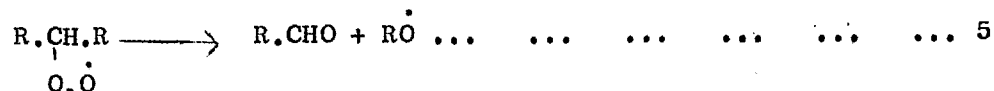
or binary combination to yield alkoxy radicals and oxygen (24,17).

$$R\dot{O}_2 + R\dot{O}_2 \longrightarrow R\dot{O} + R\dot{O} + O_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 6$$

Furthermore there is some evidence that the peroxy radicals derived from fairly large organic molecules can undergo intramolecular rearrangement (11,25-33) and thus yield products which at first sight are very difficult to account for as arising from the starting material used. These processes will clearly all be favoured relative to

reaction 4 if the initial organic compound does not contain an easily abstractable hydrogen atom.

d) Further reaction routes

The brief account given in previous sections of most of the possible concurrent and consecutive reactions which may occur in the initial stages of a gaseous oxidation reaction gives some idea of the great complexity of the process. However, there is also a further complicating factor which makes the chain reaction follow an even greater number of possible routes as reaction proceeds. This is the further reaction, generally either thermal decomposition or oxidation, of certain of the intermediate molecular species formed. Now it is well known that the rates of gaseous oxidation of most organic compounds increase autocatalytically with time (5). This phenomenon is thought to be due to degenerate chain-branching which results in the gradual production of increasing numbers of reactive free radicals in the system. Both organic peroxides (20-22) and aldehydes (34,35,23) have frequently been suggested as the species responsible for supplying these new radicals and thus causing the degenerate chain branching. Thus in the oxidation of a hydrocarbon at a relatively low temperature, chains are thought to be initiated very slowly by the reaction:

$$RH + O_2 \longrightarrow \dot{R} + H\dot{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

and propagated steadily by the chain cycle:

$$\dot{R} + O_2 \longrightarrow R\dot{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2$$

$$R\dot{O}_2 + RH \longrightarrow ROOH + \dot{R} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 3$$

The hydroperoxide may then break up slowly by homolytic fission of the fairly weak O-O bond ($\sim$ 40 K. cal.) to yield an alkoxy and a hydroxy

radical:

$$ROOH \longrightarrow R\overset{\bullet}{O} + \overset{\bullet}{O}H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 4$$

This would be a chain-branching process and thus the reaction rate would increase gradually giving rise to the autocatalysis observed.

Alternatively, the $R\overset{\bullet}{O}_2$ radical produced in step 2 may decompose to give an aldehyde and the oxidation of this aldehyde would give rise to chain-branching. This would be expressed as follows:

$$\underset{O.\overset{\bullet}{O}}{R.\overset{|}{C}H.R'} \longrightarrow R.CHO + \overset{\bullet}{O}R' \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 5$$

$$R.CHO + O_2 \longrightarrow R.\overset{\bullet}{C}O + H\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 6$$

where reaction 6 is the degenerate chain-branching process. Whatever the intermediate responsible for degenerate chain-branching, however, it is at once evident that any process which introduces into the system reactive free radicals which are different from those involved in the primary chain, will cause the production of a diversity of final products which will, in turn, make it very difficult to elucidate the full reaction mechanism. Thus the $R\overset{\bullet}{O}$ radical produced by the decomposition of the hydroperoxide can react in various ways depending upon its precise structure. It can abstract hydrogen from a reactant molecule under suitable conditions, forming an alcohol (36).

$$R\overset{\bullet}{O} + RH \longrightarrow ROH + \overset{\bullet}{R} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 7$$

If the alkoxy radical is of the type $R.CH_2\overset{\bullet}{O}$ it readily breaks down to give $\overset{\bullet}{R}$ and formaldehyde (37)

$$R.CH_2\overset{\bullet}{O} \longrightarrow \overset{\bullet}{R} + H_2CO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 8$$

If the radical is of the type $R_3C\overset{\bullet}{O}$, the following reaction can occur (38)

$$R_3C\overset{\bullet}{O} \longrightarrow \overset{\bullet}{R} + R_2CO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 9$$

Similarly, the radical $R.\overset{\bullet}{C}O$ formed by the oxidation of aldehyde can undergo several different further reactions depending on the circumstances (39,40). Thus the final products observed are usually the result of a whole sequence of consecutive and concurrent reactions, but by a detailed study of a reaction under a variety of experimental conditions, it has been found possible to suggest a reasonable reaction mechanism in many cases.
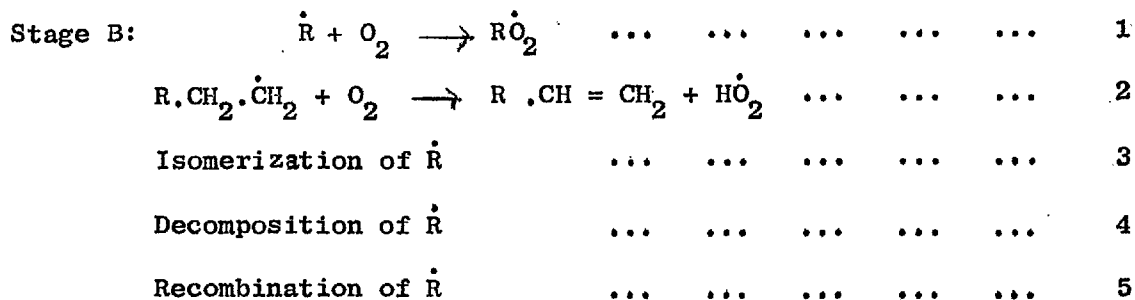
4. <u>The mechanisms of gaseous oxidation of the compounds used in</u>

   <u>this work</u>

a) <u>General</u>

The salient features of the mechanisms of gaseous oxidation of the particular fuels and additives used in this investigation will now be outlined and the reactions will be considered in the light of the general mechanisms discussed in the previous sections. The initial stages in the oxidation of a hydrocarbon or simple derivative can be summarised as follows:

Stage A: $\qquad RH + O_2 \longrightarrow \overset{\bullet}{R} + H\overset{\bullet}{O}_2$
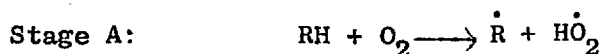
The hydrogen atom removed may have been attached to a primary, secondary, or tertiary centre, to a benzene ring, or it may have been part of a substituent group. These possibilities will be numbered 1, 2, 3, 4, 5

Stage B: $\qquad \overset{\bullet}{R} + O_2 \longrightarrow R\overset{\bullet}{O}_2$ 1

$\qquad R.CH_2.\overset{\bullet}{C}H_2 + O_2 \longrightarrow R.CH = CH_2 + H\overset{\bullet}{O}_2$ 2

$\qquad$ Isomerization of $\overset{\bullet}{R}$ 3

$\qquad$ Decomposition of $\overset{\bullet}{R}$ 4

$\qquad$ Recombination of $\overset{\bullet}{R}$ 5

If stage B occurs via step 1, then stage C can take place in the following ways:

Stage C: $\qquad$ $\dot{R}O_2 + RH \longrightarrow RO_2H + \dot{R}$ ... ... $\qquad$ 1

$\qquad\qquad$ $\dot{R}O_2 \longrightarrow$ decomposition ... ... $\qquad$ 2
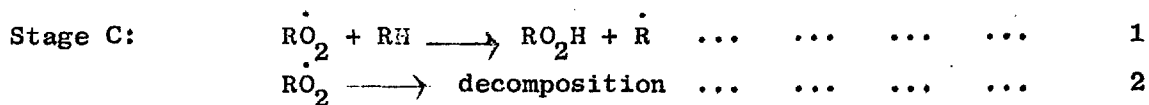
(where the groups R, R, R are small, the decomposition generally occurs according to the equation:

$$R\,R'\,R''\,C\dot{O}O \longrightarrow R\,R'\,CO + \dot{O}R''$$

and it can be thought of as proceeding through a four-centre transition state. With longer chains, transfer of a hydrogen atom to the free valency on the oxygen atom frequently occurs across rings containing five or more atoms, a hydroperoxide resulting with a free valency on a distant carbon atom. This compound may then add on a further molecule of oxygen before decomposing (32,33)).

$$2\,\dot{R}O_2 \longrightarrow 2\,\dot{R}O + O_2 \quad ... \quad ... \quad ... \quad ... \qquad 3$$

Thus the initial stages of oxidation in any system containing oxygen and a hydrocarbon or simple derivative can be denoted by three numbers, giving the type of reaction occurring in each of the two or more successive early stages, A, B and C. In all practical hydrocarbon oxidation systems most of the possible oxidation steps will occur to some extent but under the conditions actually employed, one reaction sequence will probably predominate and can be considered for simplicity to be the sole mechanism of oxidation. The mechanisms discussed in the following sections will be taken from work performed under conditions as similar as possible to those used in the present work. Thus, unless experimental conditions are mentioned, it can be assumed that the workers used a conventional static apparatus and pressures of each reactant gas of from 20 - 300 mm. Hg.

b) Fuels employed in this study

(i) Methane

The oxidation of methane has been studied in considerable detail by many workers. Thus, for example, Hoare and Walsh (41) showed that at about 500°C the effects of pressure of reactants, pressure of added inert gases, and temperature on the rate of reaction could be expressed in the form:
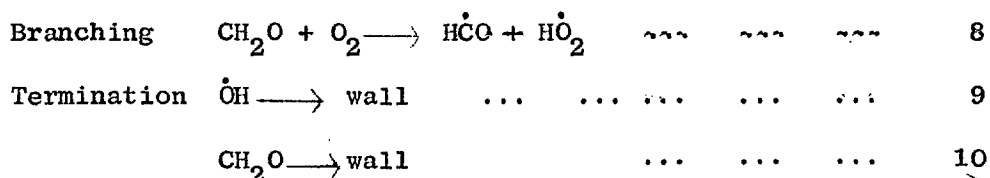
$$-\frac{dp}{dt} = k\left[CH_4\right]^m \left[O_2\right]^x \left[Total \ p\right]^t e^{-E/RT}$$

Silica reaction vessels were used, the surfaces of which were treated in the following ways: 1) "ageing" 2) heat-treatment at 1000°C 3) washing with hydrofluoric acid 4) coating with lead oxide. Depending on the type of surface present $m = 1.6 - 2.4$, $x = 1.0 - 2.0$, $t = 0.5 - 0.9$, $E = 25 - 90$ K. cal./mole. With mixtures containing high proportions of oxygen, the overall pressure change passed through a maximum and then decreased, possibly owing to the further oxidation of carbon monoxide to carbon dioxide.

Enikolopyan (42) also made a detailed study of the reaction at ca. 500°C. From an analysis of the kinetic and analytical data, the following mechanism of oxidation was proposed:

Initiation $CH_4 + O_2 \longrightarrow \dot{C}H_3 + H\dot{O}_2$ 1

Propagation $\dot{C}H_3 + O_2 \longrightarrow CH_2O + \dot{O}H$ 2

       $\dot{O}H + CH_4 \longrightarrow \dot{C}H_3 + H_2O$ 3

       $\dot{O}H + CH_2O \longrightarrow H_2O + H\dot{C}O$ 4

       $H\dot{C}O + O_2 \longrightarrow CO + H\dot{O}_2$ 5

       $H\dot{O}_2 + CH_4 \longrightarrow H_2O_2 + \dot{C}H_3$ 6

       $H\dot{O}_2 + CH_2O \longrightarrow H_2O_2 + H\dot{C}O$ 7

Branching $\quad CH_2O + O_2 \longrightarrow H\dot{C}O + H\dot{O}_2$ ～～ ～～ ～～ $\quad$ 8

Termination $\quad \dot{O}H \longrightarrow$ wall $\quad$ ... ... $\quad$ 9

$\quad\quad\quad\quad\quad CH_2O \longrightarrow$ wall $\quad\quad\quad$ ... ... $\quad$ 10
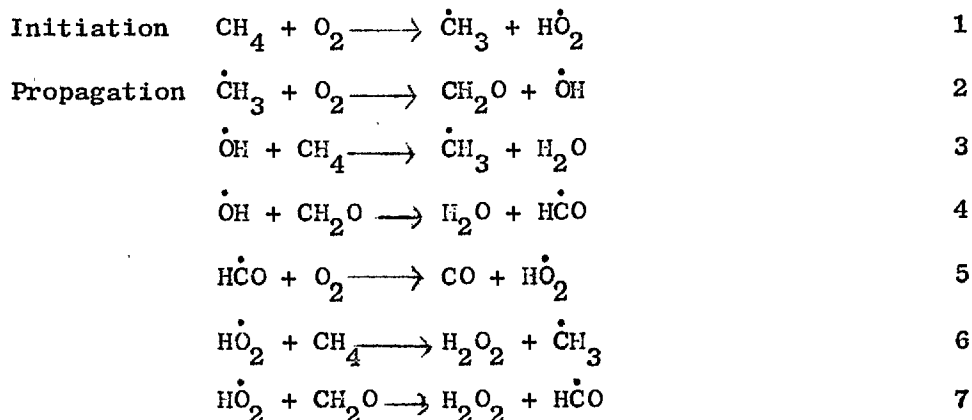
This mechanism accounts satisfactorily for most of the experimental facts. Semenov (5) has given a detailed steady-state treatment based on this reaction scheme. In terms of the general mechanisms given previously, this reaction is of type 112. As all the hydrogen atoms in methane are equivalent, only one $\dot{R}$ radical, $\dot{C}H_3$, is formed in the initiation reaction and this reacts with oxygen as in reaction 2 producing formaldehyde and a hydroxyl radical. Degenerate chain branching involves the further oxidation of formaldehyde which takes place at a much greater rate than the original initiating reaction so that autocatalysis is observed. Termination is attributed to the loss of radicals, largely $\dot{O}H$, and formaldehyde to the walls.

(ii) Ethane

Many workers have investigated the oxidation of ethane. Gray (43), during studies of the low temperature photo-sensitised reaction in a flow system, isolated high yields of ethyl hydroperoxide and thus proposed the following reaction cycle:

Initiation $\quad C_2H_6 + O_2 \longrightarrow \dot{C}_2H_5 + H\dot{O}_2$ ... ... $\quad$ 1

Propagation $\quad \dot{C}_2H_5 + O_2 \longrightarrow C_2H_5\dot{O}_2$ $\quad$ ... ... $\quad$ 2

$\quad\quad\quad\quad C_2H_5\dot{O}_2 + C_2H_6 \longrightarrow C_2H_5OOH + \dot{C}_2H_5$ $\quad$ 3
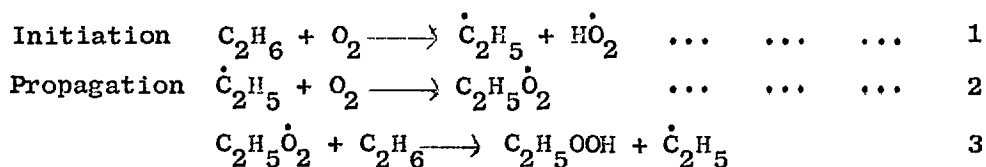
$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ Ethyl hydroperoxide

In further work, (44) the thermal oxidation of ethane was examined at ca. 400°C. The initial chain cycle appeared to be the same as in the photo-sensitised oxidation, the final products being obtained by the breakdown of this hydroperoxide:

Branching $\quad C_2H_5OOH \longrightarrow C_2H_5\dot{O} + \dot{O}H$ $\quad$ ... ... $\quad$ 4

$$C_2H_5\overset{\bullet}{O} \longrightarrow \overset{\bullet}{C}H_3 + CH_2O \quad \ldots \quad \ldots \quad \ldots \qquad 5$$

$$C_2H_5\overset{\bullet}{O} \longrightarrow CH_3CHO + \overset{\bullet}{H} \quad \ldots \quad \ldots \quad \ldots \qquad 5a$$
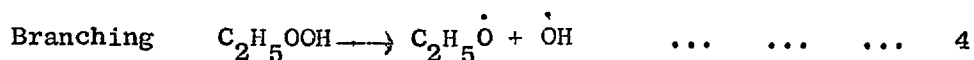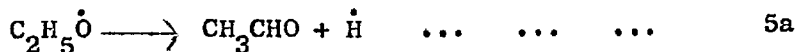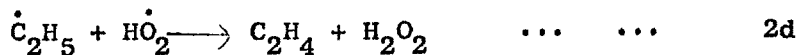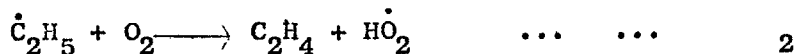
However, reaction 3 is not now thought very probable at 400°C, and a unimolecular breakdown is more likely:

$$C_2H_5\overset{\bullet}{O}_2 \longrightarrow CH_3CHO + \overset{\bullet}{O}H \quad \ldots \quad \ldots \quad \ldots \qquad 3b$$

$$\text{Branching} \quad CH_3CHO + O_2 \longrightarrow CH_3\overset{\bullet}{C}O + H\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \qquad 4b$$
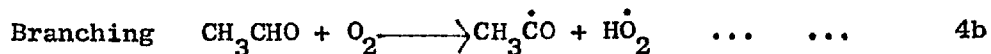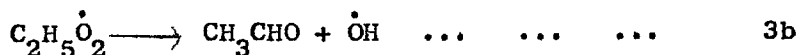
Ethylene is probably produced as follows:

$$\overset{\bullet}{C}_2H_5 + O_2 \longrightarrow C_2H_4 + H\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \qquad 2$$

$$\overset{\bullet}{C}_2H_5 + H\overset{\bullet}{O}_2 \longrightarrow C_2H_4 + H_2O_2 \quad \ldots \quad \ldots \qquad 2d$$

Thus, with the experimental data at present available it is not possible to postulate a precise reaction mechanism but the steps listed above are probably predominant in the early stages. This oxidation reaction is then mainly of type 112 although some reaction of types 12 and 111 may also occur.

(iii) Isopentane

The oxidation of isopentane is of particular interest mechanistically as this hydrocarbon is the simplest containing hydrogen atoms in the primary, secondary, and tertiary positions. The oxidation has been studied by Fersht (45) in a flow system at 300-400°C. Acetone and methyl ethyl ketone were the main products but peroxides, isobutyraldehyde, and methyl isopropyl ketone were also produced. However, alkyl monohydroperoxides were not detected and thus the mechanism proposed does not involve these intermediates.
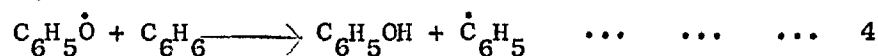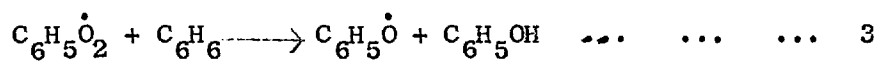
$$\text{Initiation} \quad \underset{\hspace{0.3em}CH_3}{CH_3.\overset{\bullet}{C}H.CH_2.CH_3} + O_2 \longrightarrow \underset{\hspace{0.3em}CH_3}{CH_3.\overset{\bullet}{C}.CH_2.CH_3} + H\overset{\bullet}{O}_2 \qquad 1$$

$$\text{Propagation} \quad \underset{\hspace{0.3em}CH_3}{CH_3.\overset{\bullet}{C}.CH_2.CH_3} + O_2 \longrightarrow \overset{O.\overset{\bullet}{O}}{\underset{CH_3}{CH_3.C.CH_2.CH_3}} \cdots \qquad 2$$

$$\overset{\overset{\textstyle O.\dot{O}}{|}}{CH_3 \cdot \underset{\underset{\textstyle CH_3}{|}}{C} \cdot CH_2 \cdot CH_3} \longrightarrow CH_3 \cdot CO \cdot CH_3 + CH_3 \cdot CH_2\dot{O} \qquad \cdots \quad \cdots \quad \cdots \quad 3$$

$$CH_3 \cdot CH_2\dot{O} \longrightarrow CH_3 \cdot CHO + \dot{H} \qquad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 4$$

$$CH_3 \cdot CH_2\dot{O} \longrightarrow \dot{C}H_3 + H \cdot CHO \qquad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 4a$$

$$\overset{\overset{\textstyle O.\dot{O}}{|}}{CH_3 \cdot \underset{\underset{\textstyle CH_3}{|}}{C} \cdot CH_2 \cdot CH_3} \longrightarrow CH_3 \cdot CO \cdot CH_2 \cdot CH_3 + \dot{O} \, CH_3 \qquad \cdots \quad \cdots \quad \cdots \quad 3b$$

$$CH_3\dot{O} + RH \longrightarrow CH_3OH + \dot{R} \qquad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 4b$$
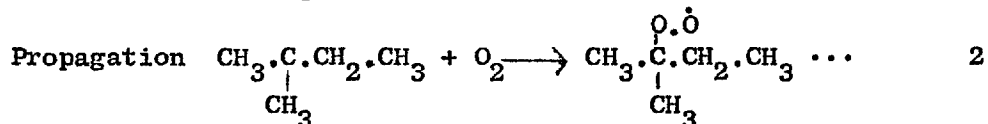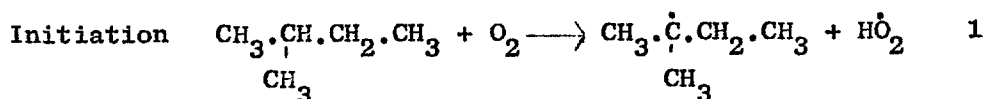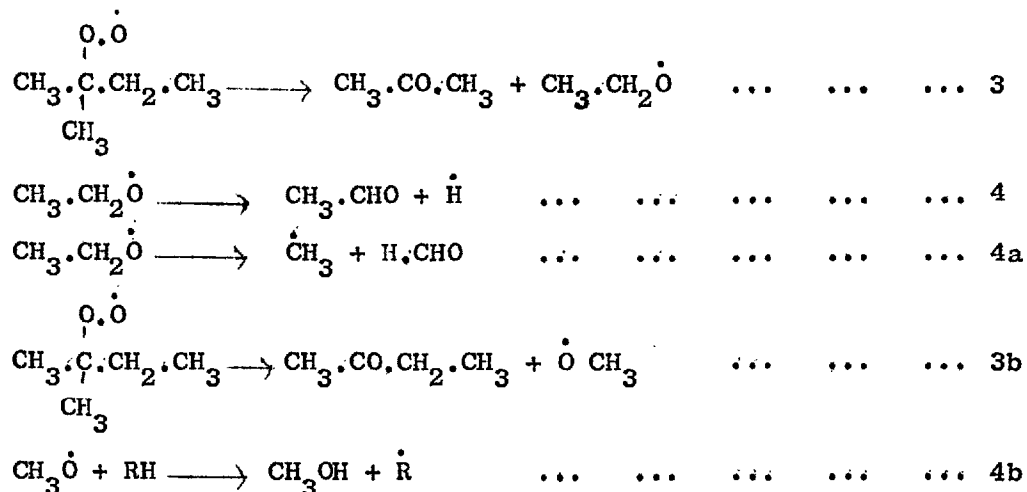
This mechanism is of type 312. It accounts for the formation of the major products, acetone and methyl ethyl ketone. Oxidation mechanisms of types 32 and 212 probably also occur to some extent. The type 32 mechanism will also lead to the formation of acetone and acetaldehyde through the decomposition of the intermediate epoxide formed by oxidation of the olefin. The minor products, isobutyraldehyde and methyl isopropyl ketone, are formed as a result of oxidation by the type 212 mechanism.

(iv) Benzene

No low temperature region of oxidation of benzene has yet been found (46-48). Norrish and Taylor (48) have studied the reaction in a flow system at 685°C. On the basis of product analysis, it was concluded that combustion proceeds by stepwise hydroxylation of the ring to the dihydroxy stage,,followed by rupture to give compounds containing one or two carbon atoms, hydrogen, and water. The following mechanism was proposed for the early stages of reaction:

$$\text{Initiation} \quad C_6H_6 + O_2 \longrightarrow \dot{C}_6H_5 + H\dot{O}_2 \qquad \cdots \quad \cdots \quad \cdots \quad 1$$

$$\text{Propagation} \quad \dot{C}_6H_5 + O_2 \longrightarrow C_6H_5\dot{O}_2 \qquad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 2$$

$$C_6H_5\overset{\bullet}{O}_2 + C_6H_6 \longrightarrow C_6H_5\overset{\bullet}{O} + C_6H_5OH \quad \cdots \quad \cdots \quad \cdots \quad 3$$

$$C_6H_5\overset{\bullet}{O} + C_6H_6 \longrightarrow C_6H_5OH + \overset{\bullet}{C}_6H_5 \quad \cdots \quad \cdots \quad \cdots \quad 4$$
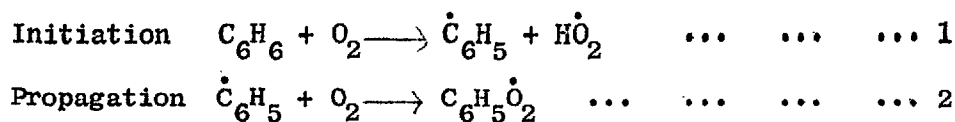
Reactions such as 3 do not necessarily occur in a single step. The reaction may be rewritten in several steps as follows:

$$C_6H_5\overset{\bullet}{O}_2 + C_6H_6 \longrightarrow C_6H_5OOH + \overset{\bullet}{C}_6H_5 \quad \cdots \quad \cdots \quad \cdots \quad 3a$$

$$C_6H_5OOH \longrightarrow C_6H_5\overset{\bullet}{O} + \overset{\bullet}{O}H \quad \cdots \quad \cdots \quad \cdots \quad 4a$$

$$\overset{\bullet}{C}_6H_5 + \overset{\bullet}{O}H + M \longrightarrow C_6H_5OH + M \quad \cdots \quad \cdots \quad \cdots \quad 5a$$
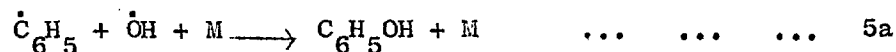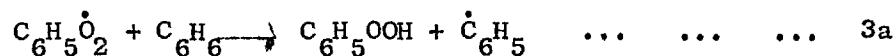
Thus the reaction mechanism is of type 411 if it is accepted that reaction 3 occurs in the stages given. Again, insufficient experimental evidence is available for a precise reaction mechanism to be put forward.

(v) Cumene (Isopropyl benzene)

The gas-phase oxidation of cumene has not been studied in detail and thus no definite mechanism can be proposed. However, the results obtained in the liquid phase oxidation (49) can be explained in terms of the mechanism:

$$C_6H_5.CH.(CH_3)_2 + O_2 \longrightarrow C_6H_5.\overset{\bullet}{C}.(CH_3)_2 + H\overset{\bullet}{O}_2 \quad \cdots \quad \cdots \quad 1$$

$$C_6H_5.\overset{\bullet}{C}.(CH_3)_2 + O_2 \longrightarrow C_6H_5.C(O\overset{\bullet}{O}).(CH_3)_2 \quad \cdots \quad \cdots \quad 2$$

$$C_6H_5.C(O\overset{\bullet}{O}).(CH_3)_2 + C_6H_5.CH.(CH_3)_2 \longrightarrow C_6H_5.C(OOH).(CH_3)_2$$
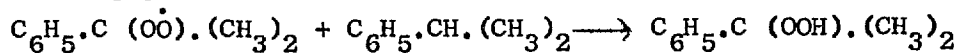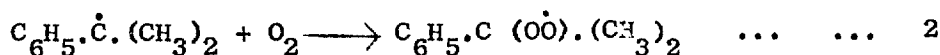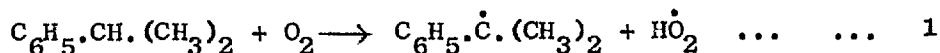
Cumene hydroperoxide

$$+ C_6H_5.\overset{\bullet}{C}.(CH_3)_2 \cdots \quad \cdots \quad \cdots \quad 3$$

It seems likely that reactions 1 and 2 will also occur in the gas phase. The reaction will then be continued by the decomposition of the peroxy radical in various ways. The oxidation is thus probably of the type 312.

(vi) Formaldehyde

The mechanism of the oxidation of formaldehyde is of
particular interest as this compound is found as an intermediate
during the oxidation of methane.   From a survey of the published data
on the reaction, Lewis and Von Elbe (4) concluded that performic acid
is an important intermediate.   This is assumed to diffuse to the walls
and there decompose into carbon monoxide, water, carbon dioxide,
hydrogen, and formic acid.   If this process is sufficiently rapid,
further gas-phase reactions of the performic acid with chain carriers
can be neglected and the reaction becomes a simple steady-state
process.   On the other hand, if the vessel surface is inactive to the
destruction of peroxides, the gas phase reactions of the performic acid
become important and the kinetics of the reaction become more complex.
The simple kinetics observed by certain workers (50) was attributed
to the presence of mercury vapour in their system which rapidly
decomposed the intermediate peroxides.   The more complex data obtained
by other workers was probably due to their use of systems in which the
intermediate performic acid was not rapidly destroyed.

The oxidation of formaldehyde at 340°C has been further
investigated by Scheer (51) who was particularly interested in the
effects of mercury vapour on the reaction.   In this work, for a vessel
contaminated with mercury or for a vessel with a clean surface,

$$2 \left(\frac{dp}{dt} \right)_i \rightleftharpoons - \left(\frac{dF}{dt} \right)_i$$

i.e. the initial rate of decrease of the formaldehyde concentration was
equal to twice the initial rate of pressure change, in agreement with

the findings of earlier workers. However, for an aged vessel,
uncontaminated with mercury vapour

$$2 \left(\frac{dp}{dt}\right)_i \quad << \quad \left|\frac{dF}{dt}\right|_i$$

and no simple relationship was apparent.   In all the experiments, the
relationship

$$-\left.\frac{dF}{dt}\right._i = k \, F_i^2$$

was obeyed.   The wide variations in the activation energies found by
the various workers are presumably due largely to the use of reaction
vessels having different surface properties.   The following reaction
mechanism was proposed:

$$\text{Initiation} \quad H.CHO + O_2 \longrightarrow \dot{C}HO + H\dot{O}_2 \qquad\qquad 1$$

$$\text{Propagation} \quad H.\dot{C}O + O_2 \longrightarrow H\dot{C}O_3 \qquad\qquad 2$$

$$H\dot{C}O_3 + H.CHO \longrightarrow H.CO_3H + \dot{H}CO \qquad\qquad 3$$

$$\text{Termination} \quad H\dot{C}O_3 + O_2 \longrightarrow CO + H\dot{O}_2 + O_2 \qquad\qquad 3a$$

$$H\dot{C}O_3 + M \longrightarrow CO + H\dot{O}_2 + M \qquad\qquad 3b$$

$$H\dot{O}_2 \longrightarrow \text{wall} \qquad\qquad 4$$
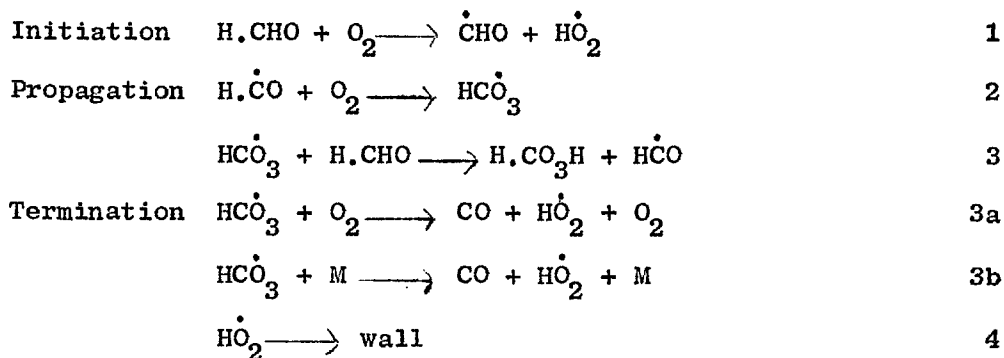
which is of type 511.   Under conditions where performic acid is rapidly
destroyed, this reaction scheme is followed by:

$$2.HCO_3H \longrightarrow 2CO + 2H_2O + O_2 \qquad\qquad 5$$

(Active surface or Mercury vapour)

$$2 \, HCO_3H \longrightarrow 2CO_2 + 2H_2 + O_2 \qquad\qquad 6$$

(Wall)
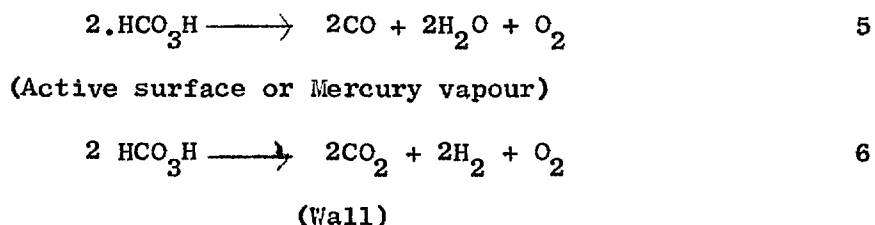
In an aged vessel, where the performic acid is not rapidly destroyed, the
following reactions are probable:

$$H.CO_3H + 2H.CHO \longrightarrow (CH_2OH)_2O_2 + CO \qquad\qquad 7$$

$$(CH_2OH)_2O_2 \longrightarrow H.COOH + CO_2 + 2H_2 \qquad\qquad 8$$

(Wall)
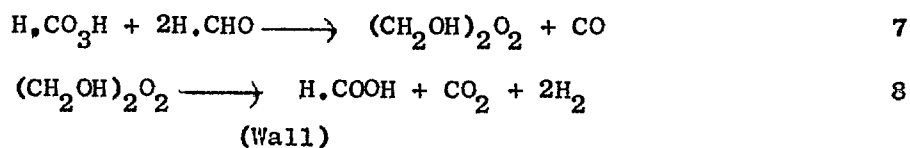
This mechanism accounts for the formation of all the products normally found in the oxidation of formaldehyde. Furthermore a steady-state treatment can be derived from it which gives rate equations which are in good agreement with those found experimentally. Thus a type 511 mechanism is here almost certainly valid.

(vii) Acetaldehyde

Acetaldehyde is very readily oxidised in the gas phase and at 120°C the main product is peracetic acid while carbon dioxide, carbon monoxide and other acids and peroxides are also obtained. The reaction has been studied by McDowell and Thomas (40,52) who proposed the following mechanism of oxidation:

Initiation $CH_3CHO + O_2 \longrightarrow CH_3\dot{C}O + H\dot{O}_2$ 1

Propagation $CH_3\dot{C}O + O_2 \longrightarrow CH_3C\dot{O}_3$ 2

$CH_3C\dot{O}_3 + CH_3CHO \longrightarrow CH_3CO_3H + CH_3\dot{C}O$ 3

Termination $2\ CH_3C\dot{O}_3 \longrightarrow (CH_3CO)_2O_2 + O_2$ 4
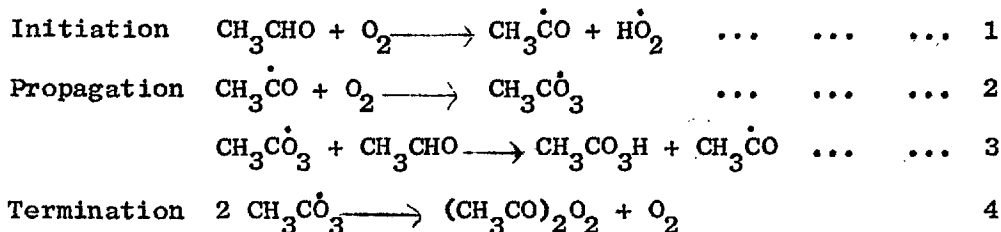
This reaction mechanism is of the type 511. Application of the steady-state treatment to this scheme gives:

$$-\frac{d}{dt}\left[CH_3CHO\right] = k\left[CH_3CHO\right]^2$$

which is in agreement with the experimental results. At the low temperatures used in this work, reactions 2 and 3 are the predominant propagation steps and peracetic acid is obtained in high yield. However some breakdown of the peracetic acid and the intermediate acetyl radical does occur to give acetic acid, carbon monoxide, and carbon dioxide:

Branching $CH_3CO_3H \longrightarrow CH_3C\dot{O}_2 + \dot{O}H$ 5

$CH_3C\dot{O}_2 + CH_3CHO \longrightarrow CH_3CO_2H + CH_3\dot{C}O$ 6

$$CH_3\overset{\bullet}{C}O_2 \longrightarrow \overset{\bullet}{C}H_3 + CO_2 \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 7$$

$$CH_3CO \longrightarrow \overset{\bullet}{C}H_3 + CO \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 8$$
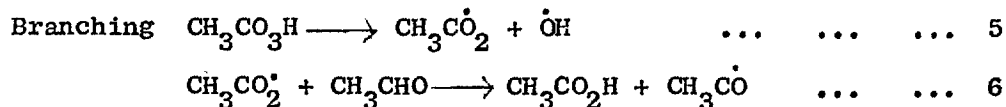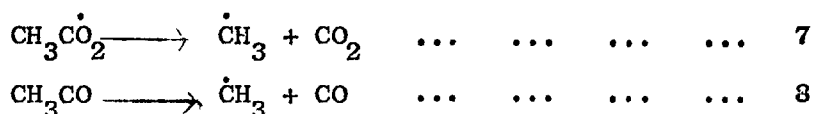
These types of breakdown occur more frequently as the temperature is increased. The reactions given above account for the formation of all the main products and thus probably include all the important reactions occurring under the experimental conditions used.

(viii) Diethyl ether

The oxidation of diethyl ether at 153°C has been investigated recently by Waddington (53). Acetaldehyde, acetic acid, ethanol, formaldehyde, methanol, and peracetic acid were detected in the products of reaction. The following oxidation mechanism was proposed:

Initiation $\quad CH_3.CH_2.O.CH_2.CH_3 + O_2 \longrightarrow CH_3.\overset{\bullet}{C}HO.CH_2.CH_3 + H\overset{\bullet}{O}_2 \quad 1$

Propagation $\quad CH_3.\overset{\bullet}{C}HO.CH_2.CH_3 \longrightarrow CH_3.CHO + CH_3\overset{\bullet}{C}H_2 \quad \cdots \quad \cdots \quad 2$
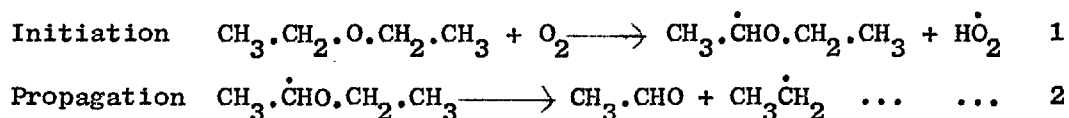
This mechanism is of type 24. These initial reactions will be followed by the oxidation of the acetaldehyde and the ethyl radicals formed in the ways previously described. The yield of formaldehyde was low compared with that of ethanol and thus the reaction:

$$CH_3CH_2\overset{\bullet}{O} \longrightarrow \overset{\bullet}{C}H_3 + H.CHO \cdots \quad \cdots \quad \cdots \quad \cdots \quad 3$$
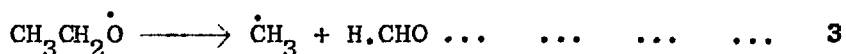
occurs infrequently compared with the competing reaction:

$$CH_3CH_2\overset{\bullet}{O} + RH \longrightarrow CH_3CH_2OH + \overset{\bullet}{R} \quad \cdots \quad \cdots \quad \cdots \quad 4$$
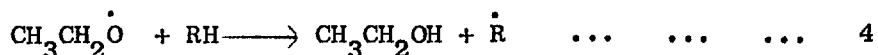
However, some hydroperoxide was also detected and thus a mechanism of type 211 probably occurs to a minor extent in parallel with the type 24 reaction.

(ix) Isopropyl alcohol

The oxidation of isopropyl alcohol has been studied by Burgess, Cullis, and Newitt (54) in a flow system. Acetone and

hydrogen peroxide were the predominant products in the early stages of the oxidation and they appeared to be formed in the following linear chain cycle:

$$\text{Initiation} \quad (CH_3)_2.CHOH + O_2 \longrightarrow (CH_3)_2\overset{\bullet}{C}OH + H\overset{\bullet}{O}_2 \quad \cdots \quad 1$$

$$\text{Propagation} \quad (CH_3)_2 CHOH + H\overset{\bullet}{O}_2 \longrightarrow (CH_3)_2\overset{\bullet}{C}OH + H_2O_2 \quad \cdots \quad 2$$

$$(CH_3)_2\overset{\bullet}{C}.OH + O_2 \longrightarrow (CH_3)_2CO + H\overset{\bullet}{O}_2 \quad \cdots \quad 3$$
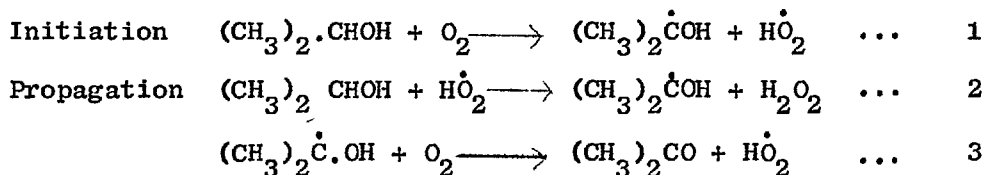
This type of mechanism is similar to type 32 but a ketone, acetone, is obtained instead of an olefin. Also $H\overset{\bullet}{O}_2$ is here postulated as an important chain-carrying species while such a process is not considered in the general mechanisms discussed initially.

A small proportion of the initial alcohol was converted into acetaldehyde and the further reaction of this compound was considered responsible for the autocatalysis observed. At this stage, the yields of the major products began to decrease and considerable amounts of methyl alcohol, formaldehyde, glyoxal, and carbon monoxide were formed, probably as a result of further reactions such as:

$$(CH_3)_2\overset{\bullet}{C}OH \longrightarrow CH_3CHO + \overset{\bullet}{C}H_3 \cdots \quad \cdots \quad \cdots \quad 4$$

$$CH_3CHO + O_2 \longrightarrow CH_3\overset{\bullet}{C}O + H\overset{\bullet}{O}_2 \cdots \quad \cdots \quad \cdots \quad 5$$

$$CH_3\overset{\bullet}{C}O \longrightarrow \overset{\bullet}{C}H_3 + CO \quad \cdots \quad \cdots \quad \cdots \quad 6$$

$$\overset{\bullet}{C}H_3 + O_2 \longrightarrow H.CHO + \overset{\bullet}{O}H \quad \cdots \quad \cdots \quad \cdots \quad 7$$
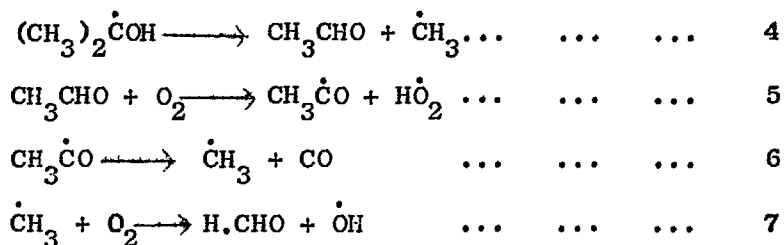
c) Additives

(i) Hydrogen bromide

The oxidation of hydrogen bromide at 400-500°C has been studied by Rosser and Wise (55). With hydrogen bromide in excess, the overall reaction was:

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$
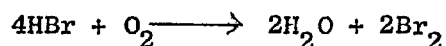
and the rate of reaction was governed by the equation:

$$\frac{d}{dt}\left[Br_2\right] = 2k\left[HBr\right]\left[O_2\right]$$

where k is the rate constant for the initiation reaction. The following reaction mechanism was proposed:

Initiation $HBr + O_2 \longrightarrow H\dot{O}_2 + \dot{B}r$ 1

Propagation $H\dot{O}_2 + HBr \longrightarrow \dot{B}r + H_2O_2$ 2

Branching $H_2O_2 \longrightarrow 2\dot{O}H$ 3

Propagation $HBr + \dot{O}H \longrightarrow H_2O + \dot{B}r$ 4

Termination $\dot{B}r + \dot{B}r \longrightarrow Br_2$ 5
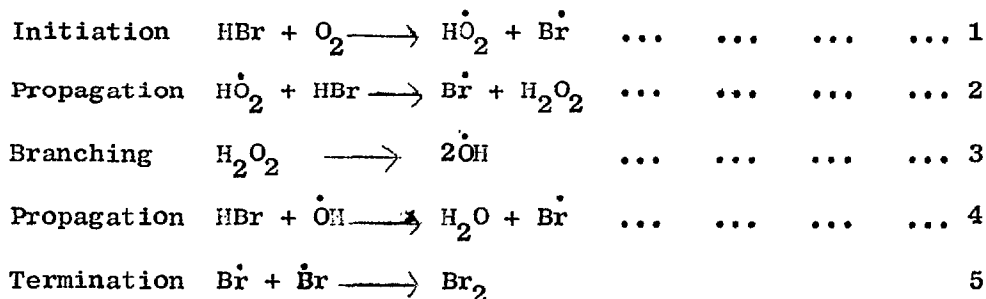
which accounts satisfactorily for the products and kinetics observed.

(ii) <u>Methyl bromide</u>

No detailed studies have been made of the oxidation of methyl bromide. Whittingham (56) studied the pressure-temperature conditions for ignition in methyl bromide-oxygen mixtures but he did not suggest any precise mechanism for the reaction. The reaction has been studied in the present work and it has been shown that bromine and hydrogen bromide are the major products. Because of the lack of experimental evidence no detailed oxidation mechanism can be proposed but from consideration of the mechanisms suggested in similar systems (42), the following reaction scheme appears plausible:

Initiation $CH_3Br + O_2 \longrightarrow \dot{C}H_2Br + H\dot{O}_2$ 1

Propagation $\dot{C}H_2Br + O_2 \longrightarrow Br.CH_2\dot{O}_2$ 2

    $Br.CH_2\dot{O}_2 \longrightarrow HBr\dot{C}O + \dot{O}H$ 3

Branching $HBr CO + O_2 \longrightarrow Br.\dot{C}O + H\dot{O}_2$ 4

    $Br\dot{C}O \longrightarrow \dot{B}r + CO$ 5

    $\dot{O}H + CH_3Br \longrightarrow H_2O + \dot{C}H_2Br$ 6

$$HO_2 + CH_3Br \longrightarrow H_2O_2 + \dot{C}H_2Br \qquad\qquad 7$$

$$\dot{Br} + CH_3Br \longrightarrow HBr + \dot{C}H_2Br \qquad\qquad 8$$

Termination $\dot{Br} + Br\dot{C}O \longrightarrow Br_2 + CO \qquad\qquad 9$
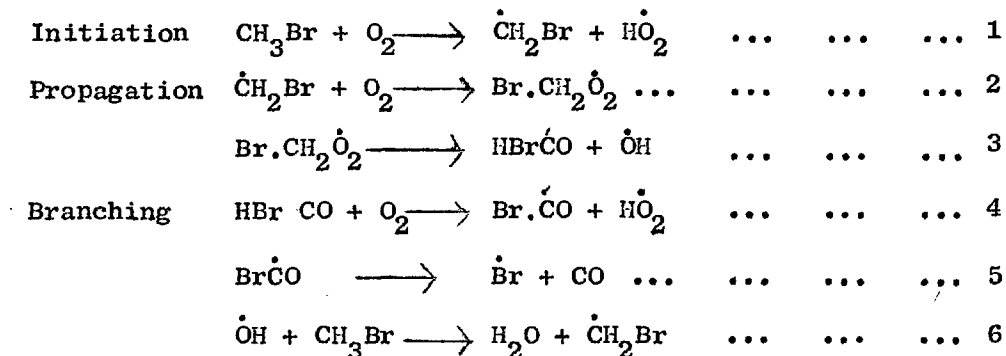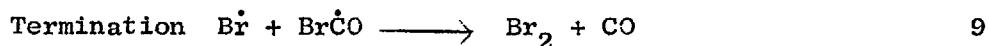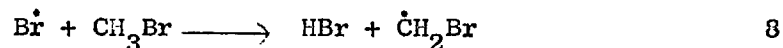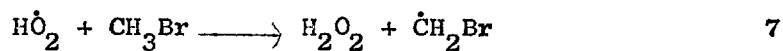
(iii) Methylene dibromide (iv) Chlorobromomethane

(v) Difluorodibromomethane

The oxidation of these compounds has not yet been studied and thus no mechanism of oxidation can be proposed.

B. THE EFFECT OF ADDITIVES ON THE GAS-PHASE OXIDATION OF ORGANIC COMPOUNDS

1. General

When a small proportion of an additive is mixed with an organic vapour and oxygen under normal reaction conditions, the additive may have no effect, or it may accelerate, retard, or inhibit the reaction. In some cases, the additive may have different effects on different phases of the reaction. Thus it may accelerate the initial stages of a reaction but retard a subsequent stage. The effect of an additive may be due solely to its physical presence in the reaction mixture or it may also participate chemically in the chain reactions occurring. Its physical presence increases the number of collisions between molecules and thus it increases the rates of reactions of higher kinetic order relative to those of lower order. For example, it increases the number of ternary collisions thus favouring radical-radical recombinations. Also it assists in maintaining radicals in the gas phase as they will take longer to diffuse to the walls. However, these effects are all proportional to the amount of additive present and the observed effect on the rate of reaction will be small

with the amount of additive normally used (0.5 - 5% by volume). This
is shown by the results obtained in this work with the acetaldehyde-
oxygen-additive and the diethyl ether-oxygen-additive systems.

Chemically, the additive may interfere with the chain reactions
occurring in the normal oxidation process. A potent additive generally
reacts readily with one of the chain carriers produced in the normal
reaction. If the species produced in this elementary step is stable
relative to other species present, then the reaction will be retarded.
If, on the other hand, the product is more reactive than the normal
chain carrier, the reaction will be accelerated. In many cases the
additive accelerates one reaction while retarding another and so the
overall effect observed may be either promotion or retardation,
depending upon the experimental conditions.

The fact that a reaction is inhibited by small quantities
of additive is powerful evidence for the reaction proceeding by a
chain mechanism and by a careful study of the inhibited reactions, it
is often possible to derive valuable information concerning the
underlying chain process (57).

a) Examples of additives

(i) Nitrogen dioxide

Nitrogen dioxide has been widely used as an additive in
oxidation systems. Thus many workers (58-60) have found that it
catalyses the reaction between hydrogen and oxygen when present in very
low concentrations, the reaction rate under given conditions increasing
sharply with nitrogen dioxide concentration. However, at higher
concentrations the rate of reaction falls as the nitrogen dioxide

concentration is increased although it remains higher than the rate of the normal reaction. These effects are thought to be caused by the additive participating in the normal chain reaction steps, accelerating some while retarding others, the resulting effect depending upon the additive concentration. However, the system is too complex for the precise mode of action of the additive to be proposed.

Nitrogen dioxide also catalyses the oxidation of methane (61) and propane (62-64) but it retards the reactions leading to cool flames in the acetaldehyde oxygen (62), diethyl ether-oxygen (65), and propane-oxygen systems (62).

It has also been found (57,66) that small quantities of nitrogen dioxide inhibit the slow oxidation of acetaldehyde, the most probable inhibiting reaction being:

$$CH_3\overset{\bullet}{C}O + NO \longrightarrow CH_3CO.NO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$
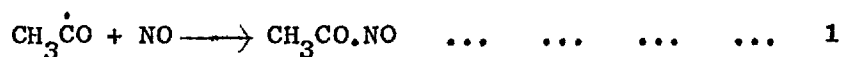
Nitrogen dioxide thus reacts either as an accelerator or as an inhibitor, depending upon the experimental conditions employed.

(ii) Amines

Many investigations have been carried out on the effect of amines on the combustion of hydrocarbons and other fuels. Thus aromatic amines inhibit the oxidation of di-isopropyl ether (67). The action of these compounds has been explained in terms of the absorption of free radicals by the cloud of π-electrons in the benzene ring, the presence of nitrogen and other groups merely modifying the properties of the ring. This theory was later shown to be unsatisfactory and an inhibition mechanism involving hydrogen transfer from the nitrogen group to high energy free radicals was proposed (68):

$$\overset{\bullet}{R} + C_6H_5NH_2 \longrightarrow RH + C_6H_5\overset{\bullet}{N}H \quad \ldots \quad \ldots \quad \ldots \quad 1$$
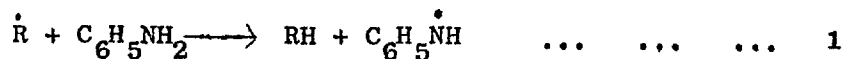
If the radical produced is relatively stable, then the rate of chain propagation is reduced and retardation or inhibition occurs. With aromatic radicals of this type, resonance stabilisation is possible so that these radicals may well be fairly stable.

Aliphatic amines also exert a definite inhibiting influence on oxidation reactions although they are far less powerful inhibitors than the aromatic amines. It has been shown that these compounds exert an inhibiting influence on the slow (69) and explosive (70) combustion of acetaldehyde. The secondary and tertiary amines were generally more effective than the primary compounds. However, the results were complicated by the formation of condensation products between the inhibitor and the fuel. It appeared that the powerful inhibiting effect was best explained in terms of surface 'poisoning' by the amine molecules. A hydrogen atom abstraction mechanism was considered unsatisfactory as it seemed unlikely that such abstraction would be particularly facile in the amines used.

Recently it has been shown (71) that amines inhibit the oxidation of diethyl ether. Here it was found that the surface of the vessel did not play an important part in the reaction. The inhibiting action was attributed to the gas-phase stabilisation of the radicals formed initially by hydrogen abstraction from the amine molecule, and also to stabilisation of these radicals through the formation of addition compounds between them and the amine involving one electron bonds.

e.g. $\ce{>\overset{\bullet\bullet}{N}.\overset{\bullet\bullet}{C}<}$
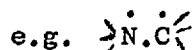
This suggestion is rather similar to that of Walsh mentioned previously.

Amines are thus powerful inhibitors of gas phase combustion
processes but their mode of action is not fully understood.

In general, then, these and other additives act by interfering
with the normal chain cycle, producing different chain carriers which
may be more or less reactive than those which normally participate in
the reaction.

2. Halogen compounds in flames

Some halogenated hydrocarbons are widely used as fire-
extinguishing materials and their flame-inhibiting properties are thus
well-established. Because of the high efficiency of these compounds
relative to inert gases, it is thought that their action is, at least
in part, chemical in origin, the compounds participating in the free-
radical reactions occurring in the flame front and thereby inhibiting
the reactions causing flame propagation. The flame-inhibiting
properties of these halogenated hydrocarbons have been studied in some
detail in the hope that some understanding might be gained of their
mode of action and that this would in turn lead to the discovery of more
efficient fire-extinguishing agents.

The earliest work was on inflammability limits. Burgoyne
and Williams-Leir (72,73) found that methyl bromide was far more
efficient than nitrogen in narrowing the inflammability limits of
many fuel/air mixtures while Simmons and Wolfhard (74,75), studying
the effect of methyl bromide and bromine on the combustion of methane-
air mixtures, concluded that the methyl bromide acted in the same way
as equivalent amounts of fuel and bromine, the bromine being the
effective inhibitor.

Burdon, Burgoyne and Weinberg (76) studied the burning of limit mixtures of hydrogen-air and carbon monoxide-air in the presence of methyl bromide and found that the limit flame temperatures were substantially raised by adding methyl bromide. This effect was attributed to the chemical intervention of methyl bromide in the flame reactions. Thus it was proposed that active hydrogen atoms might be removed by a reaction such as:

$$\overset{\bullet}{H} + CH_3Br \longrightarrow \overset{\bullet}{C}H_3 + HBr$$
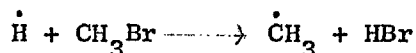
the methyl radicals produced being far less energetic in continuing the chain.

Studies have also been made of the effect of these compounds on the burning velocities of fuel-air mixtures. Garner and co-workers (77) found that various halomethanes reduced the burning velocities of propane-air mixtures, even when present in very small concentrations. For the compounds investigated, the order of effectiveness was:

$$CH_2ClBr > CH_3Br > CH_3I > CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl > HCl > H_2O$$
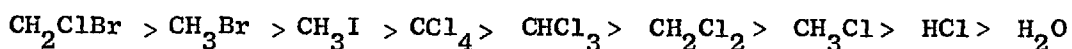
It appeared that these compounds exerted a specific chemical inhibiting effect on the reactions occurring in the flame front.

The most detailed study of flame inhibition phenomena has been carried out by Rosser, Wise, and Miller (78). It was found that the burning velocities of methane-air mixtures were substantially decreased by very small proportions of various halomethanes such as methyl bromide, methylene dibromide, chlorobromomethane, and bromoform. The reduction of flame speed obtained for a given concentration of additive was dependent on the number of halogen atoms in the molecule, methylene dibromide being roughly twice as effective as methyl bromide.

The small concentrations of additive used had little effect on the maximum flame temperature observed. A chemical inhibition mechanism of the following type was proposed:

$$H\alpha + X \longrightarrow HX + \alpha \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

fuel · · · · · · · · · · · acid

halogen · · · · · relatively stable radical

$$\beta + HX \longrightarrow H\beta + X \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2$$
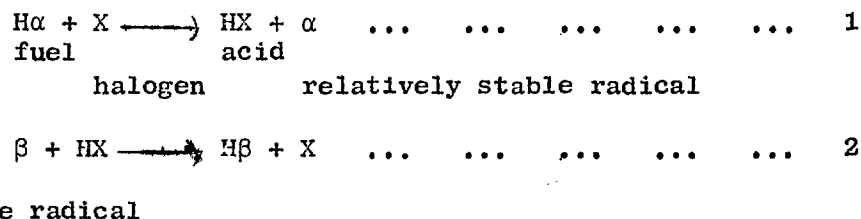
reactive radical

in which the halogen acid HX, obtained by the decomposition of the halomethane in the flame zone, reacts with an active radical β (e.g. OH, H, O) to give a fairly stable species $H\beta$ and the halogen radical X. The halogen acid is regenerated by reaction of X with a fuel molecule. In this way, active radicals are replaced by relatively stable radicals and this reduces the rate of reaction to such an extent that the heat produced is no longer able to support a flame and extinction results.

The effectiveness of the inhibition may be reduced by

a) The decomposition of the halogen acid:

$$HX \longrightarrow H + X$$

b) The oxidation of the halogen acid:

$$HX + O_2 \longrightarrow H\dot{O}_2 + X$$
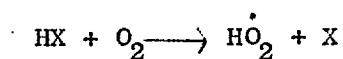
c) The failure of the additive to decompose.

Factors a) and b) will be important in unusually hot flames. A critical factor in the mechanism is the strength of the H – X bond. If it is too strong, reaction 2 will occur only slowly, while if it is too weak, HX will decompose rather than react. The almost unique ability of iodine and bromine compounds to reduce flame speed reflects this balance.

Work has also been carried out on the extinction of stationary flames by additives. Levy and co-workers (79) have obtained composition profiles through lean methane-air flames inhibited with hydrogen bromide. It was concluded that hydrogen bromide inhibits the conversion of methane to carbon monoxide but does not affect its further oxidation to carbon dioxide.

Creitz (80) found that halomethanes such as methyl bromide and trifluoromethyl bromide were far more efficient inhibitors of various diffusion flames when added to the air supply than when added to the fuel. It was thus concluded that the inhibition reaction involved the intact additive molecule and was related to the use of oxygen in the flame reactions. These facts were explained by assuming that the oxidation of a fuel occurs to some extent through the initial ionization of the fuel molecule to give a positive ion and electrons. These electrons then react with oxygen molecules to give the activated O_2^- ion. The positive and negative ions then react in the flame to give the final products observed. However, if other molecules are present in the flame zone which are more efficient at capturing electrons than oxygen, then it is conceivable that all the electrons will be removed by the additive before they are able to react with oxygen and thus the normal flame reactions will be completely inhibited. Evidence is given to show that the observed efficiency of an inhibitor is related to its capture-cross section for electrons and thus the theory appears to be a reasonable one. However insufficient experimental evidence is at present available to determine whether Creitz's theory or that of Rosser, Wise, and Miller provides the more likely explanation of the inhibiting effects in flames produced by halogen compounds.

3. Halogen compounds in slow combustion

Relatively little work has been done on the effect of halomethanes on slow combustion processes, (81-83) although several investigations have been made on the effect of halogens and halogen acids. Thus Garstang and Hinshelwood (84) found that iodine has a distinct effect on the hydrogen-oxygen reaction, promoting the surface reaction while retarding the gas phase reaction. Iodine also affects the methane-oxygen reaction. Thus small concentrations increase the induction period at 340°C but reduce it at 440°C (85). The inhibition step at low temperatures can be written:

$$\dot{H} + I_2 \longrightarrow HI + \dot{I} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

the reactive H atom being replaced by the I atom which is incapable of propagating a chain due to its low activity. At higher temperatures, the iodine molecule dissociates into radicals and these radicals are capable of abstracting a hydrogen atom from a fuel molecule:

$$RH + \dot{I} \longrightarrow \dot{R} + HI \quad \ldots \quad \ldots \quad \ldots \quad 2$$

Initiation thus occurs more readily than usual so that promotion of the reaction is observed. Bromine would be expected to show similar behaviour.

Hydrogen bromide is an active catalyst of hydrocarbon oxidations. Rust, Vaughan and co-workers (86) have studied the oxidation of many hydrocarbons in the presence of hydrogen bromide in a flow system. The catalysed reactions took place at temperatures well below the normal reaction temperatures and under these relatively mild conditions C-C bond fission was minimised and high yields of specific reaction products were obtained. Compounds containing

tertiary hydrogen atoms are readily oxidised to the corresponding hydroperoxide. Thus with isobutane the main reaction may be represented as:

$$(CH_3)_3CH + O_2 + HBr \longrightarrow (CH_3)_3COOH \quad \ldots \quad \ldots \quad \ldots \quad 3$$

10 pts   10 pts   1 pt   160°C   75% yield
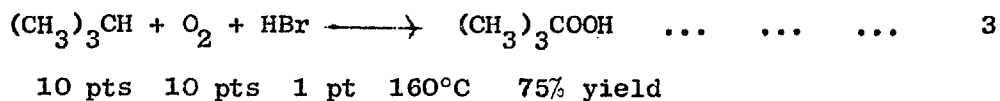
A little bromine, organic bromides, tertiary butyl alcohol, and di-tertiary butyl peroxide are also formed in side reactions. A high percentage of the catalyst can be recovered from the reaction mixture but the remainder is lost through oxidation to bromine or by the formation of organic bromides. The probable reaction mechanism for the main reaction is:

$$HBr + O_2 \longrightarrow H\dot{O}_2 + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad 4$$

$$(CH_3)_3CH + \dot{B}r \longrightarrow (CH_3)_3\dot{C} + HBr \quad \ldots \quad \ldots \quad \ldots \quad 5$$

$$(CH_3)_3\dot{C} + O_2 \longrightarrow (CH_3)_3C\dot{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 6$$

$$(CH_3)_3C\dot{O}_2 + HBr \longrightarrow (CH_3)_3COOH + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad 7$$
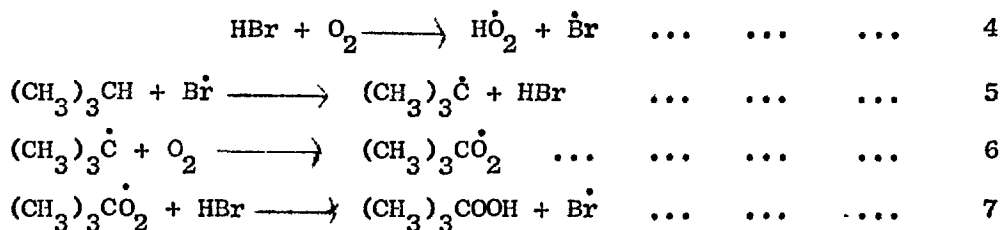
Hydrogen bromide is an efficient hydrogen donor and thus readily stabilises the peroxy radical, forming the hydroperoxide.

If the compound being oxidised contains hydrogen atoms in only primary and secondary positions, then the principal product is a ketone. Thus if propane is oxidised in the presence of hydrogen bromide, acetone is obtained:

$$CH_3.CH_2.CH_3 + O_2 + HBr \longrightarrow CH_3.CO.CH_3 \quad \ldots \quad \ldots \quad \ldots \quad 8$$

2 pts   2 pts 1 pt 190°C 75% yield
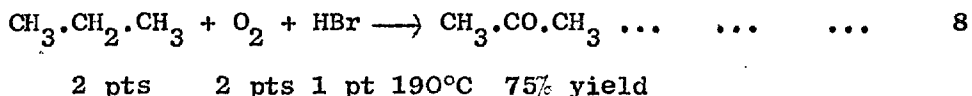
by a mechanism initially similar to that outlined above. However, the intermediate hydroperoxide decomposes to give a ketone and water:

$$(CH_3)_2CHO_2H \longrightarrow (CH_3)_2CO + H_2O \quad \ldots \quad \ldots \quad \ldots \quad 9$$
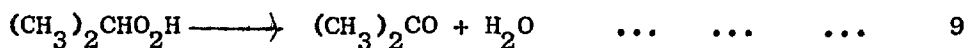
A possible mechanism for this overall reaction is:

$$\overset{\bullet}{Br} + (CH_3)_2CHO_2H \longrightarrow (CH_3)_2CO + HBr + \overset{\bullet}{O}H \quad \ldots \quad \ldots \quad 10$$

$$\overset{\bullet}{O}H + HBr \longrightarrow H_2O + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 11$$
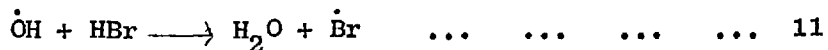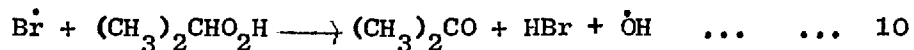
The propionic acid also obtained is probably formed by initial hydrogen abstraction from an end carbon atom giving the radical $CH_3.CH_2.\overset{\bullet}{C}H_2$ which is subsequently oxidised.

Hydrogen bromide catalysed oxidation of compounds containing only methyl groups gives largely organic acids. However, methane is not readily oxidised in this way and at the high reaction temperature required, carbon monoxide and water are the main products. Ethane, on the other hand, gives a high yield of acetic acid:

$$CH_3.CH_3 + O_2 + HBr \longrightarrow CH_3.COOH \quad \ldots \quad \ldots \quad \ldots \quad 12$$
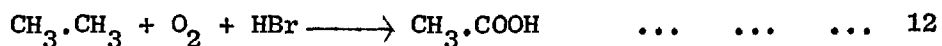
$$2 \text{ pts} \quad 2 \text{ pts} \quad 1 \text{ pt} \quad 220°C \quad 75\% \text{ yield}$$

The mechanism proposed is initially similar to that given above. However, the aldehyde produced is readily further oxidised:

$$CH_3CHO + \overset{\bullet}{Br} \longrightarrow CH_3\overset{\bullet}{C}O + HBr \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 13$$

$$CH_3\overset{\bullet}{C}O + O_2 \longrightarrow CH_3\overset{\bullet}{C}O_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 14$$

$$CH_3\overset{\bullet}{C}O_3 + HBr \longrightarrow CH_3CO_3H + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 15$$

$$CH_3CO_3H + 2HBr \longrightarrow CH_3CO_2H + Br_2 + H_2O \quad \ldots \quad \ldots \quad \ldots \quad 16$$
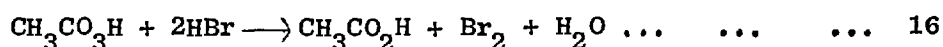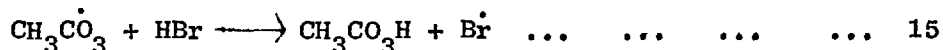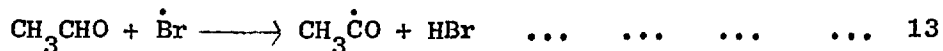
The overall reaction 16 probably proceeds in the stages:

$$RCO_3H \longrightarrow R\overset{\bullet}{C}O_2 + \overset{\bullet}{O}H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 17$$

$$R\overset{\bullet}{C}O_2 + HBr \longrightarrow RCO_2H + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 18$$

$$HBr + \overset{\bullet}{O}H \longrightarrow H_2O + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 19$$

$$2\overset{\bullet}{Br} \longrightarrow Br_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 20$$

Some ethyl bromide is also obtained by the reaction:

$$CH_3\overset{\bullet}{C}H_2 + Br_2 \longrightarrow CH_3 CH_2Br + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 21$$
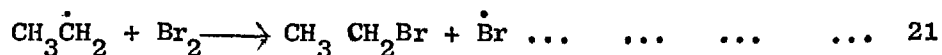
Thus compounds containing tertiary C–H bonds are the most readily oxidised and give the best yields of specific oxidation products while compounds containing only primary C–H bonds are the most difficult to oxidise and give a wide variety of products. These results would be expected in view of the independent evidence available on bond strengths. The HBr-catalysed oxidation of alkylated benzenes appears to conform to the general principals given above, at least in the early stages of reaction. However, more vigorous conditions are required for the reaction to proceed at a reasonable rate and the initial products formed undergo a complex variety of degradation and addition reactions to give a very wide range of final products.

Benzene itself is very resistant to such oxidation and no appreciable reaction occurs even at 250°C. Oxidation of toluene at 195°C gives the anticipated benzoic acid. However, appreciable amounts of benzyl bromide, phenol, and brominated phenols are also obtained. Phenol is presumably formed by breakdown of the initial hydroperoxide:

$$C_6H_5.CH_2.OOH \longrightarrow C_6H_5.OH + H_2CO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 22$$
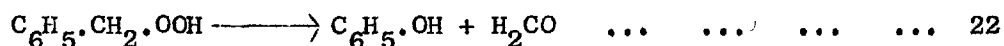
Oxidation of cumene at 195°C gives a considerable amount of acetone while phenol, acetophenone, p-cumyl phenol and p.αα dimethyl benzyl phenol are also obtained. The formation of some of these compounds can be explained by assuming various routes for the decomposition of the initially formed hydroperoxide:

$$C_6H_5.C(OOH).(CH_3)_2 \longrightarrow C_6H_5OH + CH_3.CO.CH_3 \quad \ldots \quad \ldots \quad 23$$

$$\longrightarrow C_6H_5.CO.CH_3 + CH_3OH \quad \ldots \quad \ldots \quad 24$$
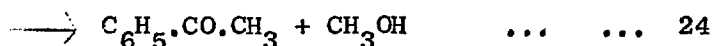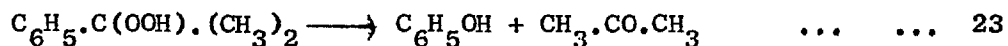
Thus in these reactions appreciable C–C bond fission occurs and no product is obtained in very high yield.

Gas-phase oxidation reactions sometimes appear to occur in several macroscopic stages, each with its own elementary mechanism (87). This is observed in the gas-phase oxidation of isobutane catalysed by hydrogen bromide (88) where the initial reaction is the production of tertiary butyl hydroperoxide. At a certain stage, however, the main reaction changes over to the oxidation of the hydroperoxide, while later on the oxidation ceases even though much reactant remains. Similar effects have been observed during the hydrogen bromide catalysed oxidation of propane (89) and ethane (90).

Maizus and Emanuel (91) have made a detailed study of the system propane + oxygen + hydrogen bromide. The accumulation of the main product, acetone, is described by the equation:

$$P_t = P \left[1 - \exp(-kt) \right]$$

where P_t = Pressure of acetone at time t

P = Pressure of acetone at completion of reaction

Thus a quasi-unimolecular law is obeyed although the system has three constituents. This is explained by assuming that some intermediate is formed rapidly in the first few seconds and this then decomposes unimolecularly, initiating the unbranched-chain oxidation of propane to acetone. The reaction ceases when the intermediate has completely decomposed. The initial stage during which this intermediate is formed is self-inhibiting so that the formation of this substance ceases while much of the reactants still remains.

The oxidation of isobutane catalysed by hydrogen bromide has also been investigated by Allen and Tipper (92). In a boric-acid coated vessel below 170°C, the overall process was largely:

$$(CH_3)_3CH + O_2 \longrightarrow (CH_3)_3COOH \quad \ldots \quad \ldots \quad \ldots \quad 25$$
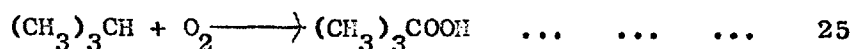
The main source of chain branching was shown to be the HBr-catalysed decomposition of the hydroperoxide. The reaction mechanism proposed was:

Branching $(CH_3)_3COOH + HBr \longrightarrow \overset{\bullet}{Br} +$ other products   26

$\overset{\bullet}{Br} + (CH_3)_3CH \longrightarrow HBr + (CH_3)_3\overset{\bullet}{C}$ 27

Propagation $(CH_3)_3\overset{\bullet}{C} + O_2 \longrightarrow (CH_3)_3C\overset{\bullet}{O}_2$ 28

$(CH_3)_3C\overset{\bullet}{O}_2 + HBr \longrightarrow (CH_3)_3CO_2H + \overset{\bullet}{Br}$ 29

Termination $(CH_3)_3C\overset{\bullet}{O}_2 + \overset{\bullet}{Br} \longrightarrow (CH_3)_3COO\ Br$ 30
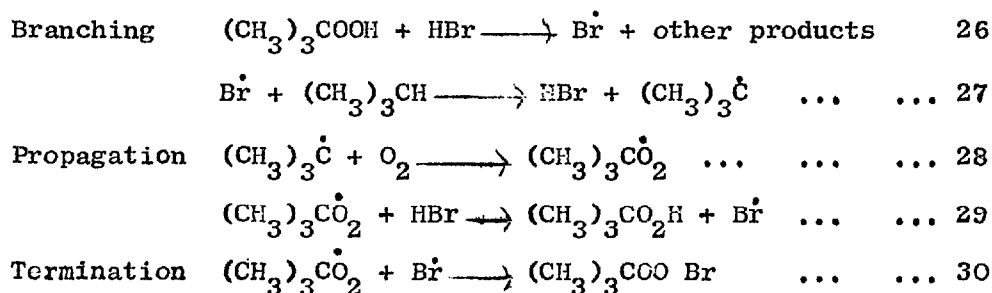
As the bond dissociation energies for $(CH_3)_3C-H$ and Br-H are approximately the same, the preferential abstraction of hydrogen atoms from hydrogen bromide is probably due to steric effects.

Thus hydrogen bromide acts as a powerful positive catalyst in the oxidation systems studied to date while free halogens sometimes accelerate and sometimes inhibit combustion. Halomethanes exert powerful inhibiting effects on flames while little evidence is available concerning their effects on slow combustion processes. It is obviously of interest to investigate these effects and thus the work described in this thesis has been carried out with this purpose in view. The thesis gives a detailed account of the effects of four different halomethanes and hydrogen bromide on the oxidation of a wide variety of different fuels.

S E C T I O N 2

EXPERIMENTAL

A. THE APPARATUS

1. The vacuum system

a) General outline

A diagram of the conventional 'static' apparatus used is
given in Fig. 1. The apparatus consisted essentially of a spherical pyrex
reaction vessel, A, suspended in an electrically heated furnace and
connected to a mercury manometer, M_2, of the open type, a pre-
mixing vessel, B, a sampling U-trap, E, analytical traps, K, and the main
vacuum line. A safety trap, D, was inserted between the manometer
and the reaction vessel to provide a pressure release in the event of a
vigorous explosion. In order to minimise the 'dead space', all the
glass tubing in the vicinity of the reaction vessel was pyrex
capillary tubing of 2 mm. internal diameter. This system was
directly connected to another mercury manometer, M_1, to the main
vacuum line, and to a series of gas storage bulbs. Oxygen was
stored in a 5 litre globe, G_4, whereas gaseous halomethanes, hydrogen
bromide, fuels, and nitrogen, were stored in 2 litre globes, (G_1, G_2,
G_3,.....) Also attached to this section of the line were another
pre-mixing vessel, C, and a small bulb, G_5, used for storing the less
volatile liquids. Pyrex tubing of 6 mm. internal diameter was used
in this section of the apparatus. The far end of the line was
connected to a system for the admission and purification of reactants.

Both the pre-mixing vessels were shielded in thick steel
chambers which had pressure-release holes drilled in their back sides
in order to prevent scattering of glass in the event of an explosion.

The pumping unit consisted of a three-stage mercury diffusion pump backed by a rotary oil pump, which provided a vacuum of about 10^{-3} to 10^{-4} mm. Hg. throughout the apparatus. Traps were inserted between the oil pump and the diffusion pump and also between the diffusion pump and the apparatus. When the system was in use, these traps were cooled in liquid nitrogen in order to prevent organic vapours entering the pumps and also to assist in obtaining a good vacuum. The vacuum in the apparatus was indicated by a small gas-discharge tube connected to the main vacuum line. The tungsten-tipped electrodes of the discharge tube were connected to the secondary terminals of an induction coil whose primary current was supplied by a 6-volt accumulator. On depression of a switch in the primary circuit a discharge was observed in the tube, the colour and intensity of this discharge being indicative of the nature and pressure of gases present in the system. During the evacuation of the system, pumping was continued until the discharge disappeared and sparking across the terminals ensued. The vacuum was then of the order of 10^{-3} to 10^{-4} mm. Hg.

KEY TO FIG. 1

A	Pyrex reaction vessel
B, C	Pre-mixing vessels
D	Safety trap
E	U trap
G_1, G_2, G_3, G_4	Gas storage globes
G_5	Liquid storage bulb
J	'Anhydrone' column
K	Analytical trap
M_1, M_2	Capillary mercury manometers
P	Platinum resistance thermometer
T	Chromel-alumel thermocouple
T_1, T_2	Cold traps
....	Region of electrical wiring

Fig.1. THE APPARATUS.

TO PUMP

TO ANALYTICAL TRAPS K & PUMP
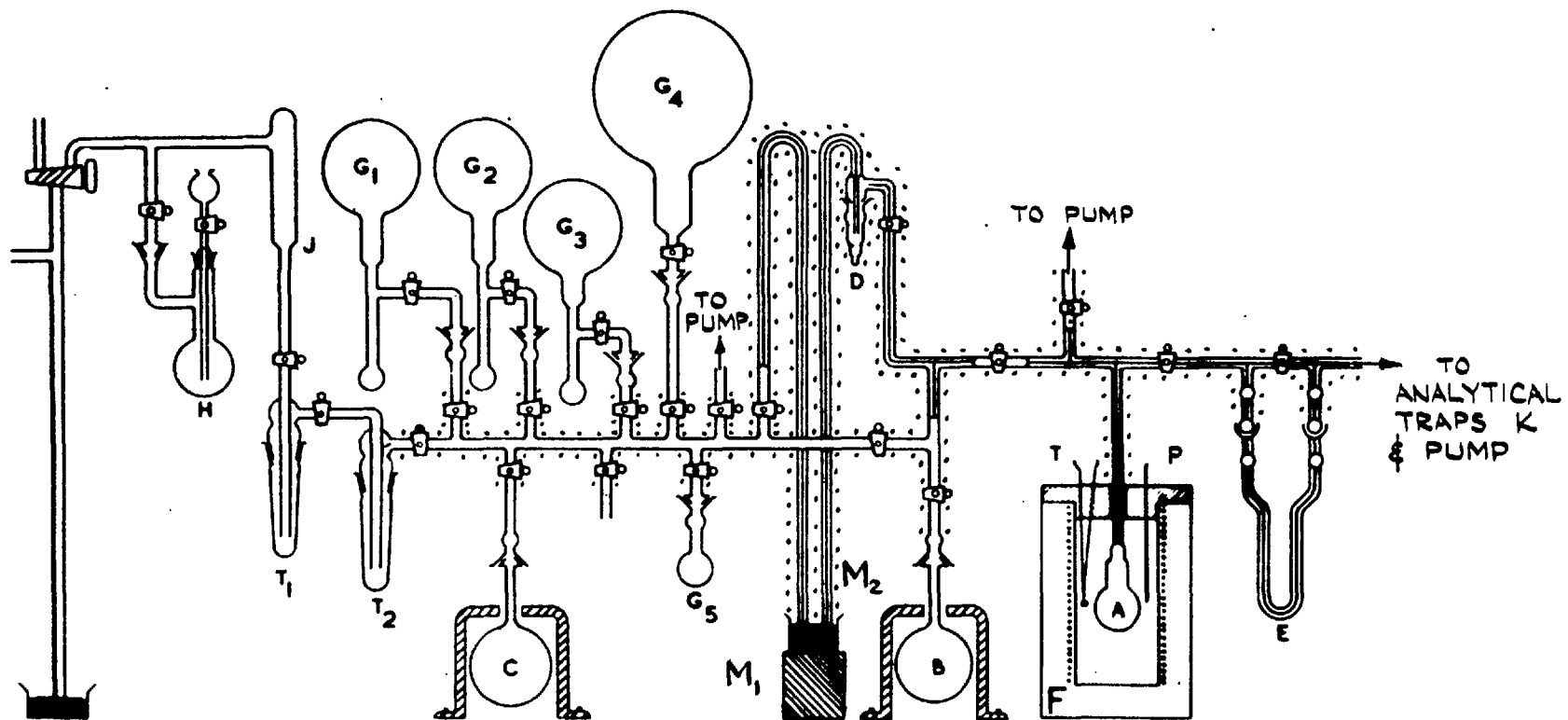
b)   The reaction vessel

A spherical pyrex reaction vessel of 200 ml. capacity was used initially.   It was cleaned with hot concentrated nitric acid, rinsed with distilled water followed by acetone and then baked at 500°C overnight before being sealed to the apparatus.   It was then heated at 450°C overnight under vacuum before use. , In the later stages of the work when experiments were being carried out at over 500°C a cylindrical silica reaction vessel of 200 ml. capacity was employed. This was initially treated in the same way as the pyrex reaction vessel.

c)   Vacuum grease

All the taps and ground glass joints were lubricated with Edwards' Silicone High Vacuum Grease, which is extremely resistant to chemical attack and possesses a low temperature coefficient of viscosity, but suffers from the disadvantage that it 'creeps' readily over glass surfaces, depositing an extremely tenacious film of silica.   Whenever taps become 'streaky' they were well cleaned with carbon tetrachloride before they were regreased and replaced in the system.

d)   Electrical heating

The glass tubing indicated in the diagram (Fig. 1) was wound with nichrome wire, resistance 18 ohm. per metre, with approximately 2 turns per centimetre length.   3 lengths of wire in parallel were connected to a 220 v. D.C. mains.   An ammeter and rheostat were placed in series with two of these lengths, and by suitable adjustment of the rheostats the total resistance of each of the three lengths was

made equal so that the same current flowed through each wire. Thus all the tubing could be maintained at approximately the same temperature which was measured on thermometers strapped to the tubing. A current of 1 amp. through each length of wire gave a temperature of about 100°C. The pre-mixing vessel, B, was heated when necessary by immersing in a thermostatic bath. The liquid used in the bath was water for temperatures up to 70°C while liquid paraffin was used at higher temperatures.

2. The furnace system

a) The furnace

The furnace, F, was constructed of welded metal and the outer casing was made of Sendanyo sheeting. The heating element consisted of nichrome wire (resistance 49 ohm.) wound on a vitreosil tube (length 30 cm., int. diam. 11.5cm) and covered with asbestos cement. The tube was also lined with a thick copper sheath to protect it against explosion and to provide a more uniform temperature distribution along the length of the furnace. The upper end of the furnace tube was closed with a thick Sendanyo 'plug'. The furnace was connected through a rheostat, ammeter, a Variac transformer, and a switch to the 230 v. A.C. mains. This is shown in Fig. 2.
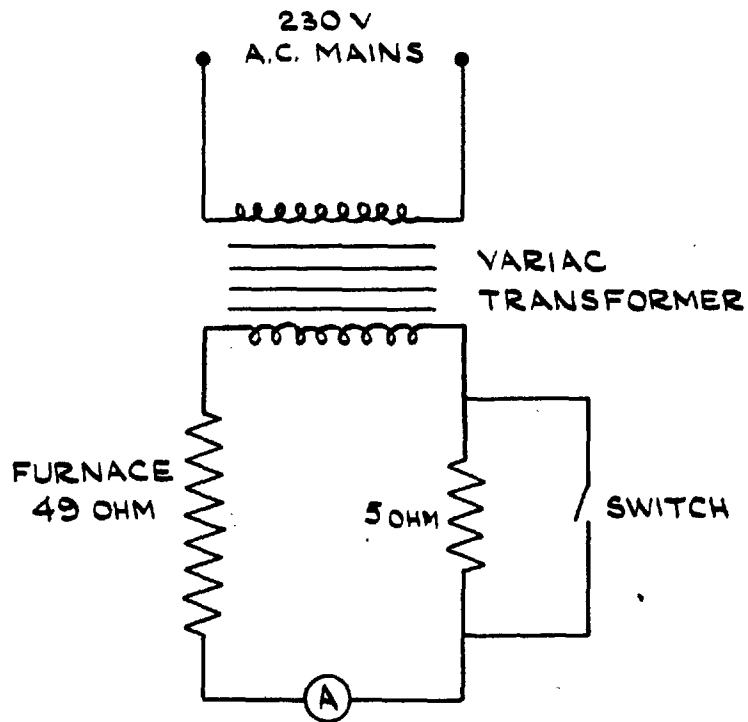
FIG. 2. THE FURNACE CIRCUIT.

b) Temperature measurement

The temperature of the furnace was measured with a spot-welded chromel-alumel thermocouple, T, which was calibrated against a standard platinum-rhodium thermocouple. The leads to the hot junction passed down a twin-hole mullite tube which could be fixed so that the tip was at the same level as the middle of the reaction vessel, while the cold junction, enclosed in a glass sheath, was immersed in melting ice. The e.m.f. produced was measured on a Cambridge thermocouple potentiometer, reading to 0.002 mv.

c) Temperature control

The furnace temperature was automatically controlled by a Wheatstone bridge circuit (93) involving a Sunvic hot-wire vacuum switch, placed in parallel with a resistance which was itself in series with the furnace resistance (Fig. 2). One arm of this Wheatstone bridge contained a platinum resistance thermometer which was fixed alongside the hot junction of the thermocouple.

To maintain the furnace at a given temperature the coarse and fine resistances of the Wheatstone bridge were adjusted so that when the temperature dropped below the required value the bridge became unbalanced and a current flowed in the amplifying circuit, closing the Sunvic hot-wire vacuum switch. Thus a current, slightly greater than that needed to give the required temperature, passed through the furnace. When the temperature attained its original value, the circuit became balanced again and the switch opened. By this means it was possible to control the temperature to within $\pm 0.5^\circ C$ for an indefinite period of time.

d)   Temperature distribution in the furnace

The distribution of temperature along the length of the furnace was measured to ensure that the reaction vessel was placed in such a position that there was only a small variation of temperature over its length.   The temperature was set at about 310°C and the furnace was left on overnight to allow thermal equilibrium to be set up.   The hot junction of the thermocouple was then moved down the furnace in 1 cm. stages and was kept stationary at each level until a constant e.m.f. was obtained.   It was subsequently raised gradually to check the readings taken on the downward journey.   Close agreement was obtained between the two sets of readings.   A graph was then drawn of depth of immersion of the thermocouple against temperature observed.   The results showed that over an 8 cm. section, the midpoint of which was 23 cm. from the top of the furnace, the temperature variation was less than $\pm$1°C.   The reaction vessel was thus suspended in the furnace with its centre at this point.   The temperature distribution in the furnace was then measured again and it was found to be little affected by the presence of the reaction vessel.   The temperature distribution with the reaction vessel in place is shown in Fig. 3.
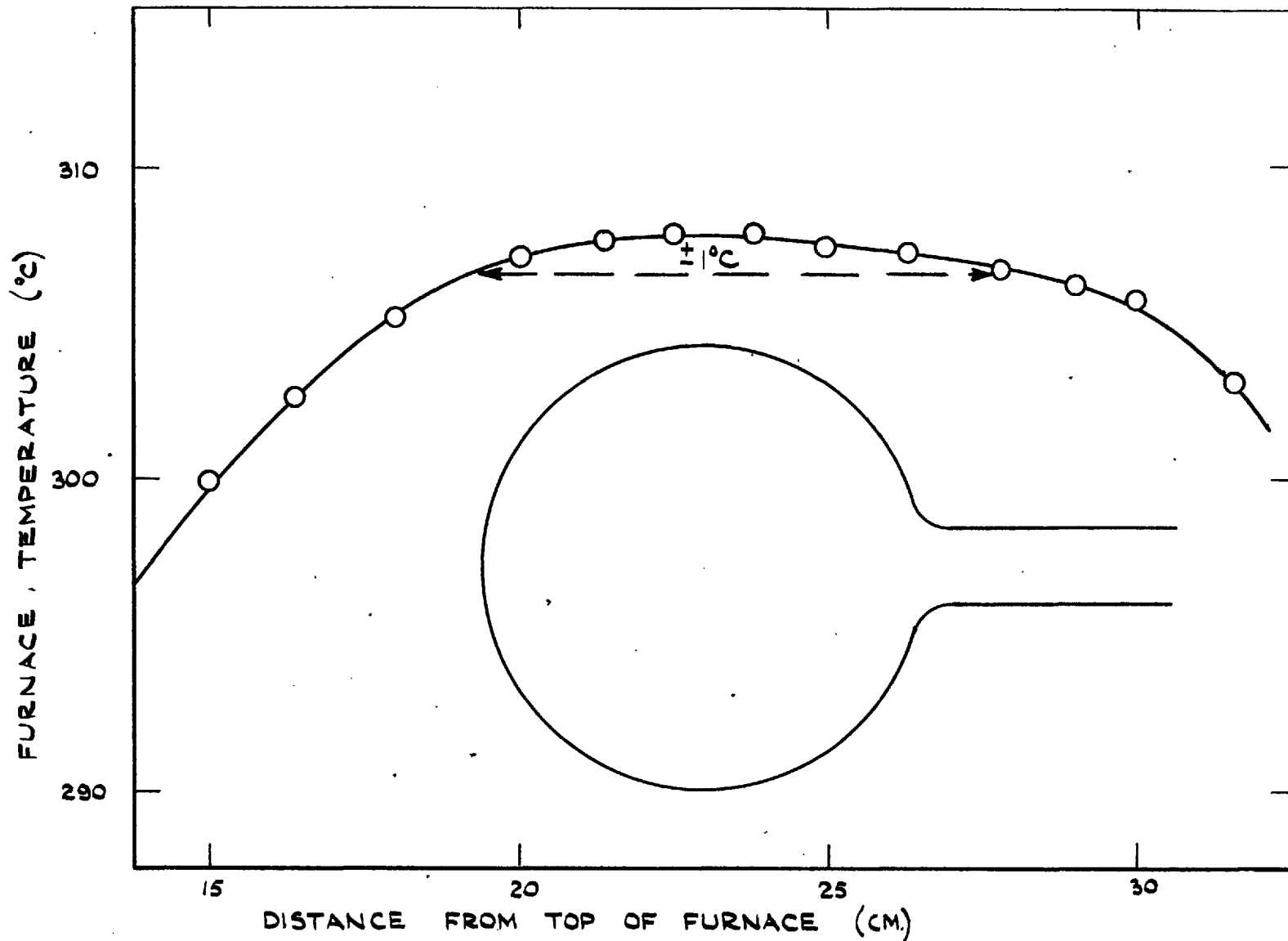
FIG. 3. TEMPERATURE DISTRIBUTION IN THE FURNACE.

B. MATERIALS

1. Fuels

    a) Diethyl ether b) Isopentane c) Benzene d) Cumene

        e) Isopropyl alcohol

The purest available commercial samples of the above liquids were introduced into the system through trap T_1 and carefully fractionated under vacuum in this trap and trap T_2 using liquid nitrogen as coolant. The low-boiling liquids, diethyl ether and iso-pentane, were then distilled into 2 litre storage globes. The higher-boiling liquids, benzene, cumene, and isopropyl alcohol, were distilled into 50 ml. bulbs.

    f) Acetaldehyde

The best available commercial sample of acetaldehyde was freshly distilled in a current of nitrogen. The middle fraction was collected in a receiver cooled in ice-salt, and then transferred to trap T_1. The sample was carefully fractionated in vacuo prior to being distilled into a 2 litre globe, blackened to prevent photo-decomposition. Liquid nitrogen was first used as a coolant but acetaldehyde is solid at this temperature (-196°C) and appreciable polymerisation occurs on freezing giving a very low yield. Solid carbon dioxide in methylated spirits was therefore used as coolant in later distillations as acetaldehyde remains a liquid at -80°C. On some occasions the yields of acetaldehyde from the external distillation were also very low. Thus it was eventually found more convenient to use freshly depolymerised paraldehyde as the source of pure acetaldehyde.

g) Formaldehyde

Formaldehyde was prepared by heating paraformaldehyde, contained in a 500 ml. cylindrical vessel, to 120°C, using wire wound on the glass as an electrical heating element.   In this way all the glass was maintained at ca. 120°C, thus preventing repolymerisation on cool surfaces, and also a large quantity of gas could be conveniently prepared.

h) Methane

Methane was obtained from a cylinder containing 99.95% pure methane supplied by Air Liquide, Belgium, and kindly loaned by Mr. A.J. Davenport.   It was introduced into a 5 litre globe on the apparatus and used without further purification.

i) Ethane

Ethane from a cylinder was purified by fractional distillation in vacuo, liquid oxygen being used as a coolant.   The final middle fraction was allowed to vaporise into 4 2-litre globes.

2. Additives

a) Methyl bromide

Methyl bromide was obtained from a cylinder and purified by fractional distillation in vacuo, solid carbon dioxide-methylated spirits being used as coolant.   The final middle fraction was allowed to vaporise into a 2-litre globe.

b) Methylene dibromide c) Chlorobromomethane

d) Dibromodifluoromethane

The above liquids were carefully fractionated in vacuo using liquid nitrogen as coolant.   The low-boiling liquid, dibromodifluoro- methane, was then distilled into a 2-litre globe.   The higher-boiling

liquids, methylene dibromide and chlorobromomethane, were distilled into 50 ml. bulbs.

e) Hydrogen bromide

Hydrogen bromide was prepared by the action of bromine on tetrahydronapthalene (94).

Tetralin (30 ml., 0.2 mole) was placed in a three-necked, 500 ml. round-bottomed flask fitted with a 50 ml. dropping funnel, entry tube, and delivery tube. The flask, A, was connected as shown in the diagram, Fig. 4, to a bubbler, B, filled with tetralin, to a U tube, C, immersed in ice-salt, and then to the main apparatus. The trap, T_2, was immersed in liquid oxygen. Nitrogen was initially bubbled through the apparatus at a steady rate for half an hour to ensure the removal of all moisture. Bromine (25 ml. 0.5 mole) was then added dropwise from the funnel, slowly over 2 hr. Hydrogen bromide was steadily produced at room temperature and was condensed in the liquid oxygen trap. Any bromine or tetralin vapour carried over by the hydrogen bromide was removed, either by the tetralin in the bubbler, or by condensation in trap C. Stepwise bromination of the tetralin occurs as far as the tetrabromo compound:

$$C_{10}H_{12} + 4Br_2 \longrightarrow C_{10}H_8Br_4 + 4HBr$$
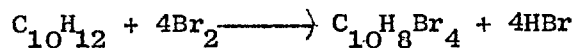
When sufficient hydrogen bromide had been collected, the tap on the apparatus was closed and the nitrogen was pumped off. The middle fraction of the condensate was then allowed to vaporise into a blackened 2 litre globe.

BROMINE

N₂

TO MAIN APPARATUS

ICE/SALT

A

B

TETRALIN

C
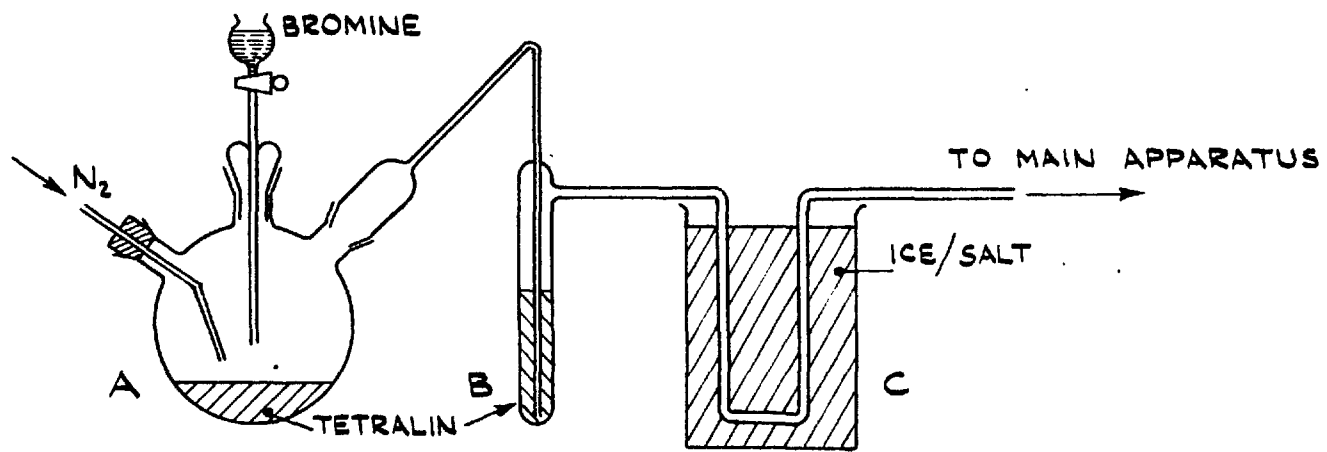
FIG. 4. APPARATUS FOR THE PRODUCTION OF HYDROGEN BROMIDE

3. Oxygen and nitrogen

These gases were obtained from cylinders, dried by passage over magnesium perchlorate, and then passed through traps at -183°C into storage globes. Oxygen was stored in a 5 litre globe while nitrogen was stored in a 2 litre globe.

C. PROCEDURE

1. Preparation of mixtures

The 'sharing factor' between the reaction vessel, A, and the pre-mixing vessel, B, was first accurately determined over a wide range of conditions of furnace temperature and gas pressure, so that if the pressure in B before sharing was known, that developed in A and B after sharing could be readily calculated. The experiments were also carried out with varying initial gas pressures in A. These calibration experiments were carried out using nitrogen.

A fuel-oxygen mixture was prepared by first admitting 100 mm. oxygen to A and then introducing fuel vapour into B to such a pressure that on opening the connecting tap, the pressure in A increased by 100 mm. The tap to the pre-mixing vessel was then closed and the change of pressure with time was observed on the manometer, readings being taken at frequent intervals. The pressure of fuel required in B was calculated from the results obtained in the 'sharing factor' experiments. Mixtures of 100 mm. oxygen/100 mm. fuel were used in nearly all the slow combustion experiments. When the spontaneous ignition of mixtures was studied mixtures of 50 mm. oxygen/50 mm. fuel were normally employed and the time delay prior to explosion was observed.

When mixtures containing high proportions of additive were used ($\geqslant$10 mm.), the additive was measured manometrically directly into the reaction vessel prior to the oxygen. Lower pressures of additive were obtained by preparing an oxygen-additive mixture in the pre-mixing vessel C of accurately known composition and then admitting such a pressure of this mixture into the reaction vessel that the desired pressure of additive was present. Pure oxygen was then added to give 100 mm. total pressure of oxygen. In this way gas mixtures containing additive concentrations as low as 0.5% by volume could be prepared with reasonable accuracy. Then the required pressure of fuel was admitted to the pre-mixer and the gases mixed by opening the connecting tap. The tap to the pre-mixer was then closed and the pressure-time curve was obtained.

This method of mixing is necessary when the effect of the pre-heating of additive-oxygen mixtures on the overall reaction is being investigated. However, in most of the work it was desirable to eliminate any effects due to this cause so that on most occasions all three reactants were pre-mixed prior to admission into the reaction vessel. As the 'sharing factor' between A and B had been determined under a wide range of conditions it was possible to calculate the pressure of gas in B required to give 100 mm. pressure in A and B on sharing at the furnace temperature employed. Thus mixtures were prepared by admitting the required pressures of additive, fuel, and oxygen successively into B. When low pressures of additive were required, a sharing technique was used. The sharing factors between the minimum volume in the line between the taps and the pre-mixer B and

also between this volume and the pre-mixers B and C were determined. These were approximately 1:10 and 1:50. Then by admitting a small known pressure of additive into the small volume and then sharing into either B or B and C, pressures of additive as low as 0.1 mm. could be introduced into B with reasonable accuracy.

2. Chemical analysis

a) The oxidation of methyl bromide

In the present work the oxidation of methyl bromide has been studied in some detail. The analytical methods employed were as follows:

(i) The estimation of hydrogen bromide and bromine

Mixtures of methyl bromide (100 mm.) and oxygen (50-400 mm.) were allowed to react at 330°C for 40 min. The products were then allowed to condense into two traps cooled in liquid nitrogen, for 5 min. The reaction vessel was then evacuated by the oil pump through the traps for 5 min. All traps were then closed and the liquid nitrogen Dewars removed, allowing the traps to warm up slowly. 50 ml. ethanol were then carefully added to each trap and the contents and washings from them were poured into two 100 ml. standard flasks. Both solutions were made up to 100 ml. with distilled water. 50 ml. of the solution from the first trap were pipetted into a conical flask, 2 ml. 10% potassium iodide solution were added, and the iodine liberated in the reaction:

$$2KI + Br_2 \longrightarrow 2KBr + I_2$$

was titrated with 0.02N sodium thiosulphate solution.

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$
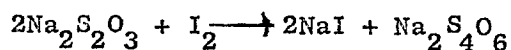
The amount of bromine present was then calculated from the relationship:

$$2Na_2S_2O_3 \equiv I_2 \equiv Br_2$$
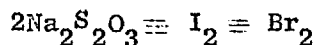
The same solution was then titrated with 0.02N sodium hydroxide solution:

$$NaOH + HBr \longrightarrow NaBr + H_2O$$
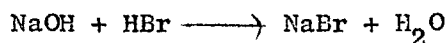
and the amount of hydrogen bromide present calculated. This was confirmed as follows: (76)

The remaining 50 ml. of the original solution were transferred to a 250 ml. conical flask with a B24 ground-glass neck and 1 ml. of pure mercury was added. The flask was glass-stoppered and vigorously shaken for 10 min. The bromine present was removed by the mercury. The solution was then titrated with 0.02N sodium hydroxide solution using methyl red as indicator. The amount of hydrogen bromide present was then calculated. The two methods gave good agreement in all cases.

The contents of the second trap were treated in the same way as those of the first trap. The amounts of hydrogen bromide and bromine detected were always very small showing that virtually all the products were trapped out in the first trap.

The above procedure was repeated with mixtures containing methyl bromide (30 mm.), oxygen (30-500 mm.) reacting for 1 hr. at 330°C. As less product was obtained, 0.006N sodium hydroxide solution and 0.005N sodium thiosulphate solution were used in the titrations.

(ii) <u>The estimation of total bromine in methyl bromide</u>

The total combined bromine present in a given pressure of methyl bromide was estimated as follows:

Methyl bromide (100 mm.) and nitrogen (100 mm.) were

introduced into the reaction vessel and left for 5 min. The methyl bromide was then trapped out and dissolved in ethanol using the standard procedure described in the previous section. The contents of the traps were then poured into 250 ml. conical flasks. 10 ml. 2% sodium hydroxide solution were then added to each flask and these were well shaken before being heated at 60°C for $1\frac{1}{2}$ hr. Under these conditions the methyl bromide is completely hydrolysed.

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$
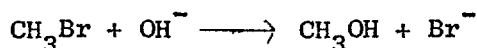
The solutions were then cooled and carefully neutralised with 2N nitric acid before being titrated with 0.05N silver nitrate solution:

$$Ag^+ + Br^- \longrightarrow AgBr$$
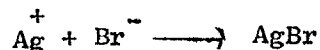
The amount of bromine produced was then calculated.

(iii) <u>The estimation of total bromine present in the products and unchanged reactants</u>

Experiments have been carried out to estimate the total bromine present in the products of a run. The bromine was present as bromine, hydrogen bromide, unchanged methyl bromide, and possibly various other organic bromides. The procedure employed was as follows:

Mixtures of methyl bromide (100 mm.), oxygen (10-400 mm.) were allowed to react for 40 min. The products were then trapped out and dissolved in ethanol. The contents of the first trap were poured into a 250 ml. conical flask containing a little granulated zinc and 2 ml. 2N nitric acid were added. The mixture was gently swirled for 10 min. The solution went colourless showing that the bromine present had been reduced to bromide. This was then decanted into another 250 ml. conical flask. The zinc was washed with distilled water and

the washings were added to the second flask. 20 ml. of 10% sodium hydroxide solution were then added and the solution was heated at 60°C for $1\frac{1}{2}$ hr., thereby hydrolysing methyl bromide and any other fairly readily hydrolysable organic bromide present. The solution was cooled and made acid with 5N nitric acid. 25 ml. 0.05N silver nitrate solution were then added and the solution well-shaken. Silver bromide was precipitated. The excess silver nitrate was titrated with 0.05N ammonium thiocyanate solution using a few drops of 40% ferric ammonium sulphate as indicator.

$$NH_4CNS + AgNO_3 \longrightarrow \downarrow AgCNS + NH_4NO_3$$
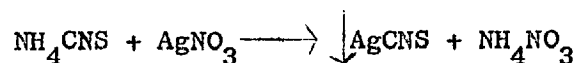
The volume of 0.05N silver nitrate solution required to precipitate the bromide could thus be calculated giving, in turn, the total amount of bromine present in the first trap. This procedure was repeated on the contents of the second trap but only very small amounts of bromide were detected showing that virtually all the products were contained in the first trap.

b) Analysis in the system acetaldehyde-oxygen-hydrogen bromide

(i) The estimation of peroxides

The method employed was that of Cullis and Newitt (95). Mixtures of acetaldehyde (100 mm.), oxygen (100 mm.) were allowed to react at 122°C for various times of from 5 min. to 1 hr. The products were then trapped out in liquid nitrogen. 50 ml. water were carefully added to each trap which were then removed, shaken up, and the contents were poured into 250 ml. conical flasks. A piece of solid carbon dioxide was added to the first flask in order to displace the air and then 1 ml. 2N sulphuric acid and 5 ml. 10% potassium iodide solution

were added. The solution was shaken up and the iodine liberated in the reaction:

$$ROOH + 2HI \longrightarrow ROH + H_2O + I_2$$
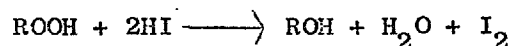
was titrated at 0°C with 0.01N sodium thiosulphate solution. The peroxide determined under these conditions is almost entirely peracetic acid, CH_3CO_3H.

This procedure was repeated on the contents of the second trap but no significant amounts of peroxide were detected.

The procedure was then repeated on mixtures of acetaldehyde (100 mm.), oxygen (100 mm.), hydrogen bromide (5 mm.), reacting for 5 min. – 1 hr. at 122°C. On these occasions, the hydrogen bromide was pre-mixed with oxygen prior to admission into the reaction vessel.

(ii) The estimation of residual acetaldehyde

Attempts were made to estimate the residual acetaldehyde present in the products of an oxidation experiment. First the silver oxide column method of Bailey and Knox was employed (96). However this involved trapping out the acetaldehyde in liquid nitrogen and as appreciable polymerisation occurred on freezing only a small proportion of the acetaldehyde originally present was actually estimated.

Gas chromatography was then employed in order to determine the acetaldehyde. A known fraction of the reaction products was shared into a U tube (cf. Section on gas liquid chromatography), the sample was swept on to the column under carefully controlled conditions, and the acetaldehyde peak area obtained was measured. Unfortunately the errors caused by adsorption of the aldehyde by the tap grease and other factors were large and thus no accurate quantitative data could be obtained.

3. Gas-liquid chromatography

a) General outline

On some occasions product analysis was carried out using gas-liquid chromatography. A Shandon apparatus was employed. A block diagram of the apparatus is shown in Fig. 5.

Hydrogen, containing 25% nitrogen, was used as the carrier gas. This mixture was introduced from a cylinder through a reducing valve and rotameter on to the column. The gas passed through the column and flowed out of the jet in the combustion chamber. Both the column and the combustion chamber were immersed in a vapour jacket. Air from a cylinder passed through a reducing valve and rotameter into the base of the combustion chamber where it diffused through porcelain beads and mixed with the hydrogen from the jet. A thermocouple (gold-palladium/platinum-iridium) was situated a few mm. above the jet. It was supported from two copper wires sheathed in glass insulators. These insulators passed through the thermocouple housing which was a hollow chromium-plated brass cylinder containing also a central chimney filled with porcelain beads and an arrangement for adjusting the height of the thermocouple relative to the jet. It fitted precisely into the combustion chamber which itself was bolted to the top of the vapour jacket. The gases were ignited by passing a high-voltage electrical discharge from the thermocouple to an earthed electrode 1 mm. away. The thermocouple was connected to a potentiometer arrangement by which the normal thermocouple output was balanced and any additional voltage was fed to another potentiometer capable of reducing this voltage by a factor of 2,5,10, or 20 as required. The final output was fed into

KEY TO FIG. 5

A   Air cylinder

B   Hydrogen/Nitrogen cylinder

C_1, C_2 Rotameters

D   Sampling U-tube

E   Column

F   Vapour jacket

G   Combustion chamber

H   Thermocouple

I   Water condenser

J   Backing off circuit

K   Sensitivity control

L   Recorder
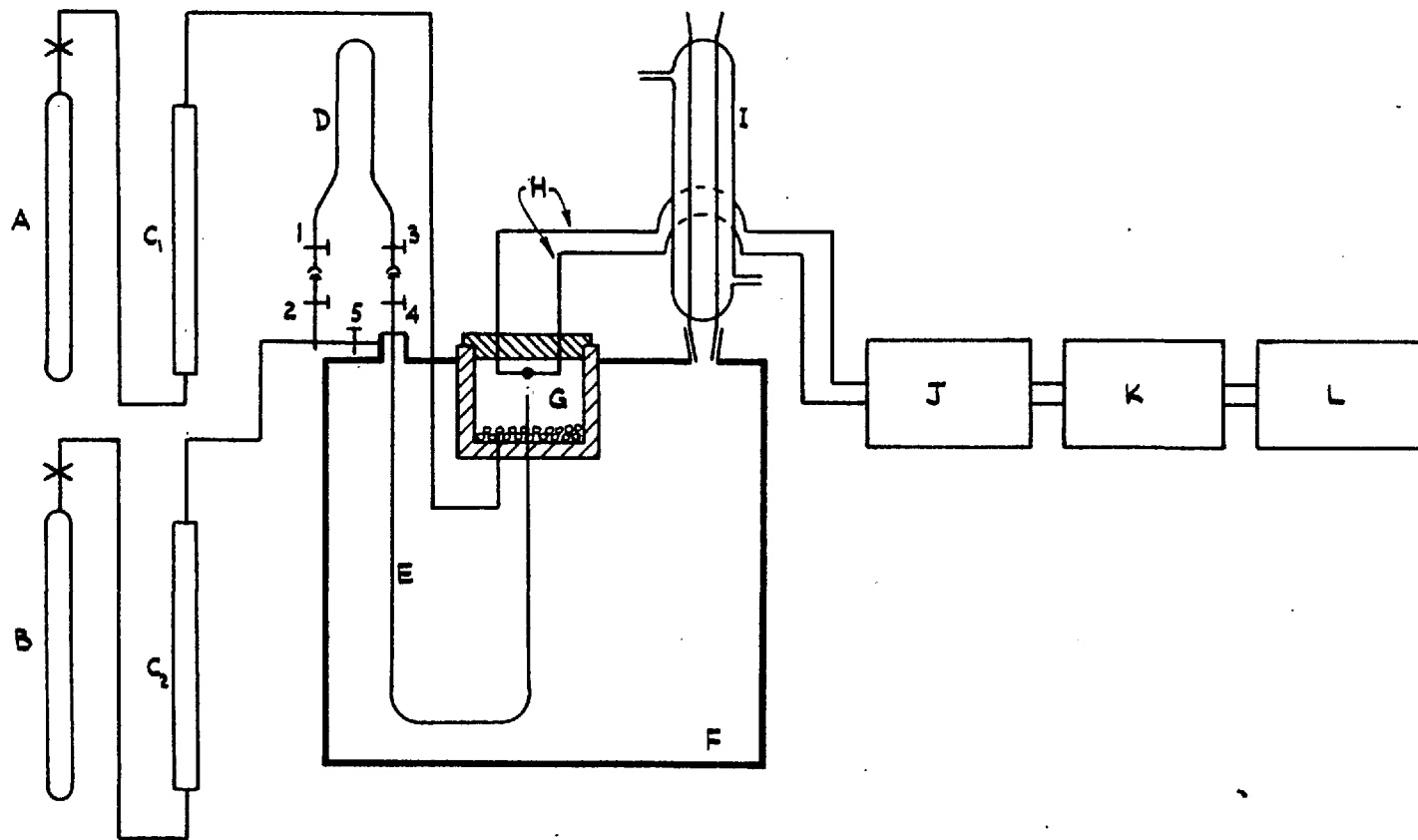
FIG. 5. BLOCK DIAGRAM OF THE VAPOUR PHASE CHROMATOGRAPHY UNIT.

a Sunvic High Speed Potentiometric Recorder (full scale deflection = 1.0 mV).

b) The sample injection system

The sample injection system consisted of a capillary glass U tube (volume ca. 1 ml.), and the arrangement of taps shown in the diagram. This set-up enabled the gaseous contents of the U tube (which could be electrically heated to ca. 100°C) to be swept rapidly on to the column.

c) The column

In the present work the column used consisted of 10% polyethylene glycol (mol. wt. 400) on embacel (40-100 mesh). Polyethylene glycol was a very suitable stationary phase for this work as it gives a good separation of a wide variety of oxygenated products while embacel was a very satisfactory supporting material since it shows no evidence of catalytic activity.

A column was prepared as follows:
25 g. embacel were impregnated with 2.5 g. polyethylene glycol dissolved in 50 ml. acetone. The mixture was well stirred and the resulting slurry was thoroughly dried by warming on a hot-plate with continuous gently stirring. The dry material was then packed into a heat-worked 12' x $\frac{1}{4}$" copper column by continuous shaking and tapping.

d) Procedure

First the air and hydrogen/nitrogen supplies were turned on and adjusted to give suitable flow rates. The level of the liquid in the vapour jacket reservoir was checked. Acetone (bp. 56°C) was normally used. The heater was then turned on and also the cold water

which flowed through the condenser above the vapour jacket. The recorder and potentiometers were switched on and the flame was ignited. The e.m.f. from the thermocouple was fed to the recorder under conditions of minimum sensitivity and 'backed-off' so that the recorder pen traversed a convenient base-line on the chart. The sensitivity control was then adjusted to the required value. When conditions had been stabilised, a smooth steady base-line was obtained on the chart. A sample of reaction products was then shared into a U tube clipped to the line. Taps 1 and 3 were closed and the U tube removed from the line and clipped on to the injection system. Taps 2,4,1,3 were then opened swiftly in that order and tap 5 was closed. The gas flow was thus diverted through the U tube sweeping the sample therein rapidly on to the column.

The various components of the mixture were normally separated on the column and thus they emerged one by one into the hydrogen flame where they burnt, producing peaks on the recorder trace. It is found that under fixed conditions a given compound always emerges from the column after a given time while the peak area is proportional to the amount of the component present. It is therefore possible to obtain a complete qualitative and quantitative analysis of the sample from the trace.

S E C T I O N 3

RESULTS

A. THE OXIDATION OF METHYL BROMIDE (at 330°C)

1. Pressure-time curves

Pressure-time curves for the reactions between various methyl bromide-oxygen mixtures at 330°C are shown in Figs. 6, 6A. Using a fixed pressure of methyl bromide, both the maximum rate of pressure change and the total pressure change increased steadily with increasing oxygen pressure.

The variation of maximum rate with oxygen pressure at fixed methyl bromide pressure is shown in Fig. 7. If it is assumed that the rate expression is of the form:

$$R = k \left[CH_3Br \right]^a \left[O_2 \right]^b$$

then, as the maximum rate observed increased roughly linearly with oxygen pressure, b = 1. From the ratio of the slopes of the two lines it is found that a $\doteqdot$ 2.

2. Estimation of hydrogen bromide and bromine

The amounts of hydrogen bromide and bromine produced by various methyl bromide-oxygen mixtures reacting for 40 mins. at 330°C were estimated in the manner described previously. The results are shown in Figs. 8, 9. They are expressed in terms of the number of bromine atoms produced, found as either bromine or hydrogen bromide, per molecule of methyl bromide in the initial mixture. Under the experimental conditions employed,

100 mm. methyl bromide $\rightleftharpoons$ 75 x 10^{-5} atoms bromine

In both cases, the amount of hydrogen bromide produced rose sharply with increasing oxygen pressure up to a maximum of 0.45, obtained with 200 mm. oxygen, 100 mm. methyl bromide and with 100 mm. oxygen, 30 mm.

methyl bromide.   The yield then decreased slightly with increasing

oxygen pressure in both cases.   The amount of bromine produced was very

small at low oxygen pressures but increased slowly as the oxygen

pressure was increased, reaching ca. 0.3 in the presence of 400 mm.

oxygen in both cases.   The total amount of bromine accounted for as

bromine and hydrogen bromide increased steadily with increasing oxygen

pressure.   However, even in the presence of 400 mm. oxygen, only ca.

70% of the bromine initially present in the methyl bromide was converted

into bromine and hydrogen bromide.   The remaining 30% was presumably

present as unchanged methyl bromide.

3.   Estimation of the bromine present in methyl bromide

The bromine present in a given pressure of methyl bromide

occupying the reaction vessel was estimated as described previously.

100 mm. methyl bromide yielded 71×10^{-5} atoms bromine on hydrolysis

as against a theoretical value of 75×10^{-5} atoms.   In view of the

probable errors, both in the experimental estimation and the

theoretical calculation, this measure of agreement was considered

satisfactory.

4.   Estimation of total bromine

The results obtained in the estimation of total bromine as

described previously are shown in the top curve in Fig. 10, where the

total number of atoms of bromine estimated per molecule of methyl

bromide initially present is plotted against oxygen pressure in the

initial mixture, the initial methyl bromide pressure being 100 mm.

For oxygen pressures greater than 300 mm. virtually all the bromine

was estimated by this method and thus it was present as bromine,

hydrogen bromide, and readily hydrolysable organic bromide, presumably unchanged methyl bromide. However, in mixtures containing less oxygen, some bromine-containing compound was produced which was not estimated by the analytical method employed. The yield of this compound was a maximum at a methyl bromide-oxygen ratio of 2:1 when one third of the bromine was not accounted for. The lower curve is the number of bromine atoms estimated as bromine and hydrogen bromide. The difference between these two curves gives the number of bromine atoms present in the products as hydrolysable organic bromide, presumably largely methyl bromide. A graph of the amount of methyl bromide remaining against initial oxygen pressure is given in Fig. 11 (see Discussion for full explanation). This shows clearly that about one-third of the methyl bromide remains unchanged in the presence of even a large excess of oxygen.
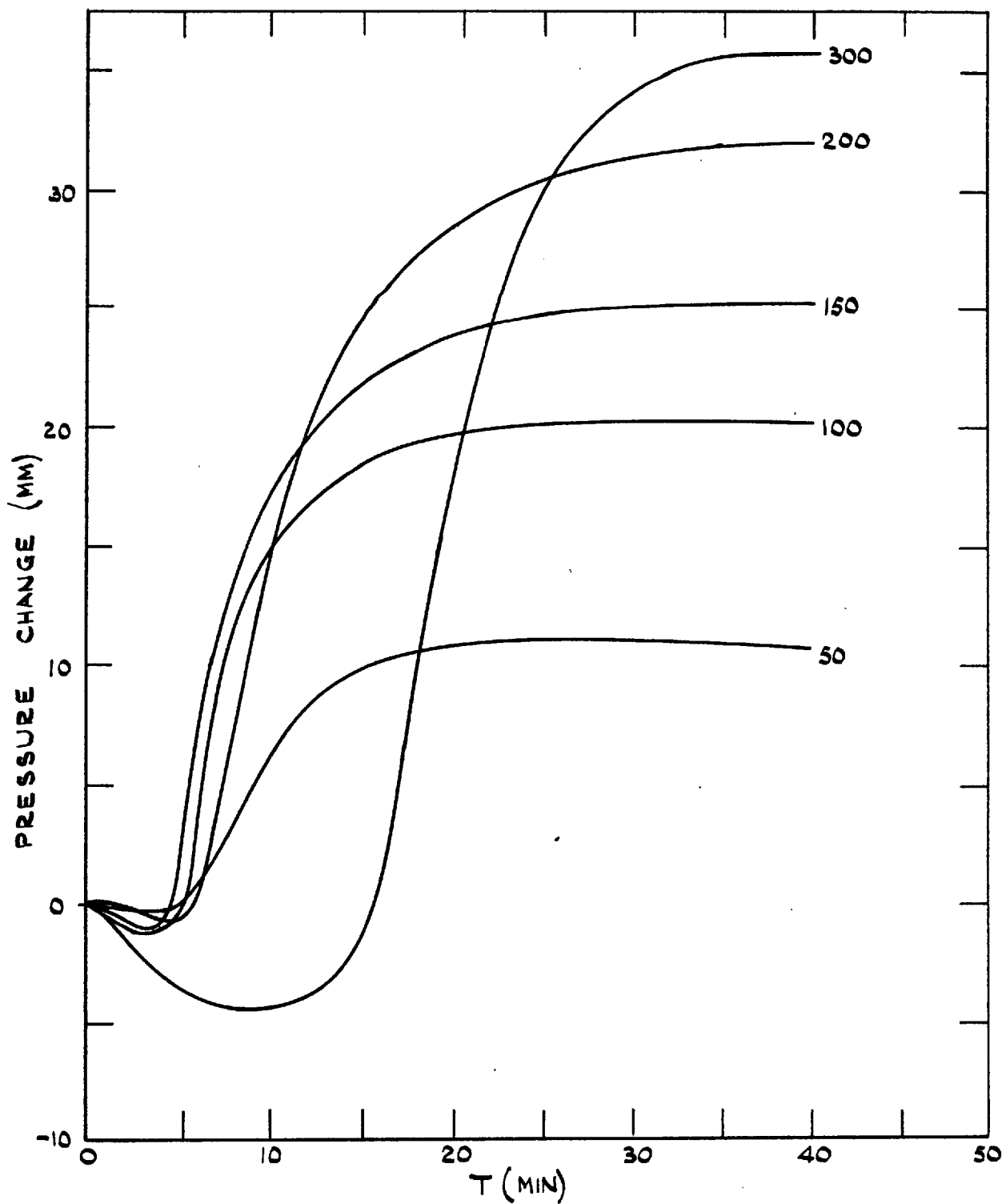
FIG.6. THE OXIDATION OF METHYL BROMIDE AT 330°C.
CH₃Br = 100 MM.   O₂ PRESSURE AS SHOWN (MM)
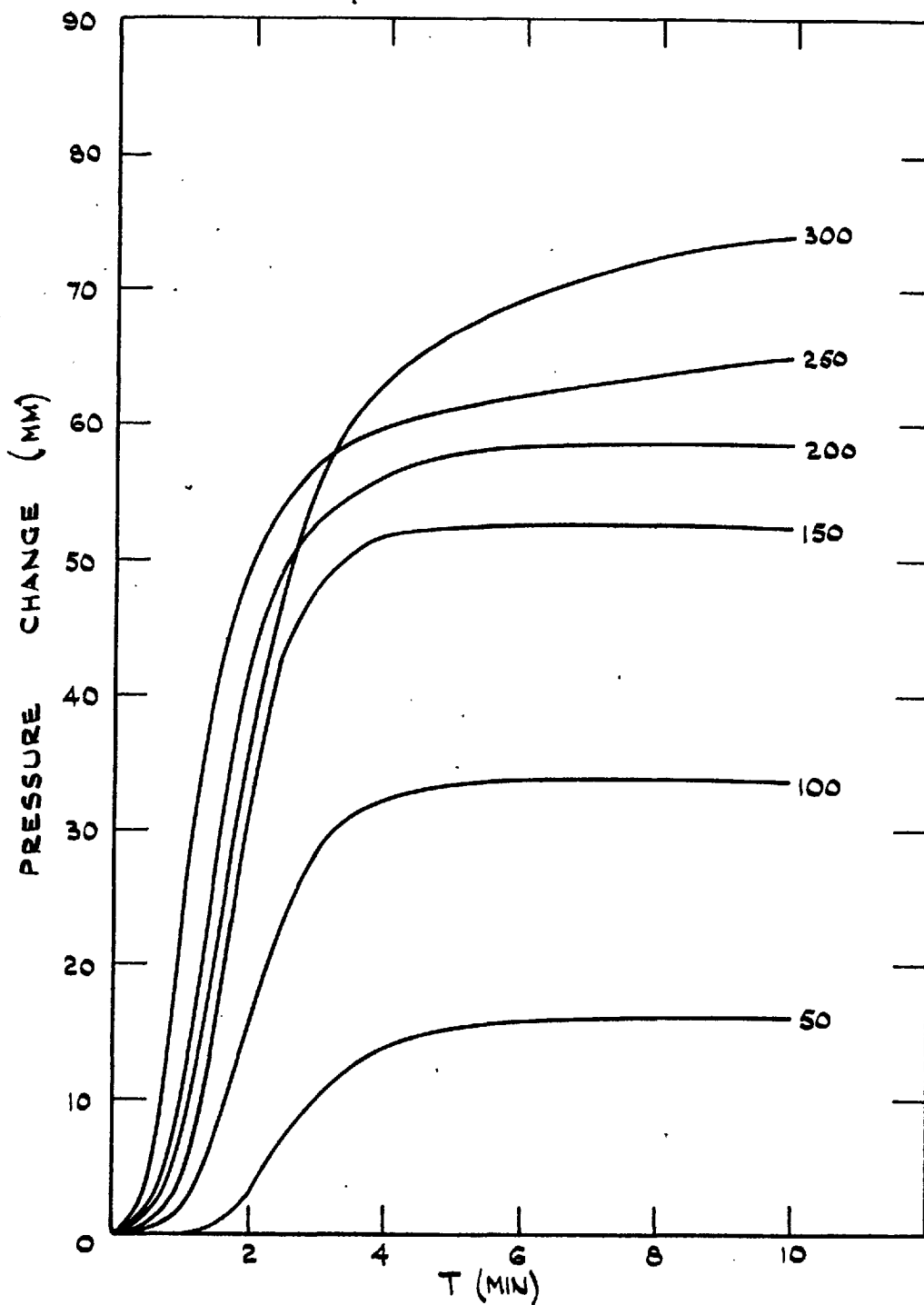
FIG. 6ᴬ THE OXIDATION OF METHYL BROMIDE AT 330°C.
$CH_3Br = 250$ MM. O_2 PRESSURE AS SHOWN (MM).
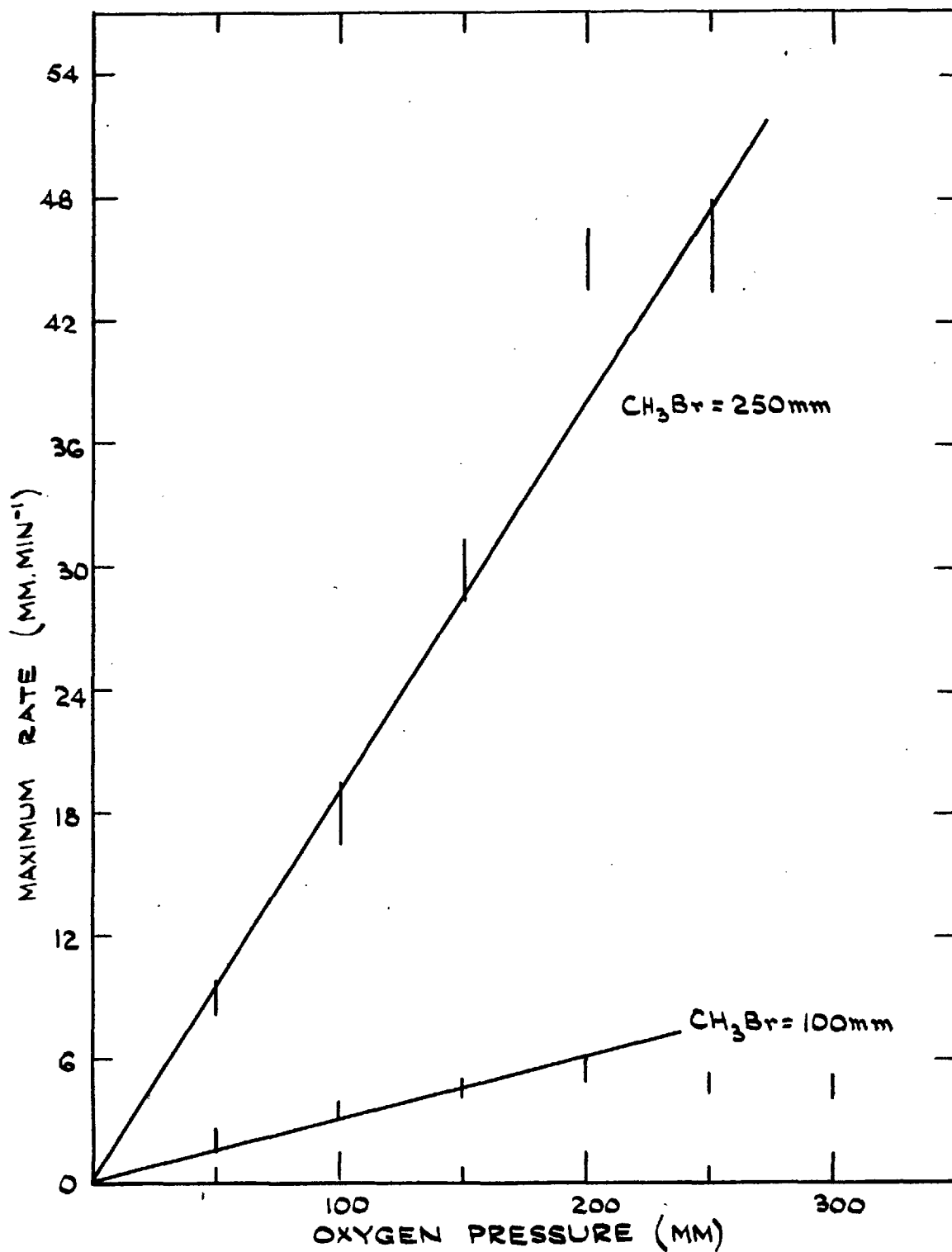
FIG. 7 THE OXIDATION OF METHYL BROMIDE AT 330°C.
THE INFLUENCE OF REACTANT PRESSURES ON
REACTION RATE.
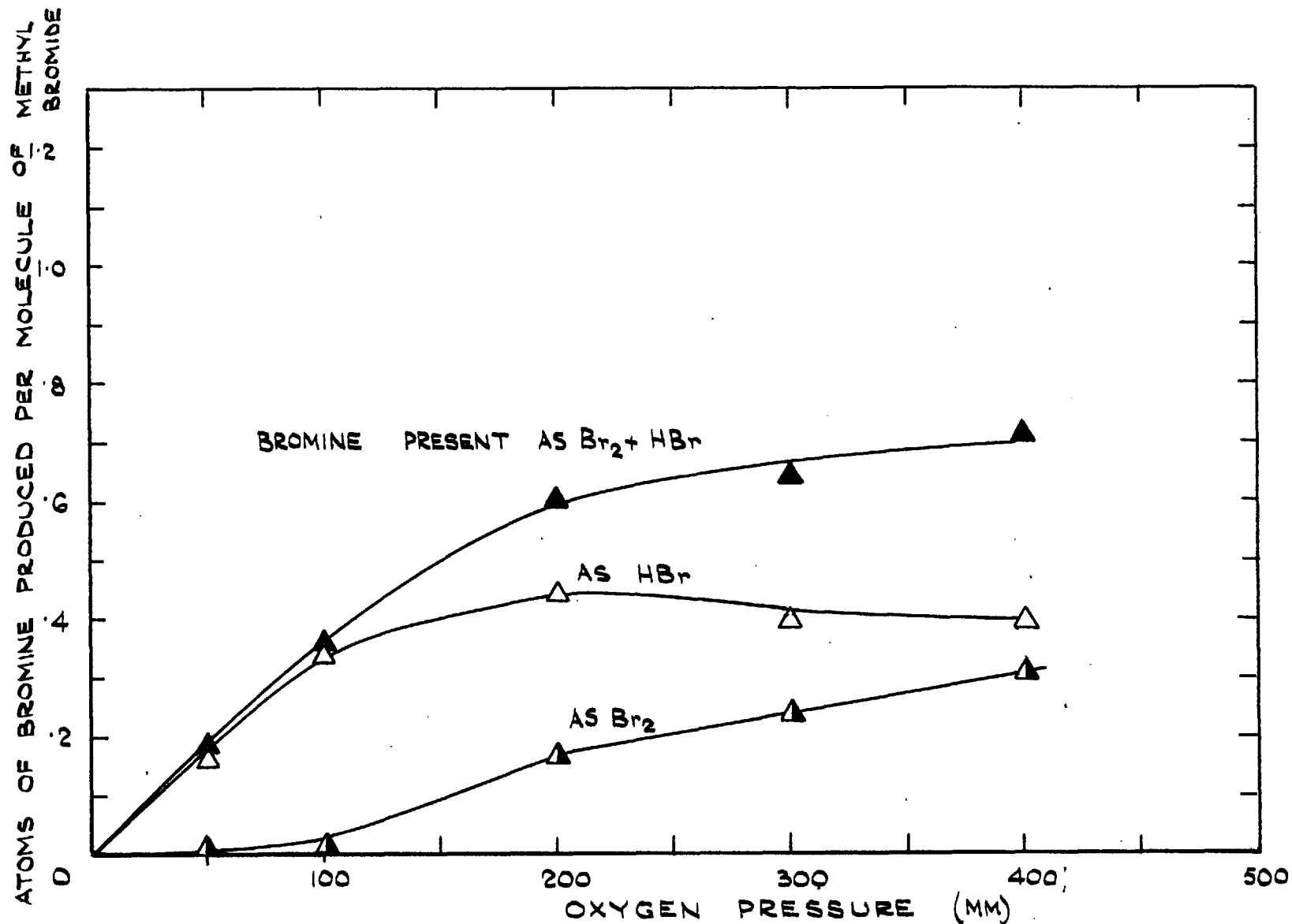
FIG. 8. THE OXIDATION OF METHYL BROMIDE AT 330°C. THE PRODUCTION OF HYDROGEN BROMIDE & BROMINE. $CH_3Br = 100$ MM.
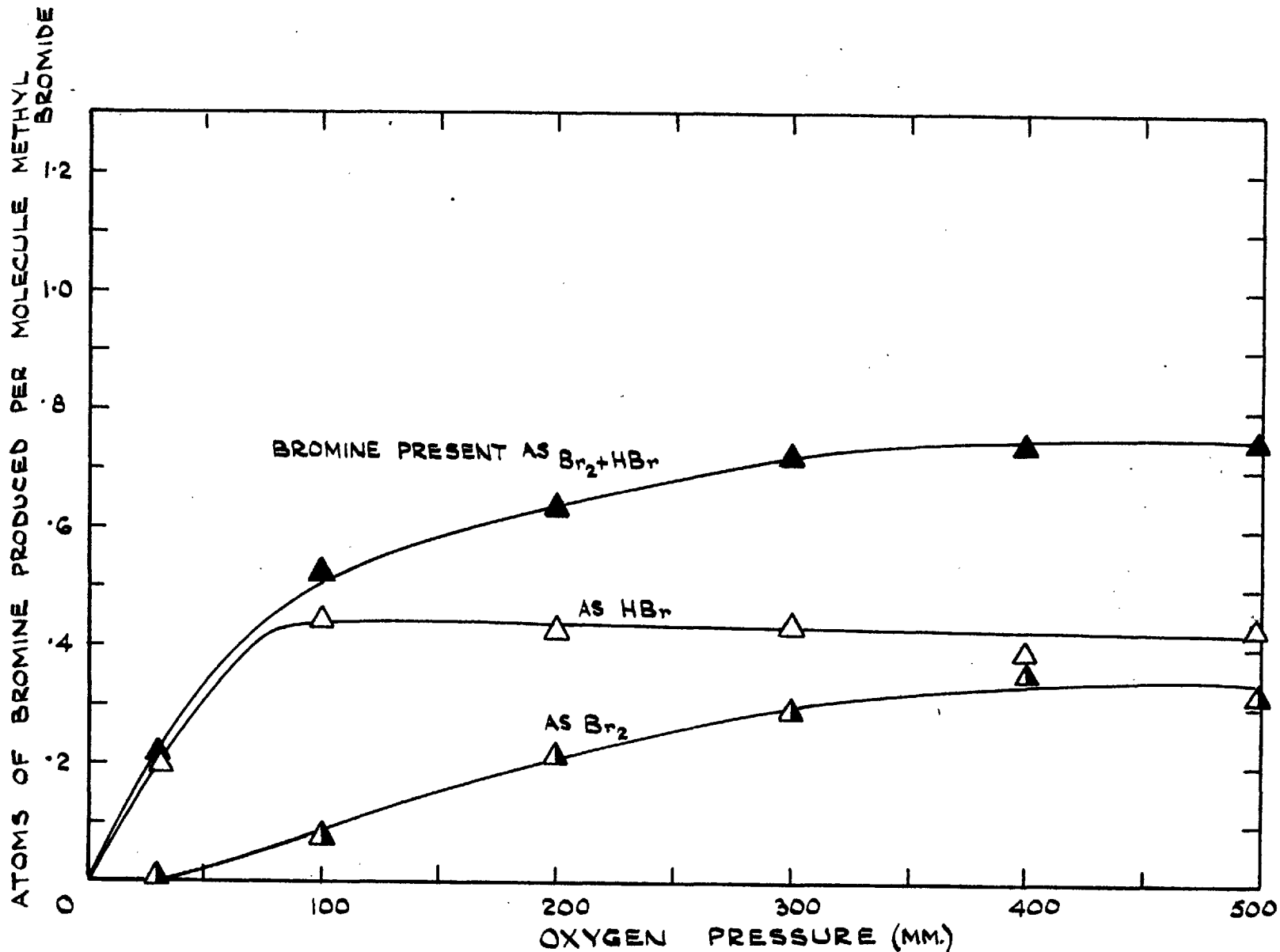
FIG.9. THE OXIDATION OF METHYL BROMIDE AT 330°C. THE PRODUCTION OF HYDROGEN BROMIDE & BROMINE. $CH_3Br = 30$ MM.
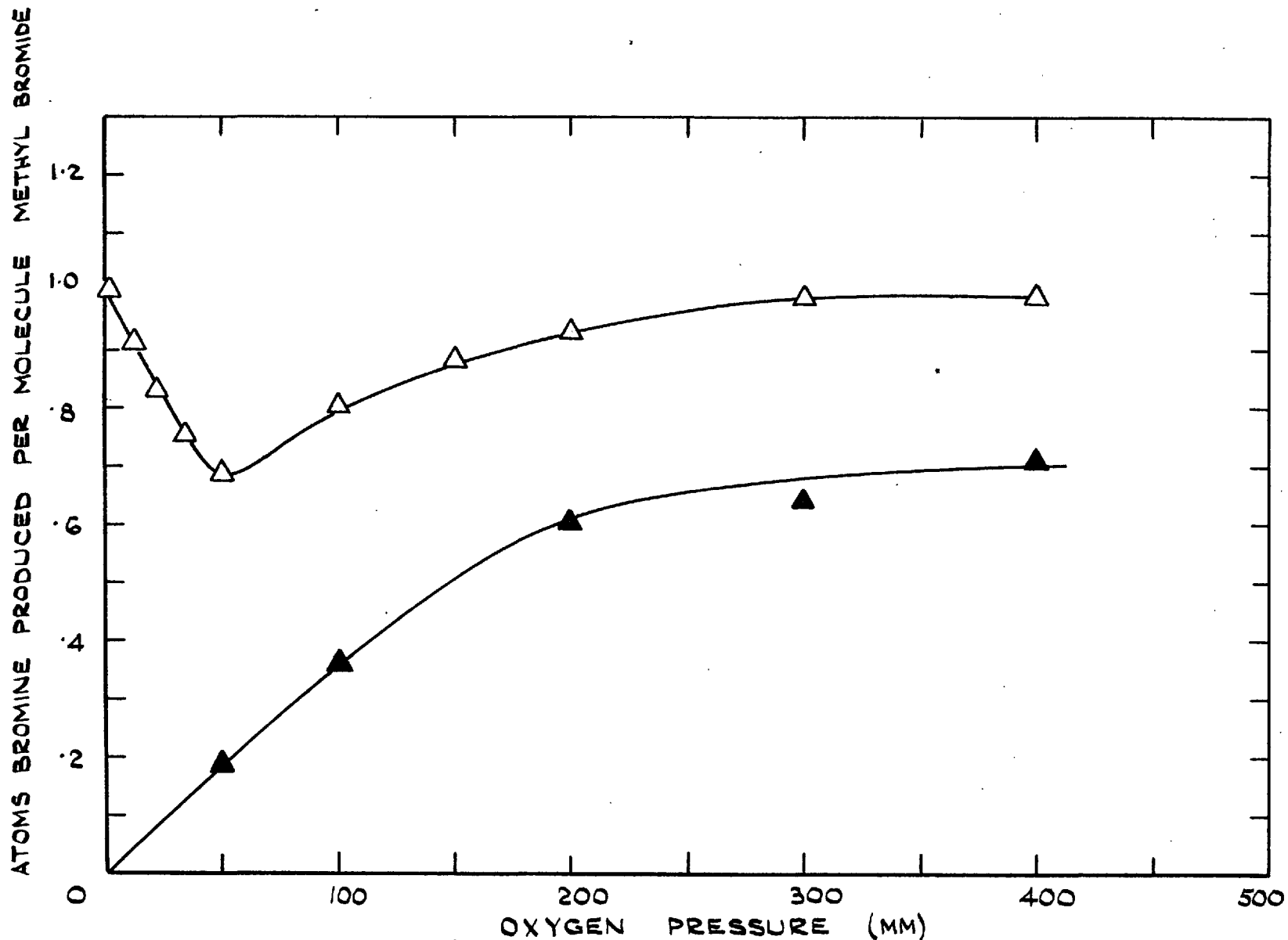
FIG.10. THE OXIDATION OF METHYL BROMIDE AT 330°C. THE PRODUCTION OF HYDROGEN BROMIDE, BROMINE, & ORGANIC BROMIDE $CH_3Br = 100MM$.
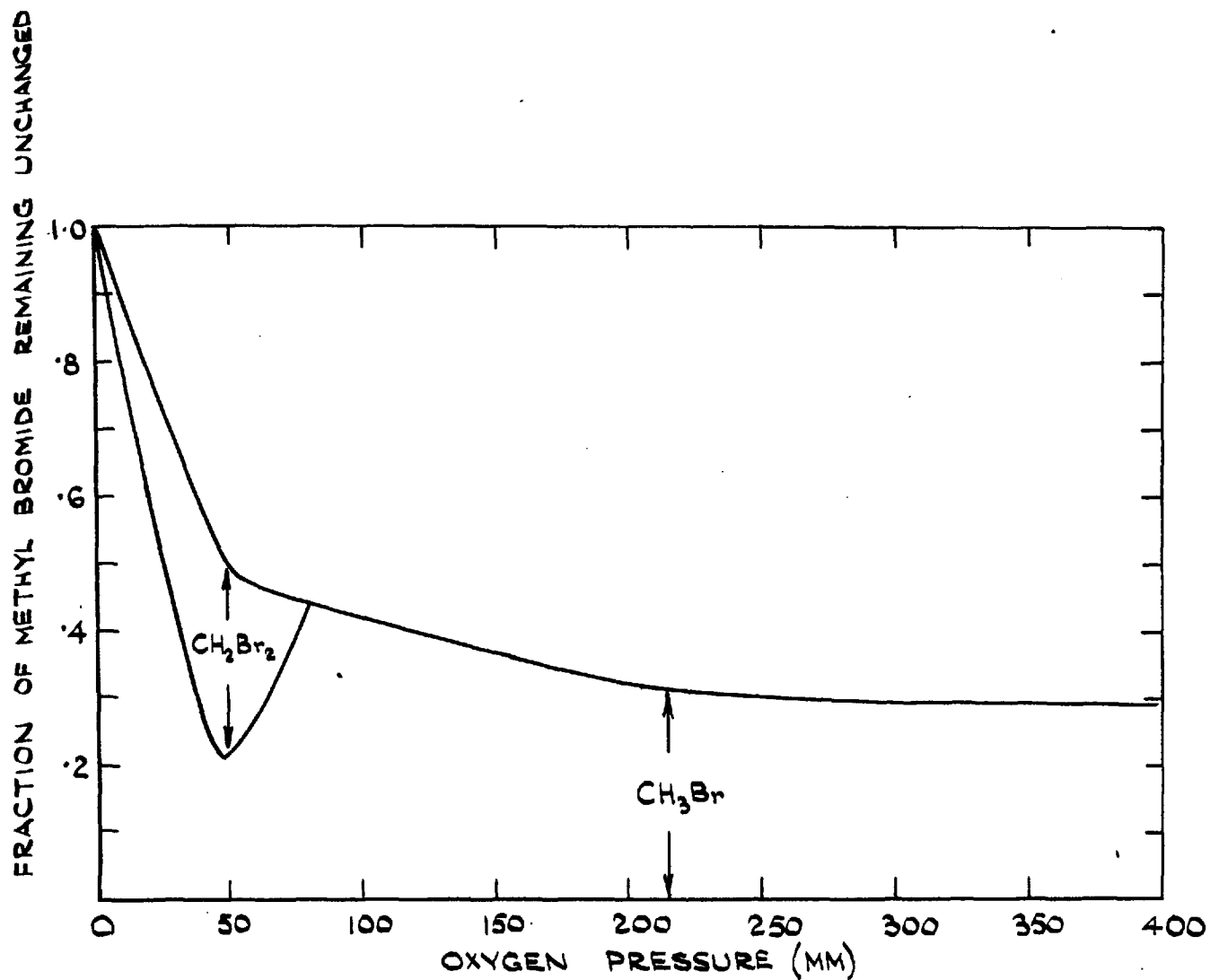
FIG.II. THE OXIDATION OF METHYL BROMIDE AT 330°C. DEPENDENCE OF THE AMOUNT OF METHYL BROMIDE REMAINING UNCHANGED ON OXYGEN CONCENTRATION. INITIAL CH_3Br = 100MM

B. THE OXIDATION OF ACETALDEHYDE (in the range 124°-225°)

1. The influence of halomethanes

a) Methyl bromide

The influence of methyl bromide on the slow combustion of acetaldehyde at 124°C, 155°C, and 188°C has been investigated. Mixtures were prepared by the first procedure described using 100 mm. acetaldehyde, 100 mm. oxygen, 2-20 mm. methyl bromide. A pressure-time curve was obtained on each occasion. The results at 155°C are shown in Fig. 12. The additive exerted a very slight accelerating influence on the reaction, the extent of the acceleration increasing as the additive concentration was increased. This slight accelerating influence is also seen in Fig. 18 where the time taken for a change in pressure of 30 mm. to occur in the normal oxidation minus the time taken for this change to occur in the presence of additive is plotted against the additive pressure for the various halomethanes used. Positive values of ΔT thus mean that the reaction is being promoted. ΔT was only very slightly affected by the pressure of methyl bromide present, 20 mm. producing a value of only one minute. The small accelerating influence of methyl bromide is also shown in Fig. 19 where the maximum rate of pressure change in the presence of additive minus the normal maximum rate is plotted against pressure of additive. In the presence of methyl bromide, the maximum rate increased approximately linearly with additive pressure. The effect was very small, however, 19 mm. methyl bromide increasing the maximum rate by only 1.5 mm. min^{-1}. The presence of methyl bromide had a similar very small promoting influence on the oxidation at 124°C and 188°C.

The effect of methyl bromide on the explosive combustion of acetaldehyde at 225°C was then investigated. As the results were not very reproducible, a large number of experiments were first carried out with mixtures of 50 mm. acetaldehyde, 50 mm. oxygen, and the time elapsing between the addition of acetaldehyde to the oxygen and the occurrence of explosion was observed. The increase in pressure resulting from the explosion was also noted. From the results obtained, the mean value (μ) and the standard deviation (σ) for both of these quantities were then calculated. This procedure gave for explosion time: $\mu = 8.5$ sec., $\sigma = 1.2$ sec., and for increase in pressure: $\mu = 68$ mm., $\sigma = 2$ mm.

The experiments were then repeated, methyl bromide at pressures of 1-50 mm. being pre-mixed with the oxygen. The results were again rather variable. As there was no obvious trend of explosion time or pressure increase with methyl bromide pressure it was considered valid to take the mean values of these quantities as representative of the separate results. Thus, in the presence of methyl bromide,

for explosion time: $\mu = 7.8$ sec., $\sigma = 0.8$ sec.

for increase in pressure: $\mu = 76$ mm., $\sigma = 4$ mm.

Methyl bromide may therefore have had a slight accelerating effect on the reaction but because the results vary so widely no definite conclusions can be drawn. It does seem probable, however, that the presence of methyl bromide increased the pressure change occurring during the reaction. It was presumably decomposed to some extent during the passage of the flame.

The effect of pre-heating the methyl bromide-oxygen mixtures prior to introducing the acetaldehyde was then studied. 20 mm. methyl bromide was pre-mixed with 50 mm. oxygen and heated at 225°C for times ranging from 1-14 hrs. 50 mm. acetaldehyde was then added and the explosion time and pressure increase on explosion were observed. Again the results were rather variable but there was no obvious trend with increased time of pre-heating and thus the mean values were considered representative of this series of results as before. For explosion time: $\mu = 8.0$ sec., $\sigma = 0.4$ sec; for increase in pressure: $\mu = 76$ mm., $\sigma = 5$ mm; These values are almost identical with those obtained without pre-heating and thus it appears that pre-heating of the additive-oxygen mixture had no effect on the results.

As relatively large amounts of additive were used in these experiments, some 'inert gas' influence would have been expected. Thus a parallel series of experiments were carried out using 5-50 mm. nitrogen in order to see if an inert gas did have any effect on the explosive reaction. The results were again rather variable with no apparent trend. On calculating the means as before, the results obtained were as follows: for explosion time: $\mu = 8.0$ sec., $\sigma = 1.2$ sec; and for pressure increase: $\mu = 69$ mm., $\sigma = 3$ mm. These results are very similar to those obtained with the normal oxidation reaction and thus even fairly high concentrations of nitrogen had no pronounced effect on the explosive oxidation of acetaldehyde under these conditions. The results of these experiments are summarised in Table 1.

TABLE 1

The Explosive Oxidation of Acetaldehyde at 225°C

The Influence of Methyl Bromide and Nitrogen

$CH_3CHO = 50$ mm., $O_2 = 50$ mm.

Additive	Explosion time (sec.)		Increase in pressure (mm.)	
	μ	σ	μ	σ
None	8.5	1.2	68	2
CH_3Br (1–50 mm.)	7.8	0.8	76	4
20 mm. CH_3Br With pre-heating	8.0	0.4	76	5
N_2 (5–50 mm.)	8.0	1.2	69	3

The explosive combustion of a stoichiometric mixture of 50 mm. acetaldehyde, 125 mm. oxygen at 225°C was then investigated. This mixture exploded with a bright flash after ca. 13 sec. Experiments were then performed with 10-50 mm. methyl bromide pre-mixed with the oxygen. The results obtained are shown in Fig. 13. The explosion time decreased steadily as the methyl bromide concentration was increased, a mixture containing 50 mm. methyl bromide exploding after 10 sec. Methyl bromide thus exerted a small but definite promoting influence on the oxidation under these conditions. The pressure increase observed on explosion increased sharply with increasing concentration of additive. This pressure increase was presumably caused by the extensive decomposition of the methyl bromide during the explosion.

b) Methylene dibromide c) Chlorobromomethane

d) Difluorodibromomethane

The influence of methylene dibromide, chlorobromomethane, and difluorodibromomethane on the oxidation of acetaldehyde at 155°C has been investigated. All three reactants were pre-mixed prior to admission into the reaction vessel. Mixtures of 100 mm. acetaldehyde 100 mm. oxygen, 2-50 mm. additive were used and the pressure-time curve was observed on each occasion. The results are shown in Figs. 14, 16, 17. With methylene dibromide, the influence of 5-25 mm. on the oxidation of mixtures of 100 mm. acetaldehyde, 250 mm. oxygen was also investigated. The results are shown in Fig. 15. In every case the additive exerted a slight promoting influence on the reaction, the maximum rate of pressure decrease increasing steadily although only slightly as the additive pressure was increased. This

is clearly shown also in Fig. 19 where the increase in maximum rate is plotted against additive pressure. With all four halomethane additives, the maximum rate observed increased roughly linearly with additive pressure. The observed order of effectiveness of the additives for increasing the maximum rate was:

$$CH_2Br_2 > CF_2Br_2, \ CH_3Br > CH_2BrCl$$
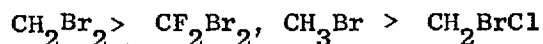
but the differences were only small.

The influence of the additives on the oxidation is also shown in Fig. 18. In all cases $\triangle T$ increased roughly linearly with additive pressure, the order of promoting effectiveness being:

$$CH_2Br_2 > CH_2BrCl > CH_3Br > CF_2Br_2$$
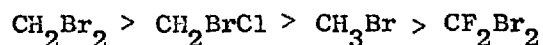
but the differences were again small. Thus all the additives exerted a small promoting influence on the reaction, the extent of the promotion increasing with increasing pressure of additive. However, in view of the small differences observed and the sensitivity of the results to small changes in temperature and surface conditions, it can only be concluded that all four additives had approximately the same small effect on the reaction.

Methylene dibromide had virtually the same effect on the oxidation of 100 mm. acetaldehyde, 250 mm. oxygen as it did on the oxidation of 100 mm. acetaldehyde, 100 mm. oxygen.
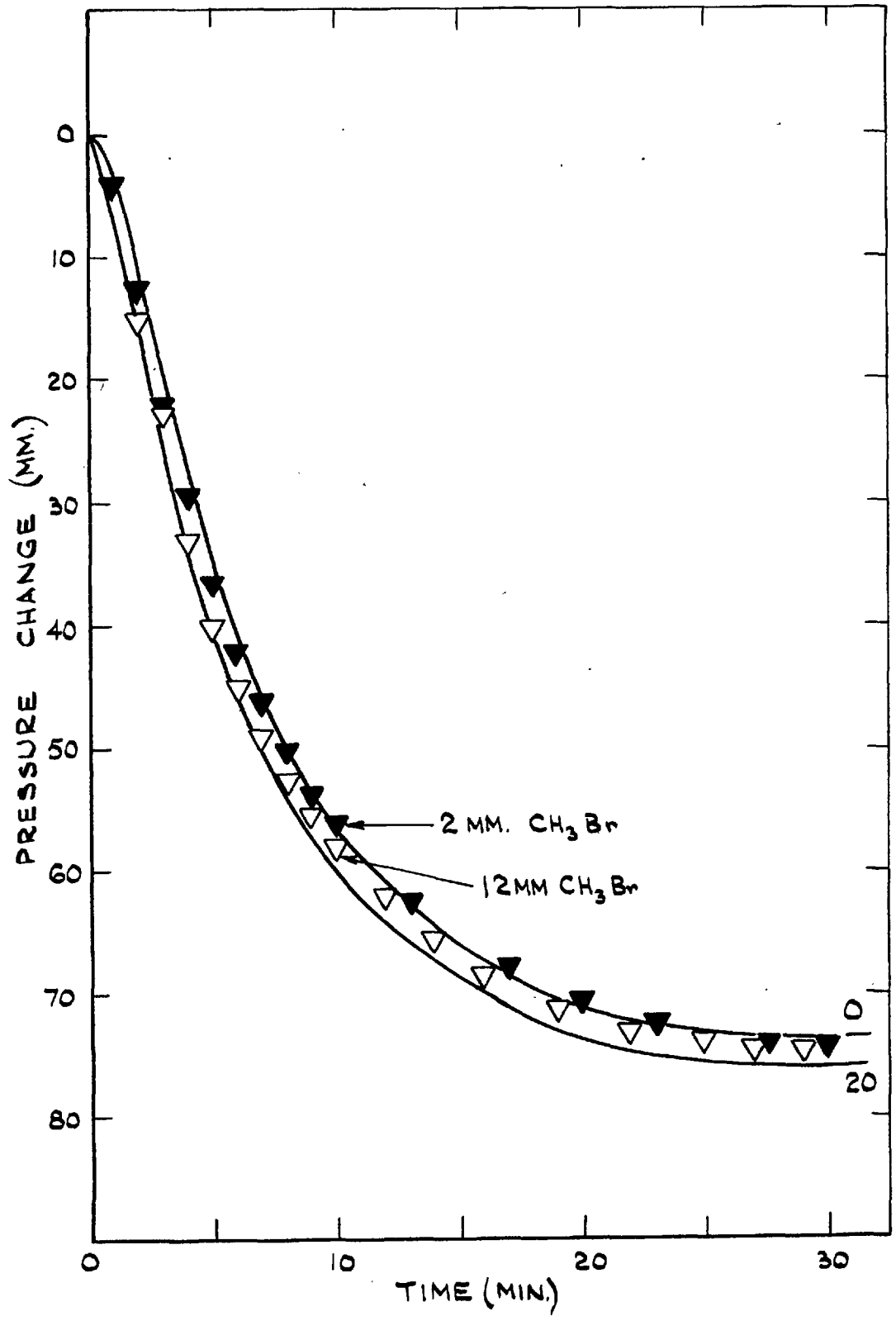
FIG. 12. THE OXIDATION OF ACETALDEHYDE IN THE
PRESENCE OF METHYL BROMIDE.
PRESSURE—TIME CURVES.
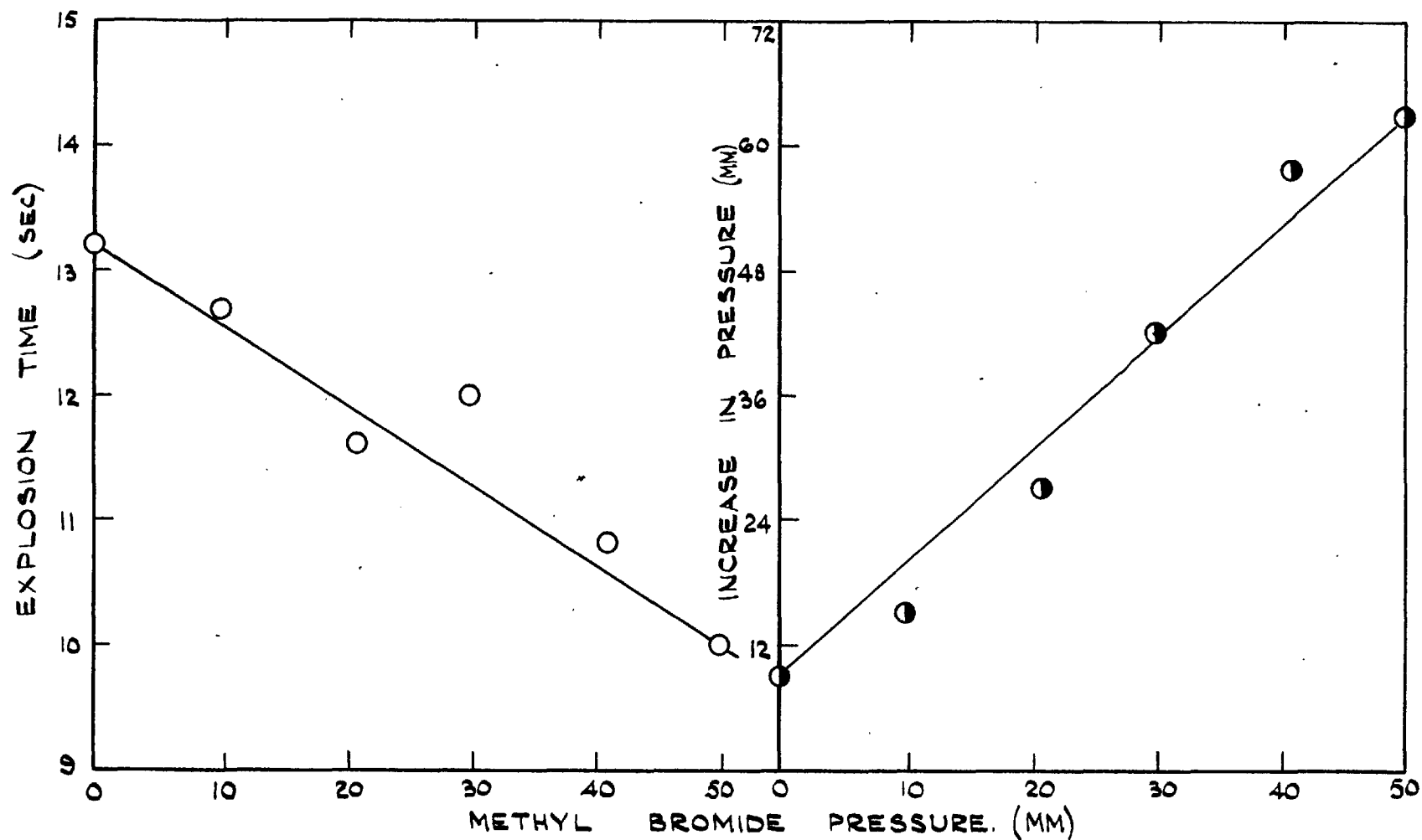T = 155°C. CH_3CHO = 100 MM. O_2 = 100 MM. CH_3Br AS SHOWN (MM)

FIG.13. THE OXIDATION OF ACETALDEHYDE IN THE PRESENCE OF METHYL BROMIDE THE DEPENDENCE OF EXPLOSION TIME AND PRESSURE INCREASE ON ADDITIVE PRESSURE. T= 225°C. CH₃CHO = 50 MM. O₂ = 125 MM.
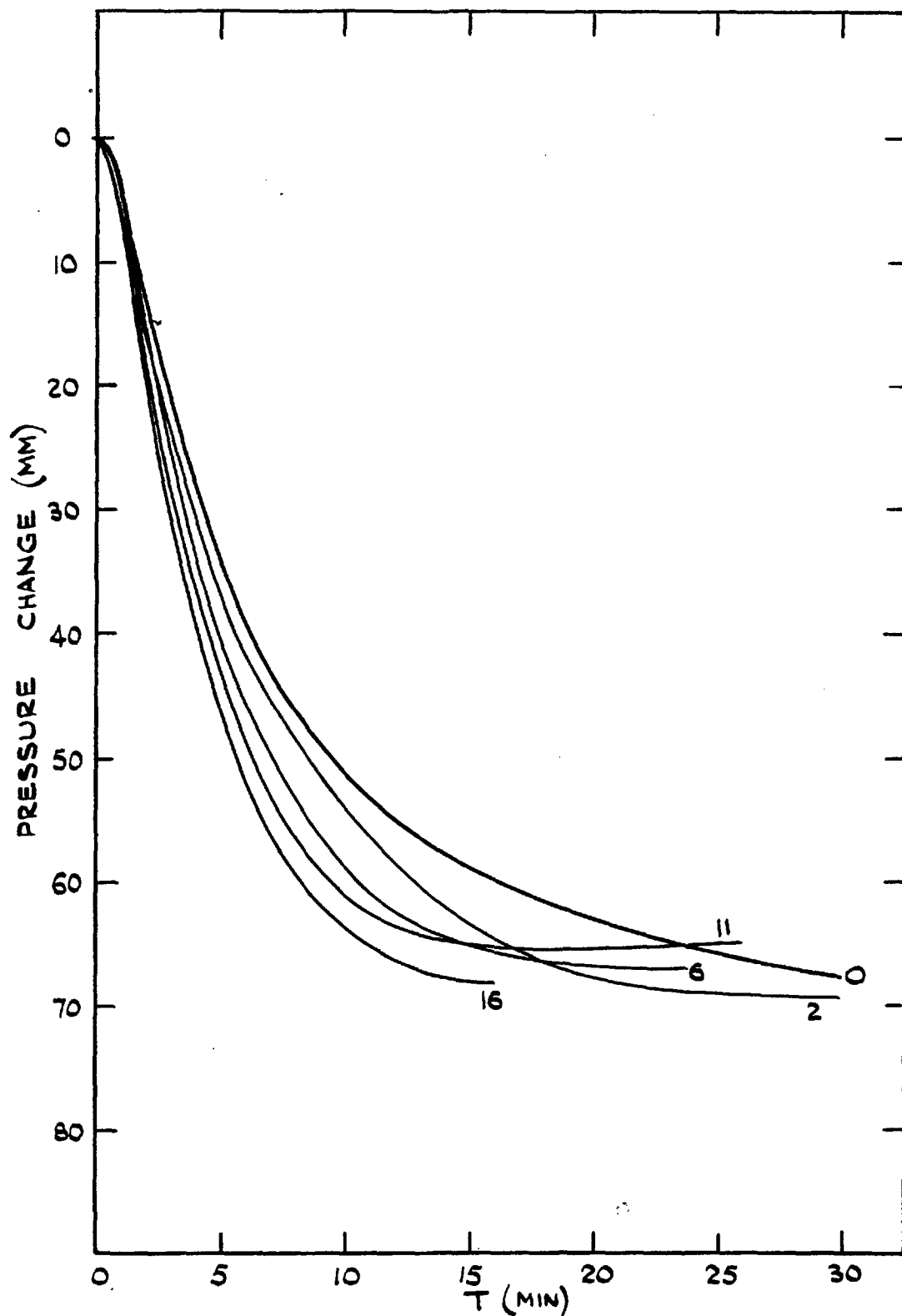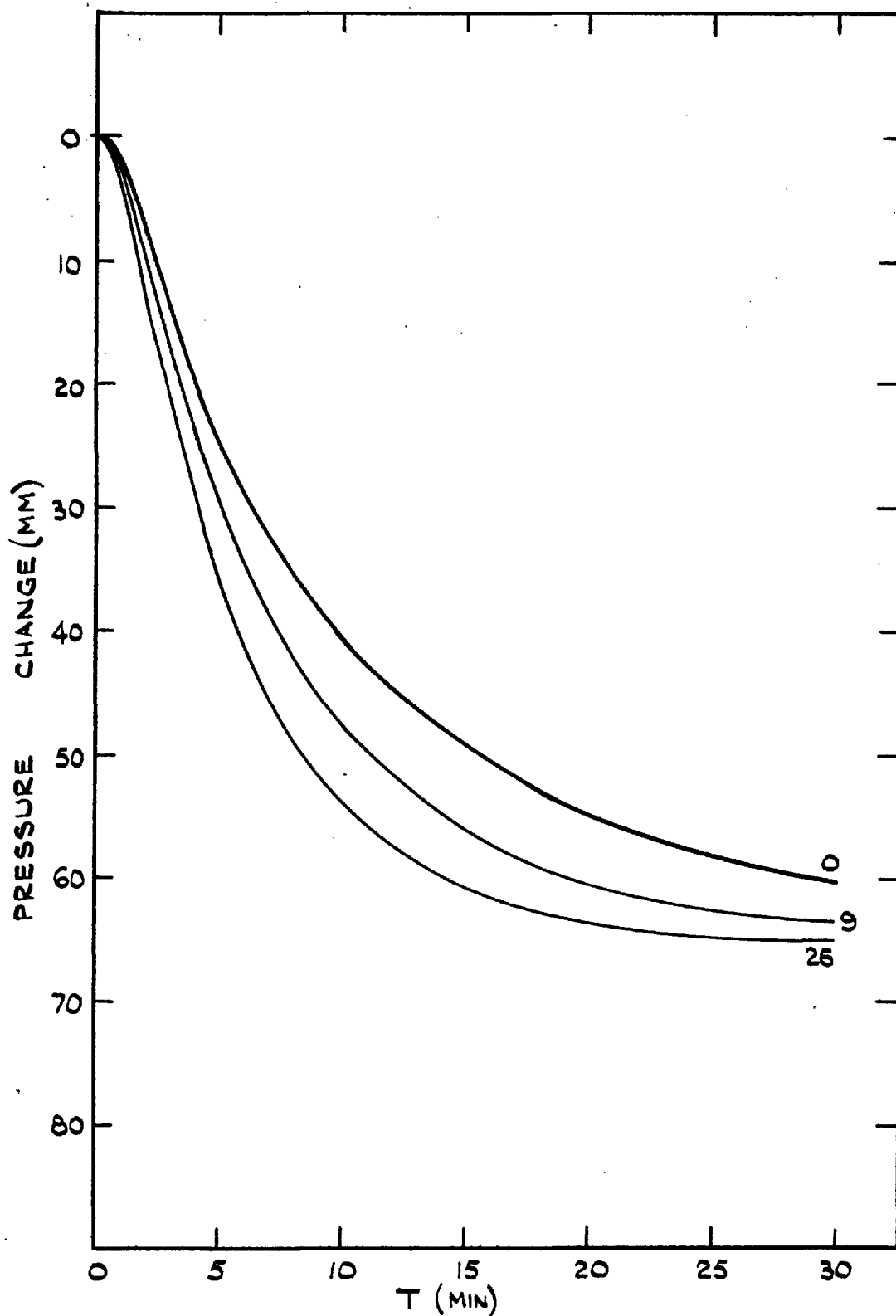
FIG. 14. THE OXIDATION OF ACETALDEHYDE IN THE PRESENCE OF METHYLENE DIBROMIDE. PRESSURE - TIME CURVES. $T = 155°C$. $CH_3CHO = 100$ MM. $O_2 = 100$ MM CH_2Br_2 AS SHOWN (MM).

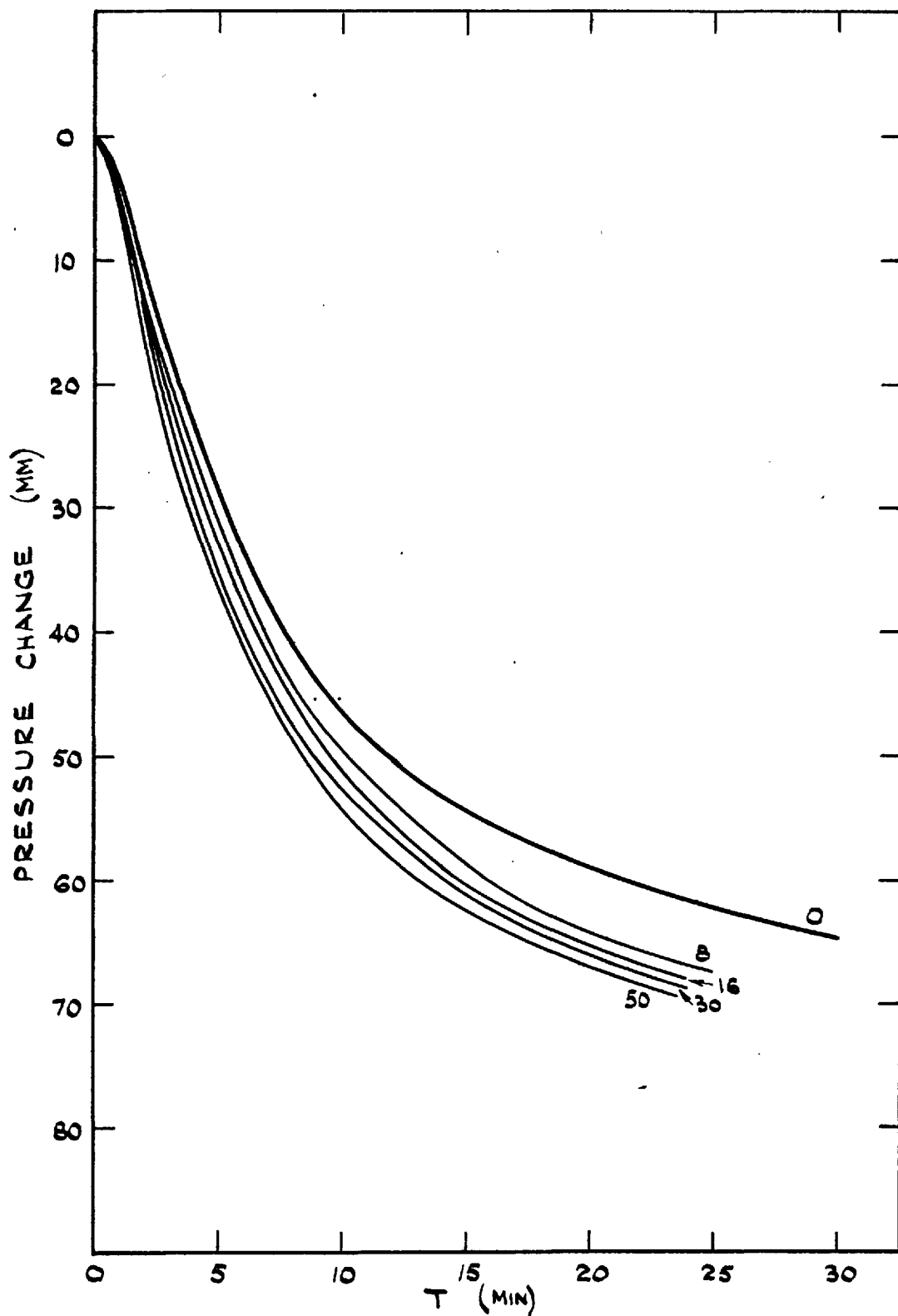FIG.15. THE OXIDATION OF ACETALDEHYDE IN THE PRESENCE OF METHYLENE DIBROMIDE. PRESSURE - TIME CURVES. T= 155°C. CH₃CHO = 100 MM. O₂ = 250 MM. CH₂Br₂ AS SHOWN (MM).

FIG. 16. THE OXIDATION OF ACETALDEHYDE IN THE
PRESENCE OF CHLOROBROMOMETHANE. PRESSURE-
TIME CURVES. T = 155°C. CH_3CHO = 100 MM.
O_2 = 100 MM CH_2BrCl AS SHOWN (MM).
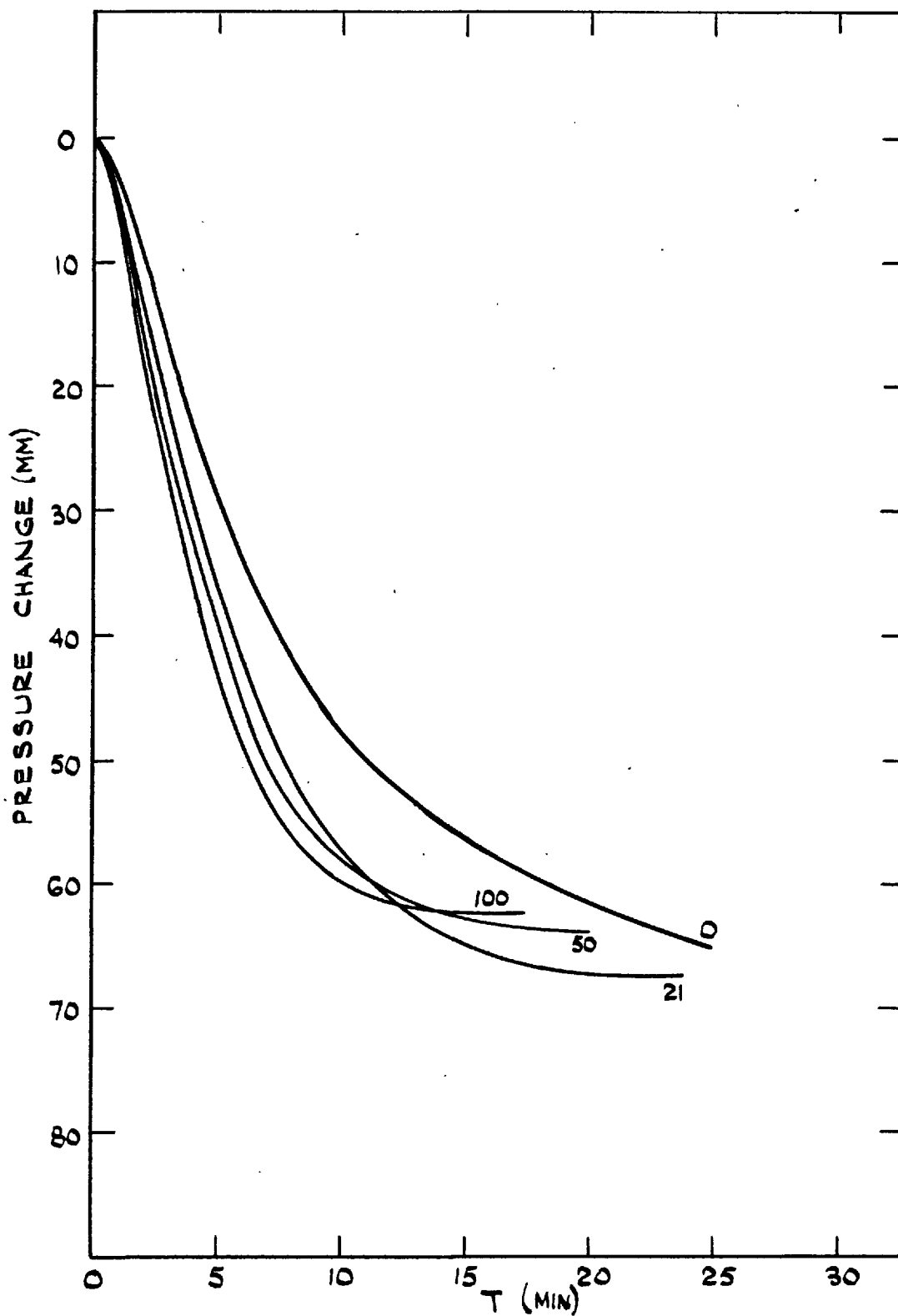
FIG. 17. THE OXIDATION OF ACETALDEHYDE IN THE
PRESENCE OF DIBROMODIFLUOROMETHANE.
PRESSURE - TIME CURVES. T = 155°C. $CH_3CHO = 100$ MM.
$O_2 = 100$ MM. CF_2Br_2 AS SHOWN (MM)

FIG.18. THE EFFECT OF VARIOUS ADDITIVES ON THE OXIDATION OF ACETALDEHYDE.
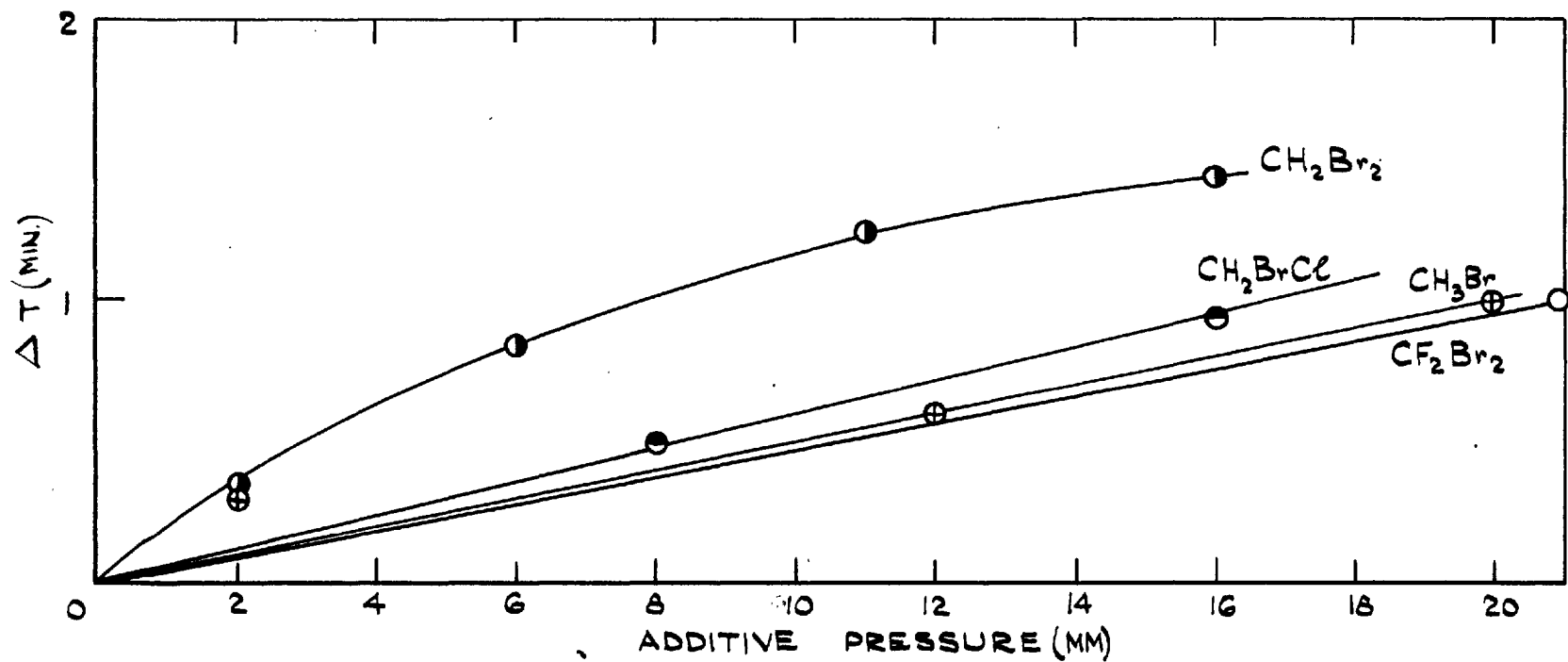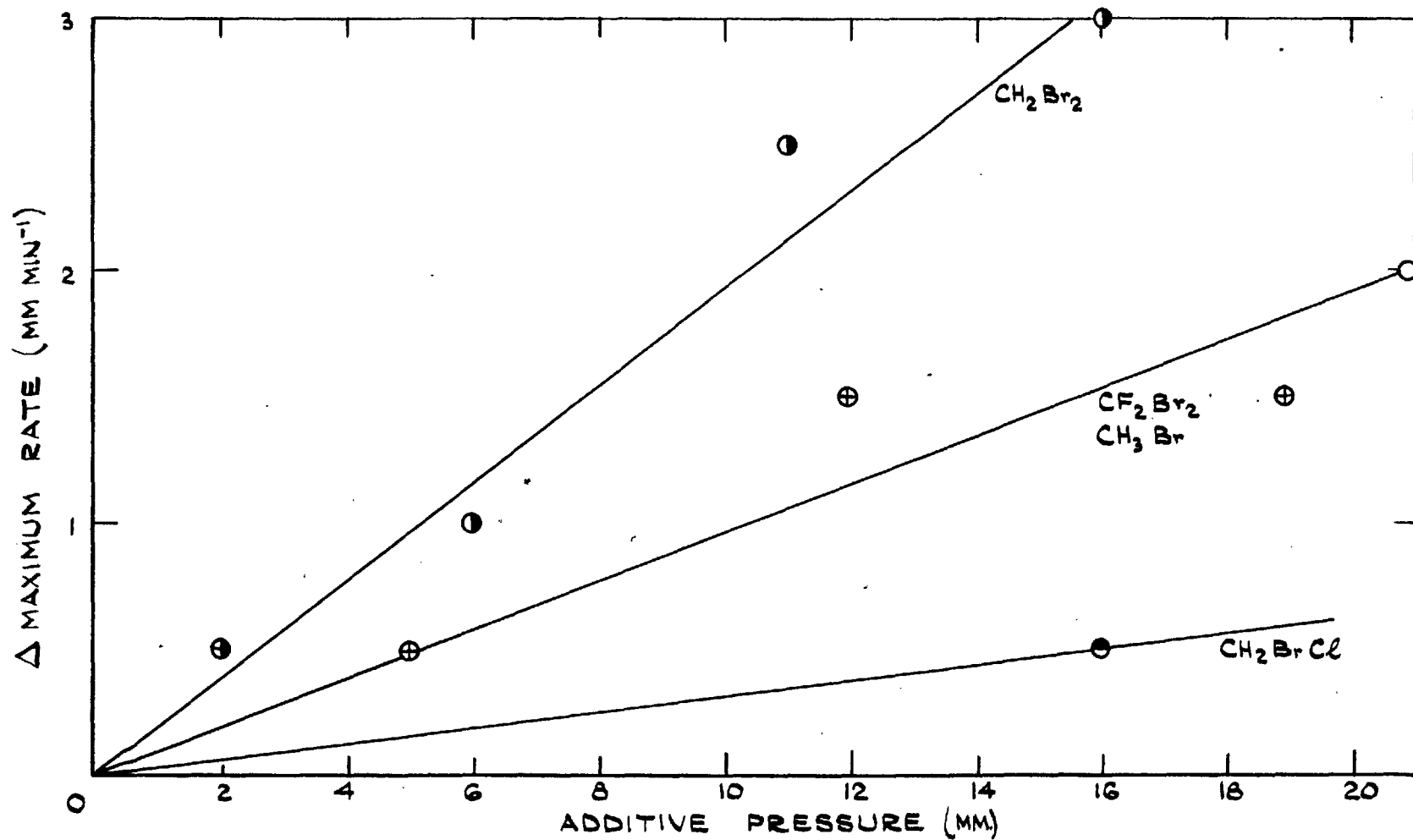T = 155°C. $CH_3CHO = 100$ MM. $O_2 = 100$ MM.

FIG. 19. THE OXIDATION OF ACETALDEHYDE. THE INFLUENCE OF ADDITIVE PRESSURE ON MAXIMUM RATE. T= 155°C. $CH_3CHO = 100$ MM. $O_2 = 100$ MM.

2. The influence of hydrogen bromide

a) 122°C

(i) Pressure-time curves

The influence of hydrogen bromide on the oxidation of acetaldehyde at 122°C has been investigated. Hydrogen bromide (5-100 mm.) was introduced into the reaction vessel followed by oxygen (100 mm.) and then acetaldehyde (100 mm.). The pressure-time curves were then obtained. Some are shown in Fig. 20. The presence of hydrogen bromide increased the maximum rate appreciably, this rate increasing steadily as the hydrogen bromide concentration was increased. The graph of the maximum rate of pressure change plotted against hydrogen bromide pressure is the continuous line shown in Fig. 21. The theoretical treatment given in the Discussion (Section C.1.b.) leads to the dotted line shown in the figure.

(ii) Estimation of peracetic acid

The amount of peracetic acid produced in these reactions was then studied using the analytical procedures described previously. The results are shown in Figs. 22, 23. With acetaldehyde-oxygen mixtures alone, the yield of peracetic acid increased linearly with time and with pressure decrease. The slopes obtained were respectively 0.66×10^{-5} moles per minute and 0.91×10^{-5} moles per millimetre. From the volume of the reaction vessel and the dead space it was calculated that the input of acetaldehyde was 1.09×10^{-5} moles per millimetre.

The experiments were then carried out using 5 mm. hydrogen bromide pre-mixed with the oxygen prior to admission into the reaction vessel. Under these conditions of mixing, the initial rate of reaction

was not appreciably increased, the reaction proceeding at an
approximately normal rate for about 5 minutes. The rate then increased
markedly for a short time before falling off almost to nothing. This
behaviour contrasted strongly with the immediate sharp increase in the
rate of reaction which occurred when the reacting mixture was prepared
by adding the hydrogen bromide first to the evacuated vessel, followed
by acetaldehyde and then oxygen.

The yield of peracetic acid was determined after various
times as before. It was assumed that the amount of bromine produced
was so small that it did not appreciably affect the estimation.
Again, the amount of peracetic acid formed increased linearly with time,
at least up to 40 min., but the yield obtained after 60 min. suggested
that the rate of formation of peracid decreased appreciably after
about 40 min. The initial rate of formation of peracetic acid in the
presence of hydrogen bromide was appreciably greater than in the normal
oxidation, the slope on this occasion being 0.91×10^{-5} moles per
minute. The yield of peracetic acid again increased linearly with
millimetres pressure decrease, the slope being 0.75×10^{-5} moles per
mm., which was distinctly smaller than in the absence of additive.

(iii) <u>Estimation of residual acetaldehyde</u>

Attempts were made by the methods previously described to
estimate the acetaldehyde remaining unchanged in the products of a
run. However, no reliable data could be obtained because of the
large errors involved in the methods employed.

b) <u>At 225°C</u>

The influence of hydrogen bromide on the explosive oxidation
of acetaldehyde at 225°C has been investigated. A mixture of 50 mm.

acetaldehyde, 50 mm. oxygen exploded after ca. 9 sec. at 225°C. On pre-mixing 2-50 mm. hydrogen bromide with the oxygen prior to the addition of the acetaldehyde, explosion occurred after 2-3 sec. The order of introduction of the reactants was varied. Thus oxygen was added to mixtures of acetaldehyde and hydrogen bromide, but this had little effect on the explosion time observed. Hydrogen bromide therefore had a powerful promoting influence on the oxidation under these conditions.
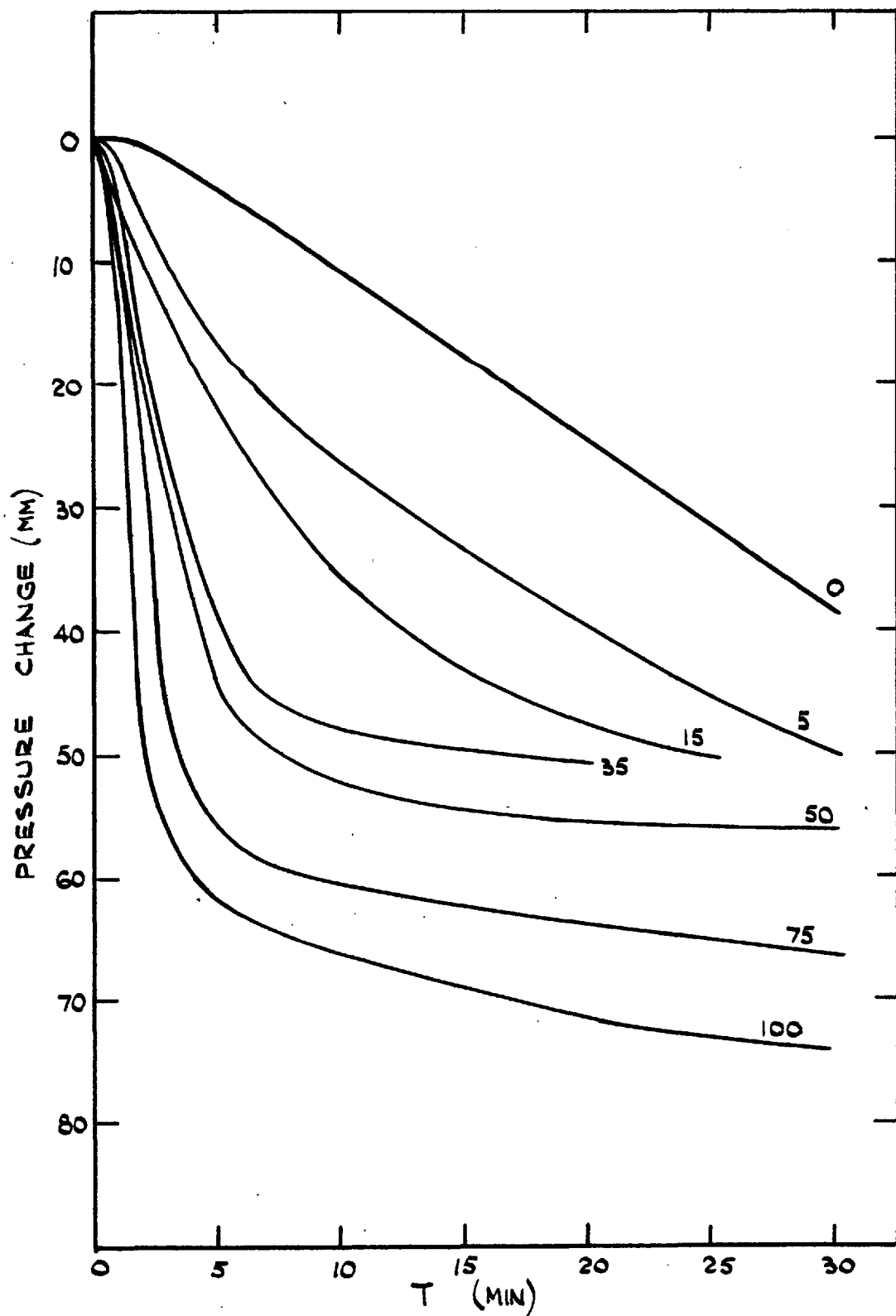
FIG.20. THE OXIDATION OF ACETALDEHYDE IN THE
PRESENCE OF HYDROGEN BROMIDE.
PRESSURE-TIME CURVES. T= 122°C.
$CH_3CHO = 100$MM. $O_2 = 100$MM. HBr AS SHOWN (MM)
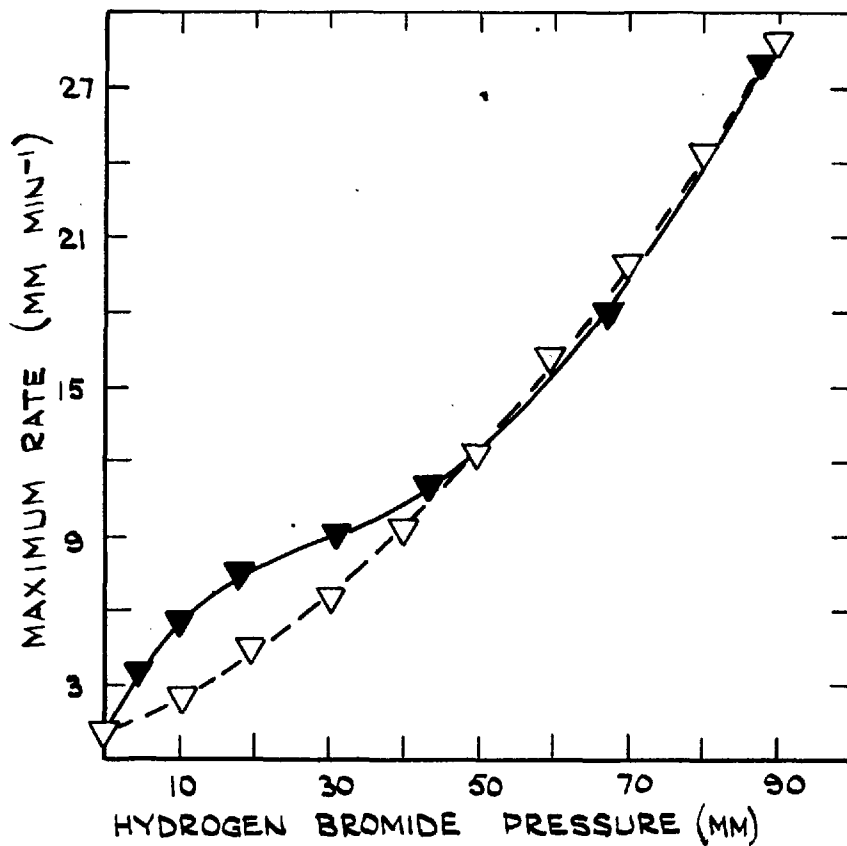
FIG.21. THE OXIDATION OF ACETALDEHYDE IN
THE PRESENCE OF HYDROGEN BROMIDE.
THE EFFECT OF HYDROGEN BROMIDE PRESSURE
ON MAXIMUM RATE. T=122°C.
$CH_3CHO = 100\,MM.$ $O_2 = 100\,MM.$
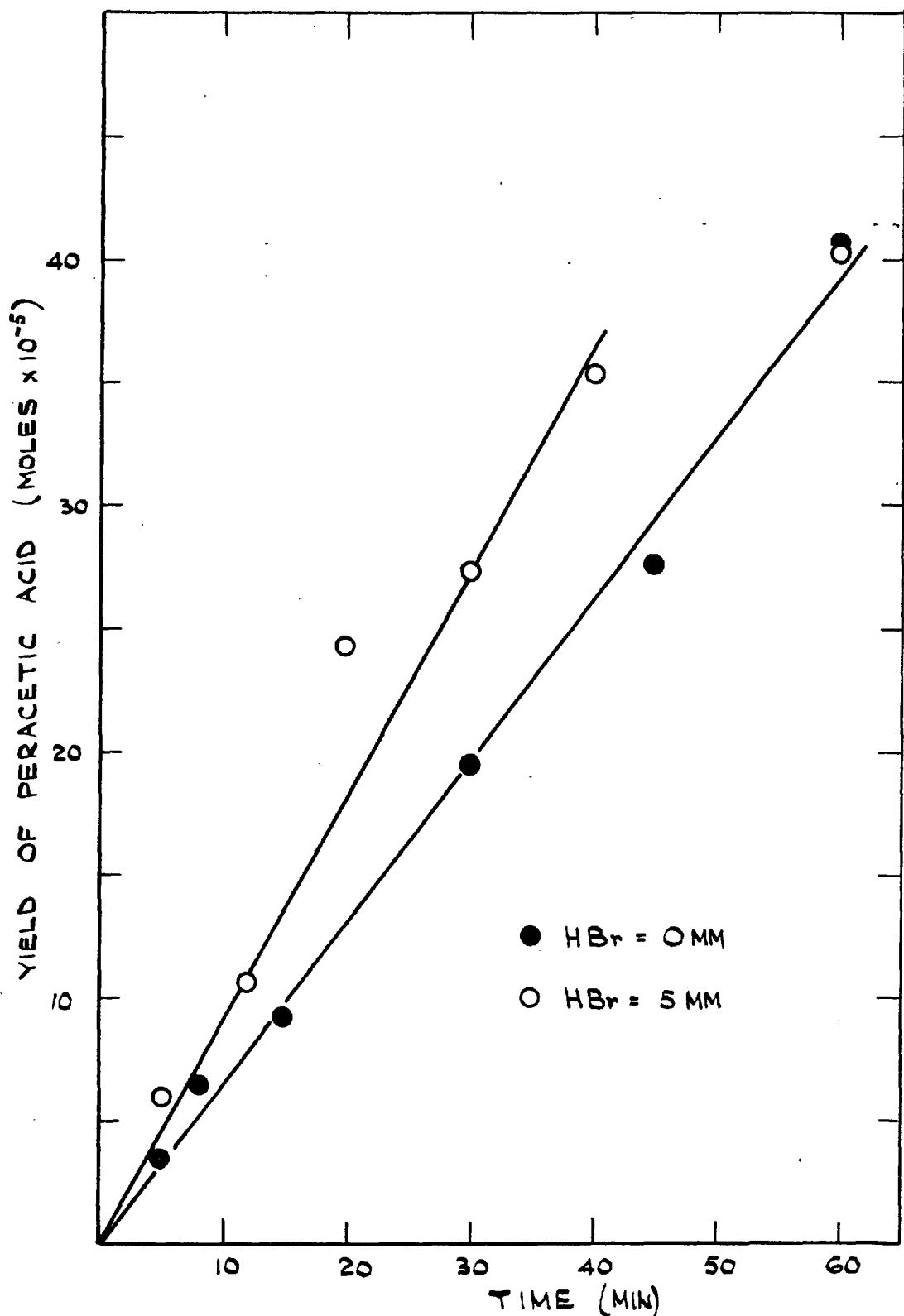
FIG.22. THE OXIDATION OF ACETALDEHYDE IN THE PRESENCE OF HYDROGEN BROMIDE, THE YIELD OF PERACETIC ACID AS A FUNCTION OF TIME. T=122°C. CH_3CHO=100MM. O_2=100MM. HBr AS SHOWN.

FIG.23. THE OXIDATION OF ACETALDEHYDE IN THE PRESENCE OF HYDROGEN BROMIDE. THE RELATIONSHIP BETWEEN YIELD OF PERACETIC ACID AND PRESSURE DECREASE. T = 122° C. CH_3CHO = 100 MM. O_2 = 100 MM. HBr AS SHOWN.

C. THE OXIDATION OF DIETHYL ETHER (at 155°C)

1. The influence of halomethanes

The influence of methyl bromide, methylene dibromide,
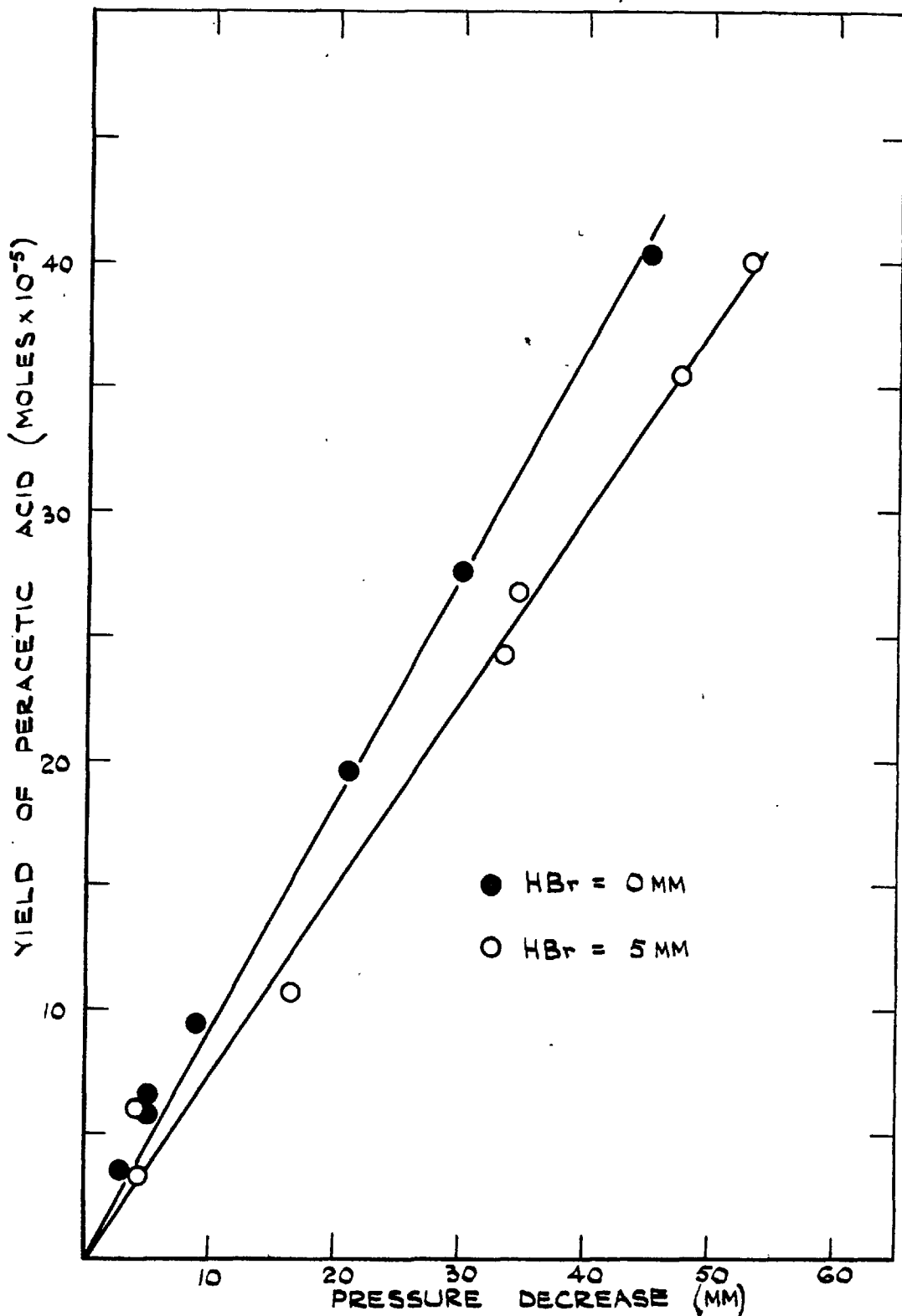chlorobromomethane, and difluorodibromomethane on the oxidation of
diethyl ether at 155°C has been investigated.   In these experiments
and in all subsequent ones all three reactants were pre-mixed prior to
admission into the reaction vessel.   Mixtures of 100 mm. diethyl
ether, 100 mm. oxygen, 2-50 mm. additive were employed and the pressure-
time curves were observed on each occasion.   The results are shown
in Figs. 24-27.   The presence of methyl bromide or difluorodibromomethane
caused the pressure to decrease initially at a slightly slower rate than
in the normal reaction while the presence of methylene dibromide or
chlorobromomethane caused the pressure to decrease initially rather
faster than normally.   The extent of the change in rate of pressure
decrease increased steadily as the additive pressure was increased in
most cases.   These effects are clearly shown in Fig. 28 where the time
taken for the pressure to decrease by 5 mm. (dotted line), 10 mm.
(continuous line) in the normal reaction minus the time taken for the
pressure to decrease by 5 mm., 10 mm. in the reaction occurring in the
presence of additive, is plotted against additive pressure.   Positive
values of ΔT thus mean that the additive is promoting the reaction.
A pressure change of 10 mm. did not occur in the presence of 8 mm.
methyl bromide and so this graph could not be plotted.   Considering the
effects observed at 5 mm. pressure change, it is seen that
chlorobromomethane had no effect on the reaction, methylene dibromide
had a slight promoting influence, while methyl bromide and

difluorodibromomethane had a roughly equivalent retarding influence. ΔT increased linearly with additive pressure in all cases.

At 10 mm. pressure change, difluorodibromomethane still exerted a pronounced retarding effect while chlorobromomethane and methylene dibromide had a roughly equivalent accelerating effect on the reaction. All the curves exhibited minima and the pressure then increased quite sharply. All pressures of all the additives increased slightly the maximum rate of this pressure increase except for high pressures of difluorodibromomethane which caused a very large increase in this rate of pressure increase. This pressure increase also occurred progressively earlier as the pressure of additive was increased. This is shown in Fig. 29 where the time taken for the pressure change to become zero again in the normal oxidation minus the time taken for the pressure change to become zero again in the presence of additive is plotted against the additive pressure. Here also positive values of ΔT mean that the additive is promoting the reaction. The results are rather scattered but it is seen that all pressures of all the additives promoted the reaction. As the additive pressure was increased, the extent of the promotion increased but the promoting influence of the additive per unit concentration decreased. The order of effectiveness of the additives in promoting the pressure increase was:

$$CF_2Br_2 > CH_3Br > CH_2BrCl > CH_2Br_2$$
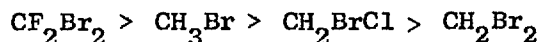
However, the differences between the effects of the various additives were small.

2. The influence of nitrogen

Nitrogen (10-20 mm.) had no effect on the pressure time curve for the oxidation of diethyl ether (100 mm. diethyl ether, 100 mm. oxygen) at 155°C.
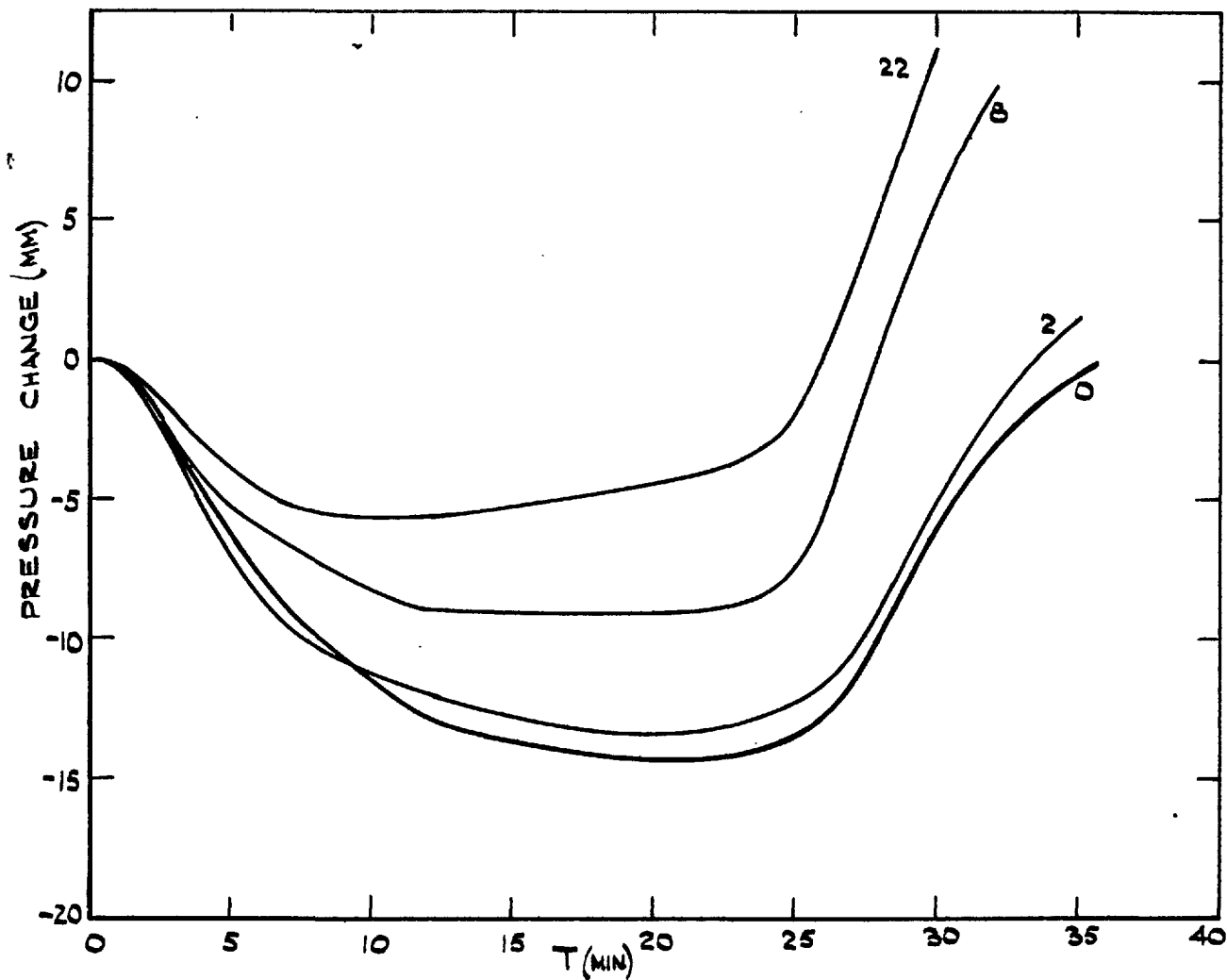
FIG. 24. THE OXIDATION OF DIETHYL ETHER IN THE PRESENCE OF
METHYL BROMIDE. PRESSURE-TIME CURVES.
$T = 155°C$ $(C_2H_5)_2O = 100MM$. $O_2 = 100MM$. CH_3Br AS SHOWN (MM)
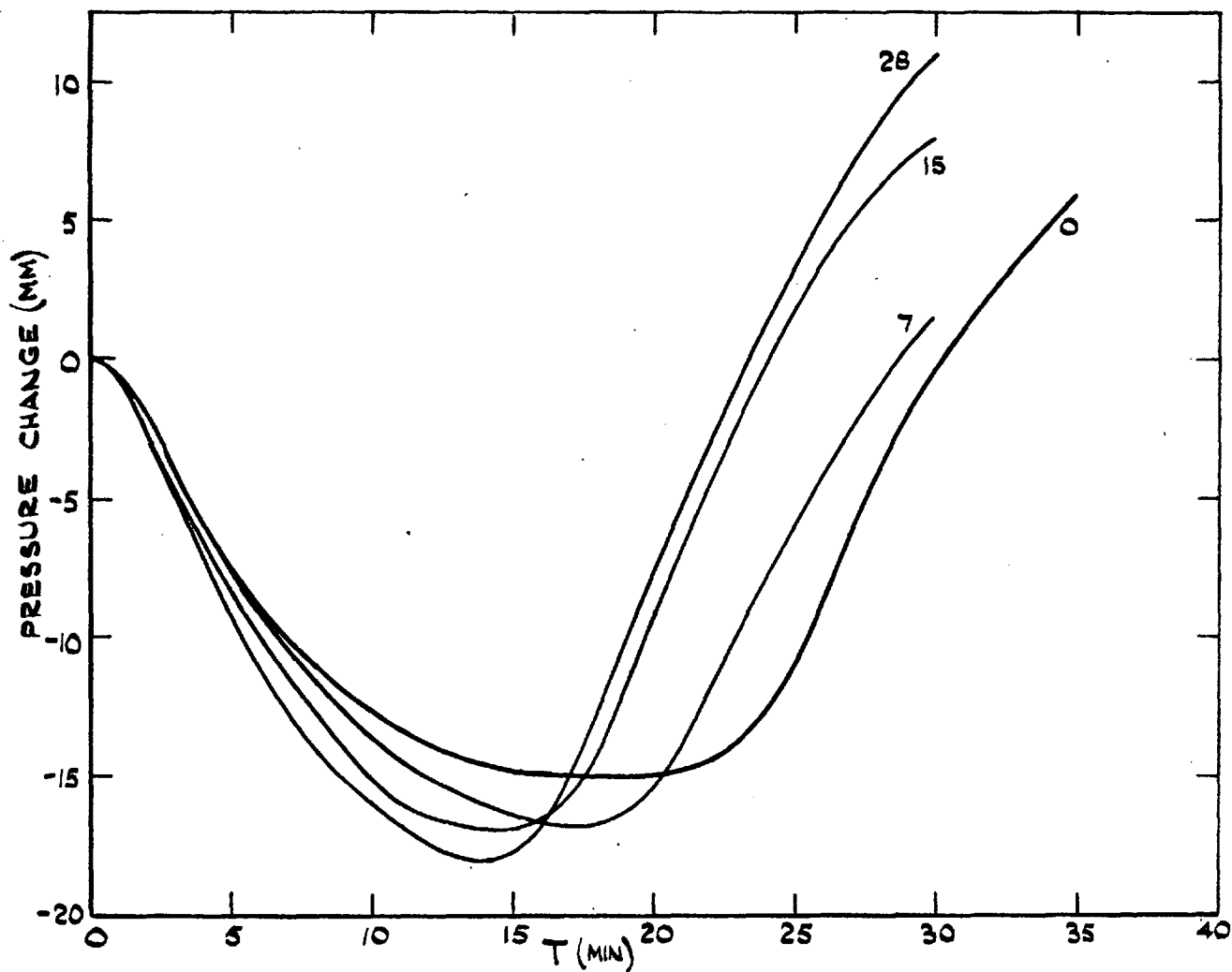
FIG. 25. THE OXIDATION OF DIETHYL ETHER IN THE PRESENCE OF
METHYLENE DIBROMIDE. PRESSURE-TIME CURVES.
T=155°C $(C_2H_5)_2O$ =100MM. O_2=100MM. CH_2Br_2 AS SHOWN (MM).
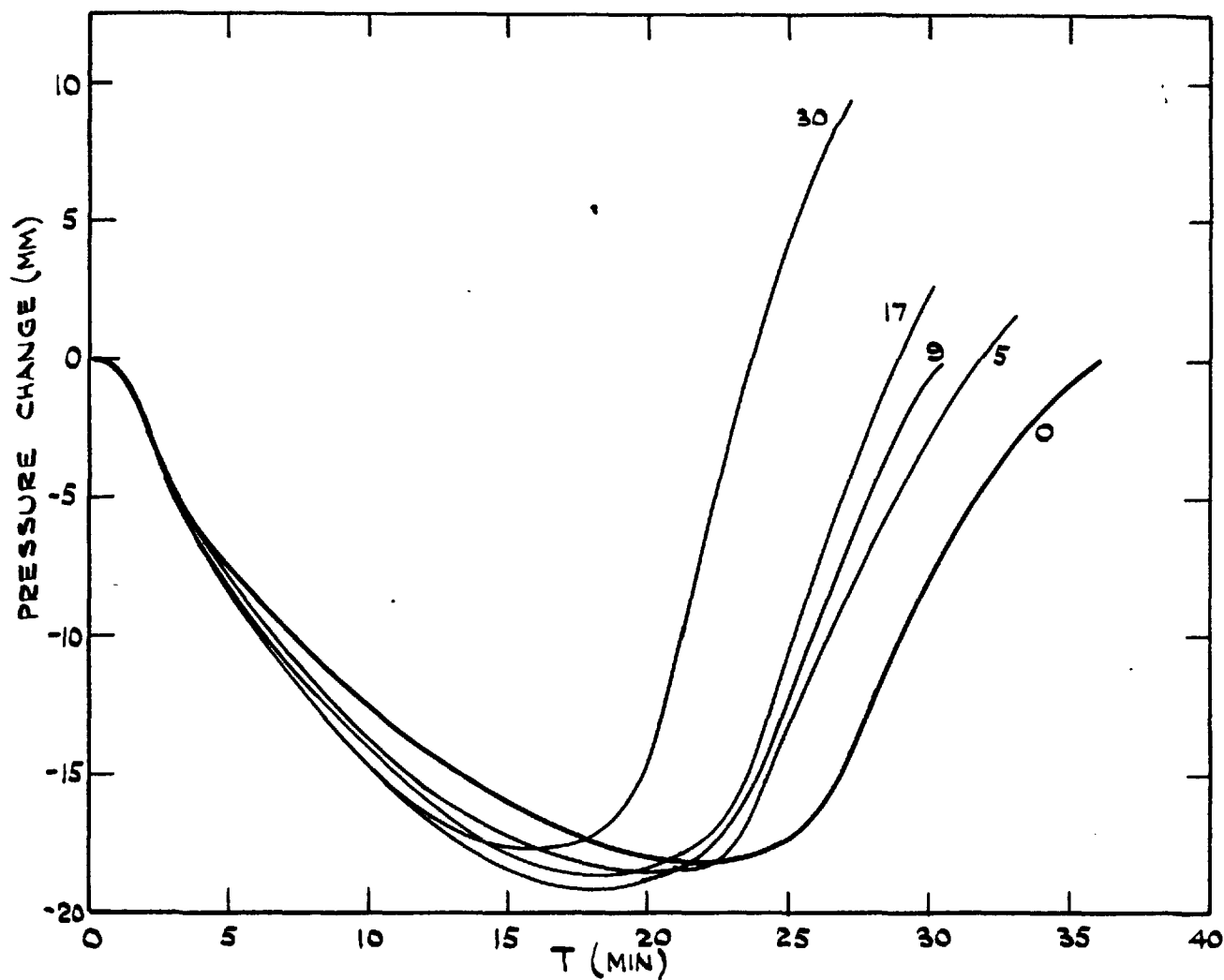
FIG. 26. THE OXIDATION OF DIETHYL ETHER IN THE PRESENCE
OF CHLOROBROMOMETHANE. PRESSURE—TIME CURVES.
T=155°C (C₂H₅)₂O = 100MM. O₂ = 100MM. CH₂Br Cℓ AS SHOWN(MM)
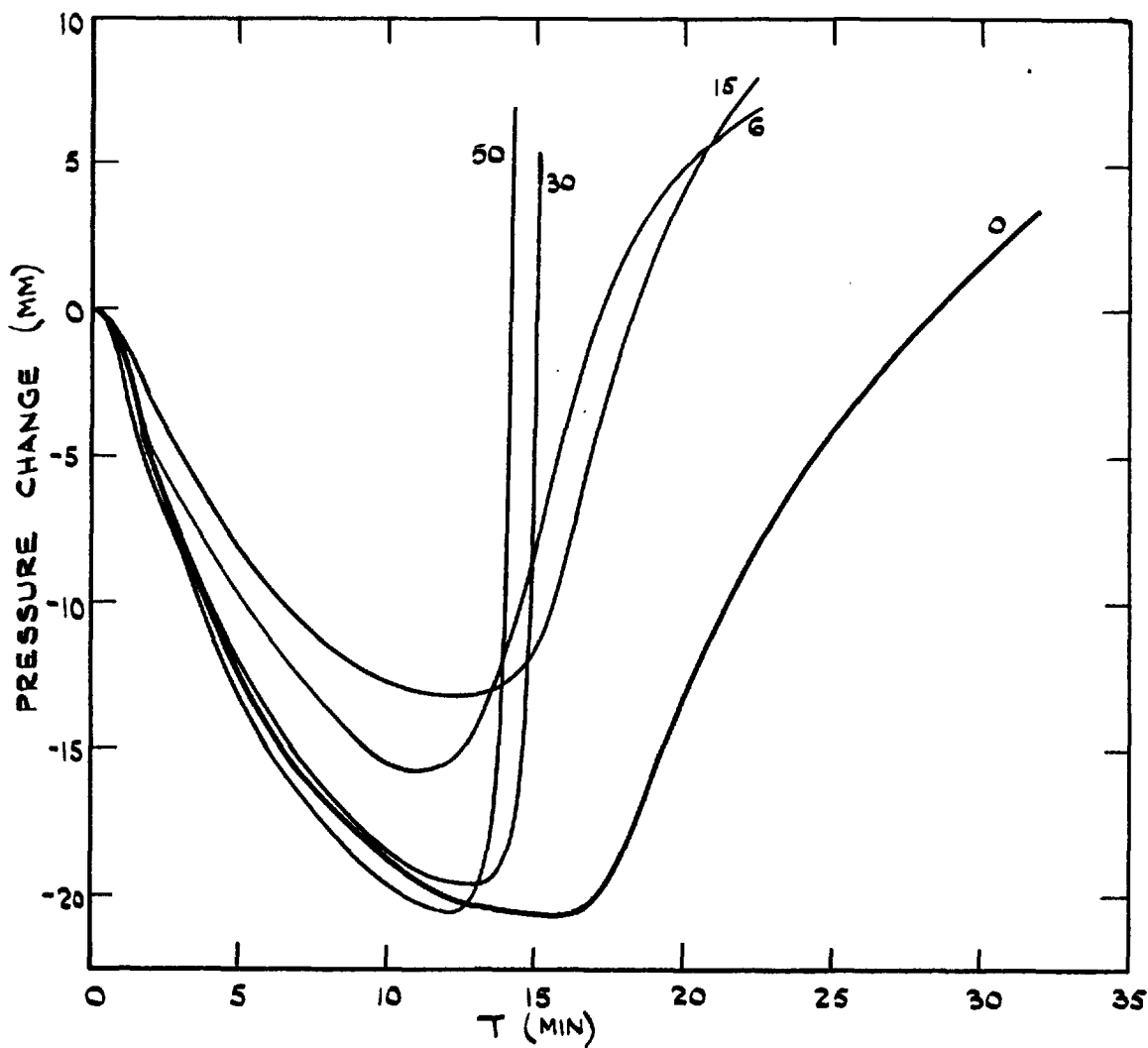
FIG. 27. THE OXIDATION OF DIETHYL ETHER IN THE
PRESENCE OF DIFLUORODIBROMOMETHANE.
PRESSURE - TIME CURVES. T = 155°C.
$(C_2H_5)_2O = 100$ MM. $O_2 = 100$ MM. CF_2Br_2 AS SHOWN (MM).
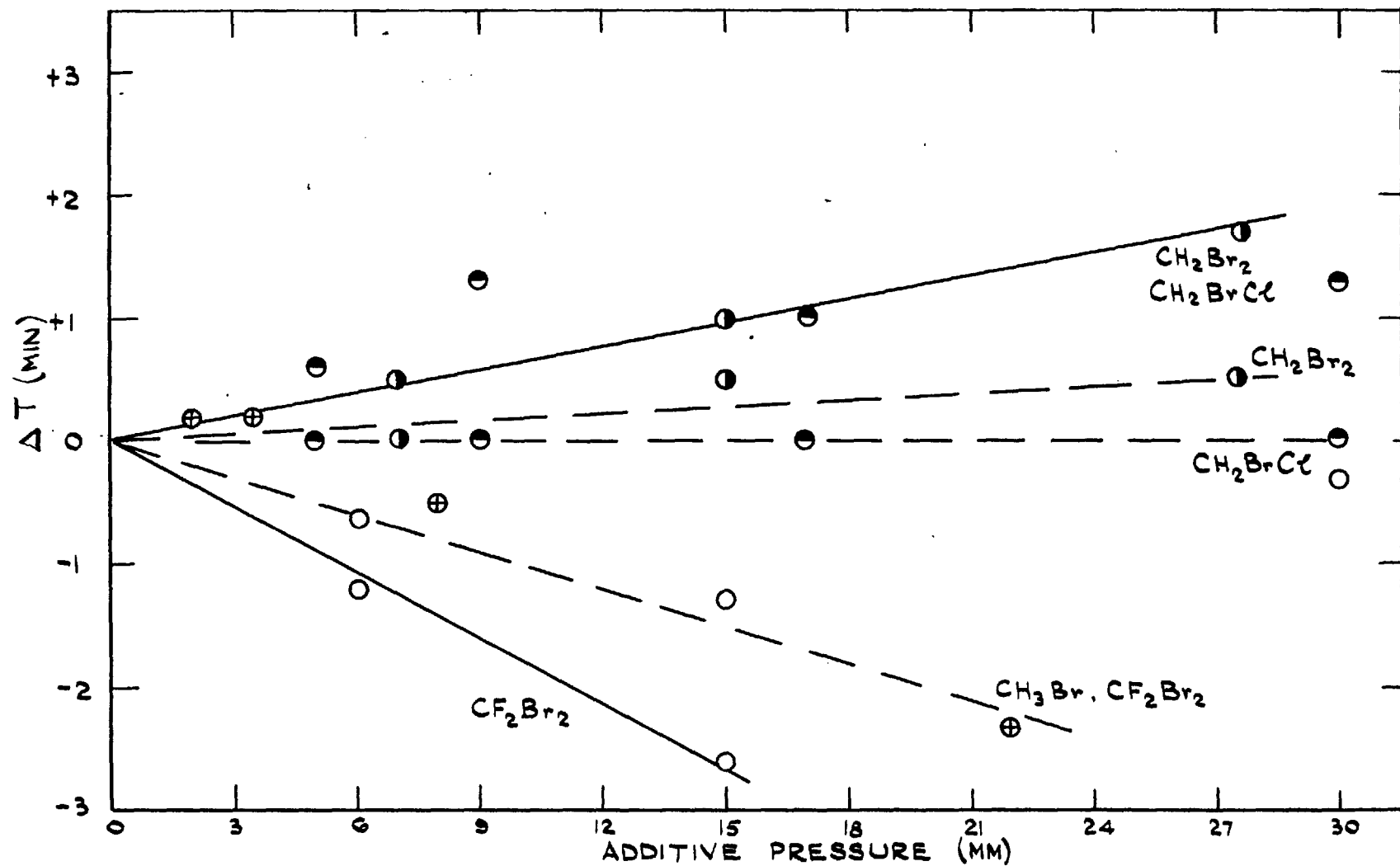
FIG. 28. THE OXIDATION OF DIETHYL ETHER IN THE PRESENCE OF HALOMETHANES.
T = 155°C (C₂H₅)₂O = 100 MM. O₂ = 100 MM.
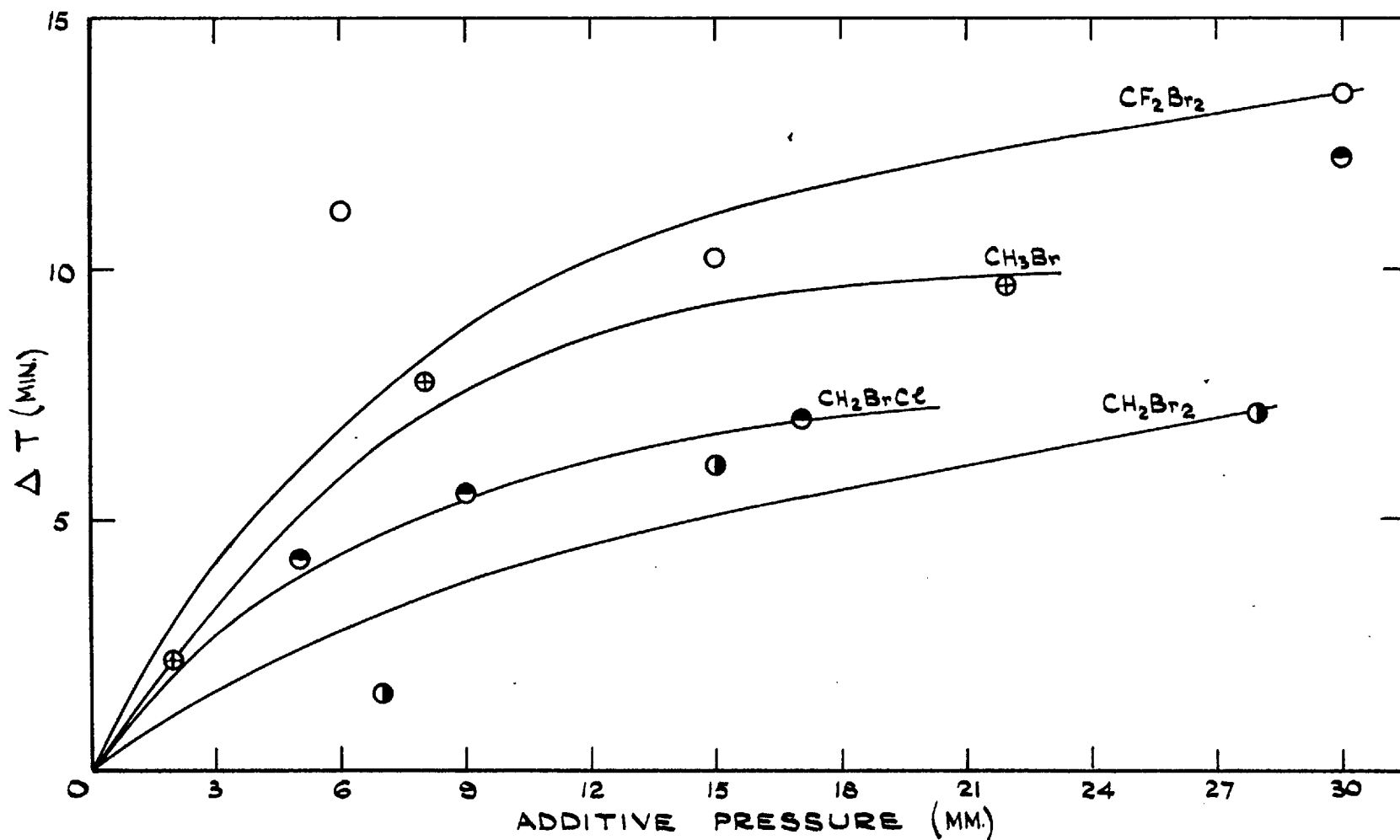
FIG. 29. THE OXIDATION OF DIETHYL ETHER IN THE PRESENCE OF HALOMETHANES. $T = 155°C$ $(C_2H_5)_2O = 100$ MM. $O_2 = 100$ MM.

D. THE OXIDATION OF ISOPENTANE (at 283°C)

1. The influence of halomethanes

The influence of methyl bromide and difluorodibromomethane
on the oxidation of isopentane (at 283°C) has been studied. Mixtures
of 100 mm. isopentane, 100 mm. oxygen, 10-50 mm. additive were used.
The pressure-time curves for the reactions were observed and also
product chromatograms were obtained immediately the pressure change
ceased. The pressure-time curves obtained are shown in Figs. 30,31.
Both additives promoted the reaction markedly, their presence increasing
the maximum rate observed and also causing the main pressure change
to occur earlier. The extent of the promotion would probably have
increased steadily with additive pressure in a fully-aged vessel but
under the conditions employed 10-15 mm. additive had a greater promoting
effect than 20-30 mm. However, 50 mm. additive had the greatest
effect in both cases. Dibromodifluoromethane had a more powerful
promoting effect than methyl bromide, 50 mm. of this additive causing
the maximum rate to occur 26 min. earlier than in the normal reaction,
while 50 mm. methyl bromide caused the maximum rate to occur only 6 min.
earlier. The maximum pressure change observed increased progressively
with additive pressure.

The product chromatograms of the normal reaction and of the
reaction in the presence of additive were virtually identical in all
cases except for the additional peak (with methyl bromide) or hollow
(with difluorodibromomethane) due to the additive.

2. The influence of nitrogen

Nitrogen (10-50 mm.) had no effect on the pressure-time
curve of the reaction between 100 mm. isopentane, 100 mm. oxygen.
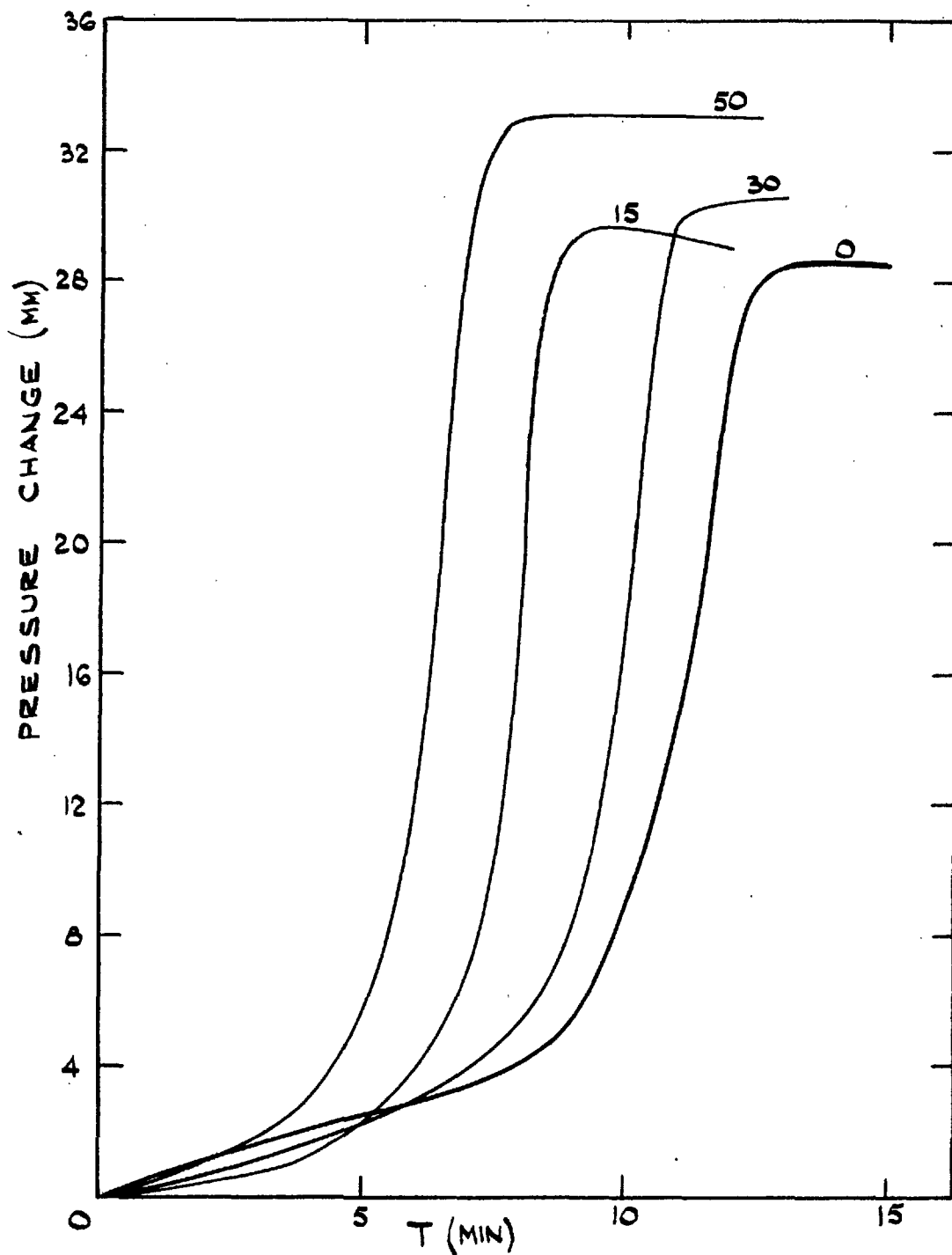
FIG. 30. THE OXIDATION OF ISOPENTANE IN THE
PRESENCE OF METHYL BROMIDE.
PRESSURE-TIME CURVES. T = 283°C.
$(CH_3)_2 CH.CH_2.CH_3 = 100 MM.$ $O_2 = 100 MM.$ $CH_3 Br$ AS SHOWN (MM)
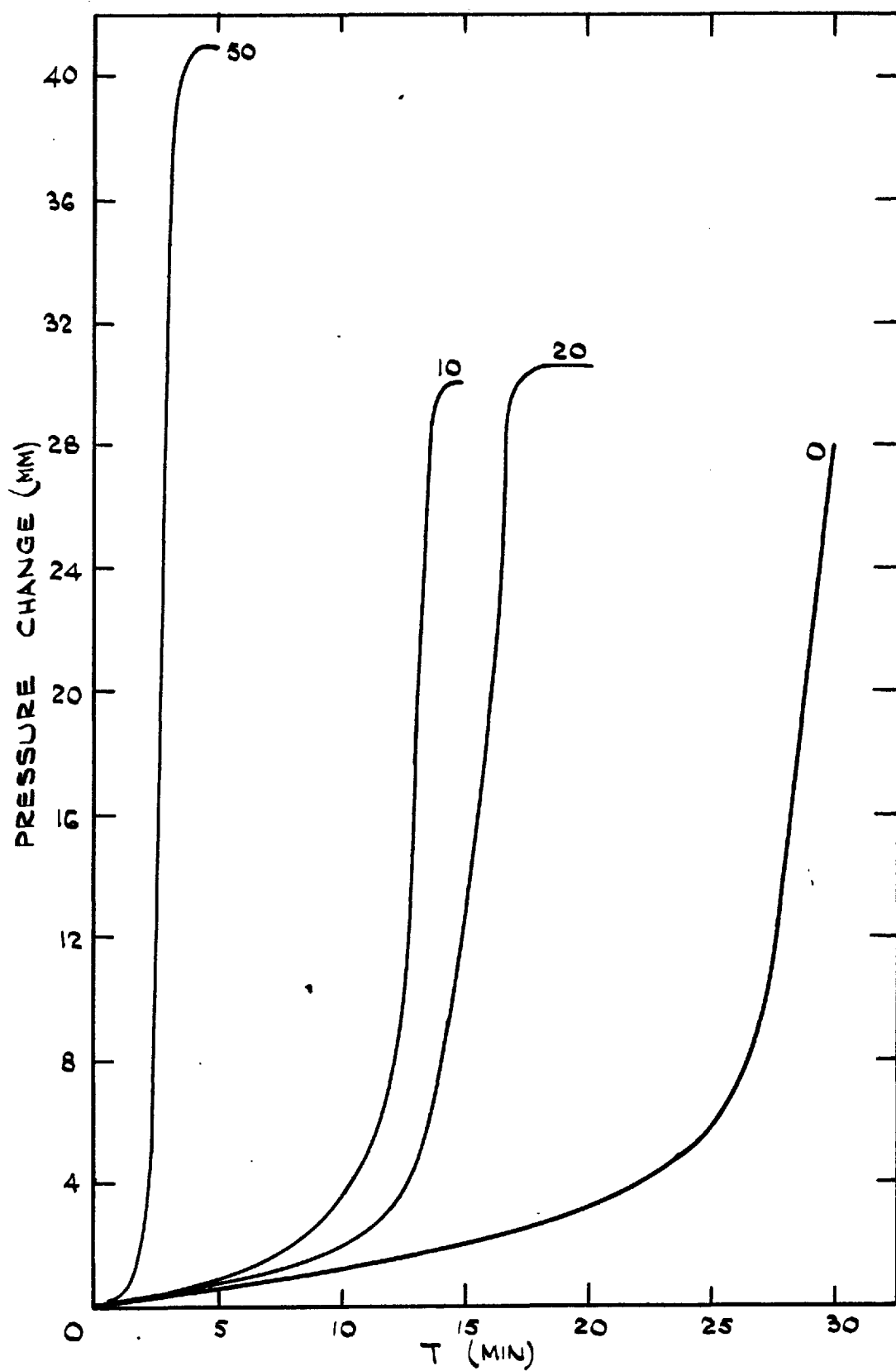
FIG.31. THE OXIDATION OF ISOPENTANE IN THE PRESENCE OF DIBROMODIFLUOROMETHANE. PRESSURE - TIME CURVES.
$T = 283°C$ $(CH_3)_2 CH.CH_2.CH_3 = 100MM.$ $O_2 = 100 MM$
CF_2Br_2 AS SHOWN (MM).

E. THE OXIDATION OF FORMALDEHYDE

1. At 315°C

a) The influence of halomethanes

The influence of methyl bromide and dibromodifluoromethane
on the oxidation of formaldehyde at 315°C has been investigated.
Mixtures of 100 mm. formaldehyde, 100 mm. oxygen, 0.5-10 mm. additive
were employed and the pressure-time curves observed on each occasion.
The results are shown in Figs. 32-34. All parts of the apparatus
coming into contact with formaldehyde were electrically heated to 120°C
in order to prevent the formaldehyde polymerising in the line. A
large number of formaldehyde-oxygen runs had to be carried out before
fairly reproducible pressure-time curves were obtained. Even then,
the curve for the normal oxidation changed steadily from one day to the
next, the oxidation proceeding at a progressively slower rate. However,
the change was sufficiently small for any large effect of additive
to be easily observable.

With methyl bromide as additive some concentrations retarded
the initial reaction slightly while others promoted it to a small
extent. These effects are seen in the pressure-time curves in Fig. 32
and also in Fig. 35 where graphs of the time taken for a pressure change
of 5, 10 mm. to occur in the reaction in the presence of additive
minus the time taken for a pressure change of 5, 10 mm. to occur in the
normal oxidation is plotted against the additive pressure. Positive
values of ΔT thus mean that the additive retarded the reaction. At
pressure changes of 5 mm. and 10 mm. the presence of methyl bromide
at pressures of 0.5-10 mm. produced only small values of ΔT varying from

- 0.8 min. to + 0.4 min.   In both cases the results were rather
scattered but a mean line was the zero abscissa.   Also the additive
had no effect on the maximum rate observed in the reaction.   Thus
although appreciable effects were observed in particular runs, considering
the results as a whole it must be concluded that methyl bromide had
no definite effect on the .oxidation of formaldehyde under these
conditions.

The presence of dibromodifluoromethane (0.5-6 mm.) retarded
the oxidation appreciably, maximum retardation being observed with 1 mm.
additive.   The presence of 0.5 mm. additive reduced the maximum rate
observed from 1.5 mm. min.$^{-1}$ to 1.0 mm. min.$^{-1}$ but the maximum rate was
not further reduced by higher pressures of additive.   The retarding
influence of difluorodibromomethane is clearly shown in Fig. 35 where
it is seen that the presence of 1 mm. caused the time taken for a
pressure change of 5 mm. to occur to increase by 3.7 min.   The retarding
influence then decreased at higher additive pressures.

b)   The influence of hydrogen bromide

Pressures of hydrogen bromide of 0.5-2 mm. retarded the
reaction appreciably (Fig. 34) while 5 mm. additive promoted the
reaction initially but the reaction rate fell below that of the normal
reaction after about ten minutes.   Again the maximum retarding
influence was observed with 1 mm. additive.   0.5 - 1 mm. additive
reduced the maximum rate slightly from 1.5 mm. min.$^{-1}$ to 1.0 mm. min.$^{-1}$
while 2 - 5 mm. additive did not affect the maximum rate.   From
Fig. 35 it is seen that 1 mm. hydrogen bromide increased the time
required for a pressure change of 5 mm. to occur by 3.5 min. but 5 mm.

accelerated the reaction, decreasing this time by 1.3 min. At a pressure change of 10 mm., 1 mm. additive had the most pronounced retarding effect but all pressures of hydrogen bromide retarded the reaction to some extent.

c) Influence of nitrogen

Nitrogen (12-30 mm.) had no effect on the pressure-time curve of the reaction between 100 mm. formaldehyde, 100 mm. oxygen at 315°C.

2. At 515°C

a) Slow combustion

The influence of methyl bromide, difluorodibromomethane, and hydrogen bromide on the slow oxidation of formaldehyde at 515°C has been studied. Mixtures of 12 mm. formaldehyde, 40 mm. oxygen, 0.1 - 5 mm. additive were used. In the normal oxidation a pressure change of 4 mm. occurred in $\frac{1}{2}$ minute. The addition of 0.1 - 5 mm. of any of these additives had no noticeable effect on the pressure-time curve of the reaction.

b) Spontaneous ignition

The influence of methyl bromide and hydrogen bromide on the spontaneous ignition of formaldehyde/oxygen mixtures has been investigated. Mixtures of 23 mm. formaldehyde, 23 mm. oxygen, 0.1 - 6 mm. additive were used. The results are shown in Fig. 36. Both methyl bromide and hydrogen bromide promoted the ignition. Thus while a formaldehyde/oxygen mixture alone exploded after 5.8 secs., the presence of 6 mm. methyl bromide caused the mixture to explode after 5.0 secs., The promoting effect was thus a small one. Hydrogen

bromide was a rather more efficient promoter, the presence of 2 mm. causing the explosion to occur after 4.2 sec. Both additives caused the final pressure to increase steadily with pressure of additive as shown in the figure.
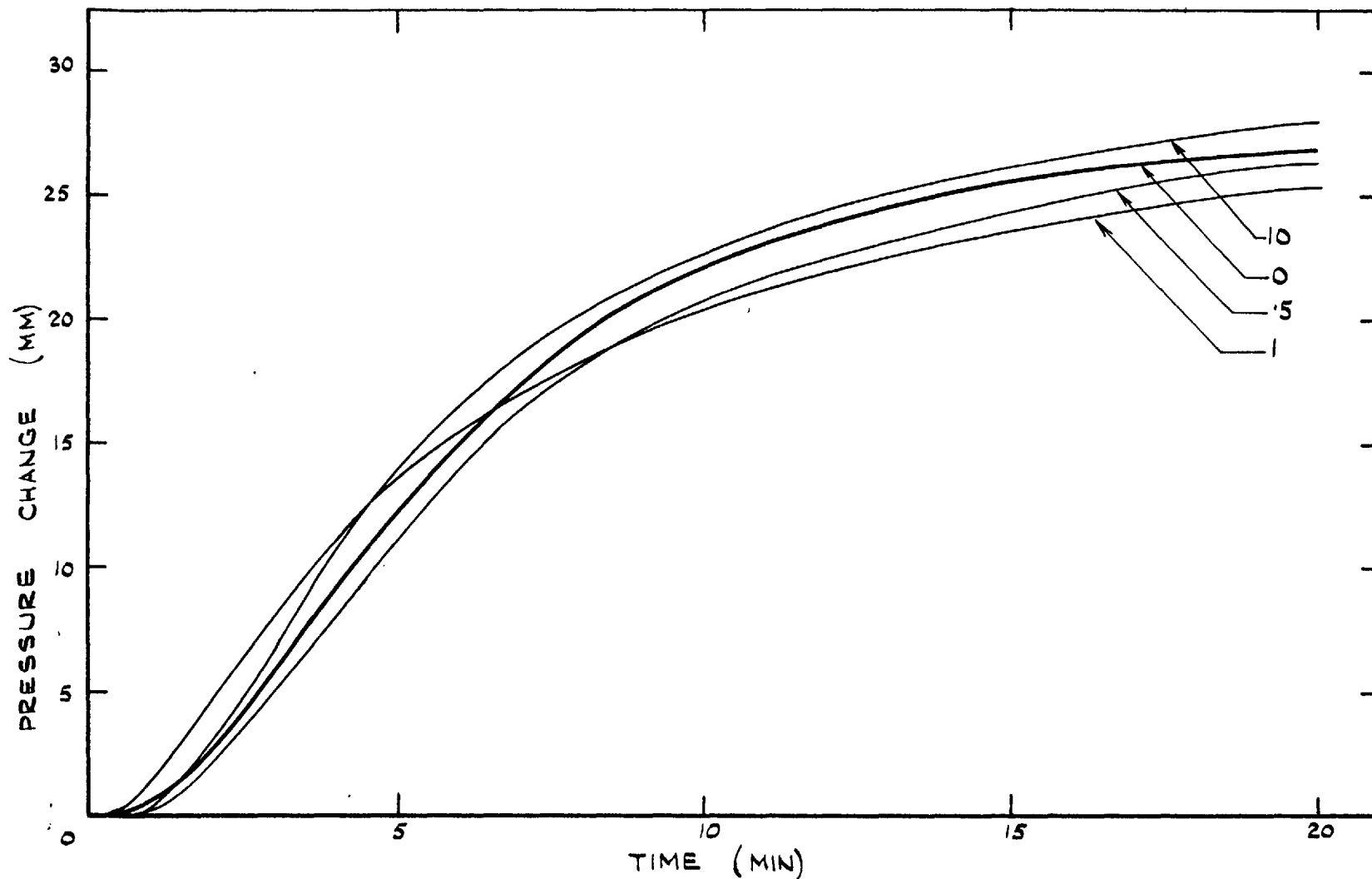
FIG.32. THE OXIDATION OF FORMALDEHYDE IN THE PRESENCE OF METHYL BROMIDE.
PRESSURE—TIME CURVES. T= 315°C. HCHO=100MM. O_2 = 100MM. CH_3Br AS SHOWN (MM).
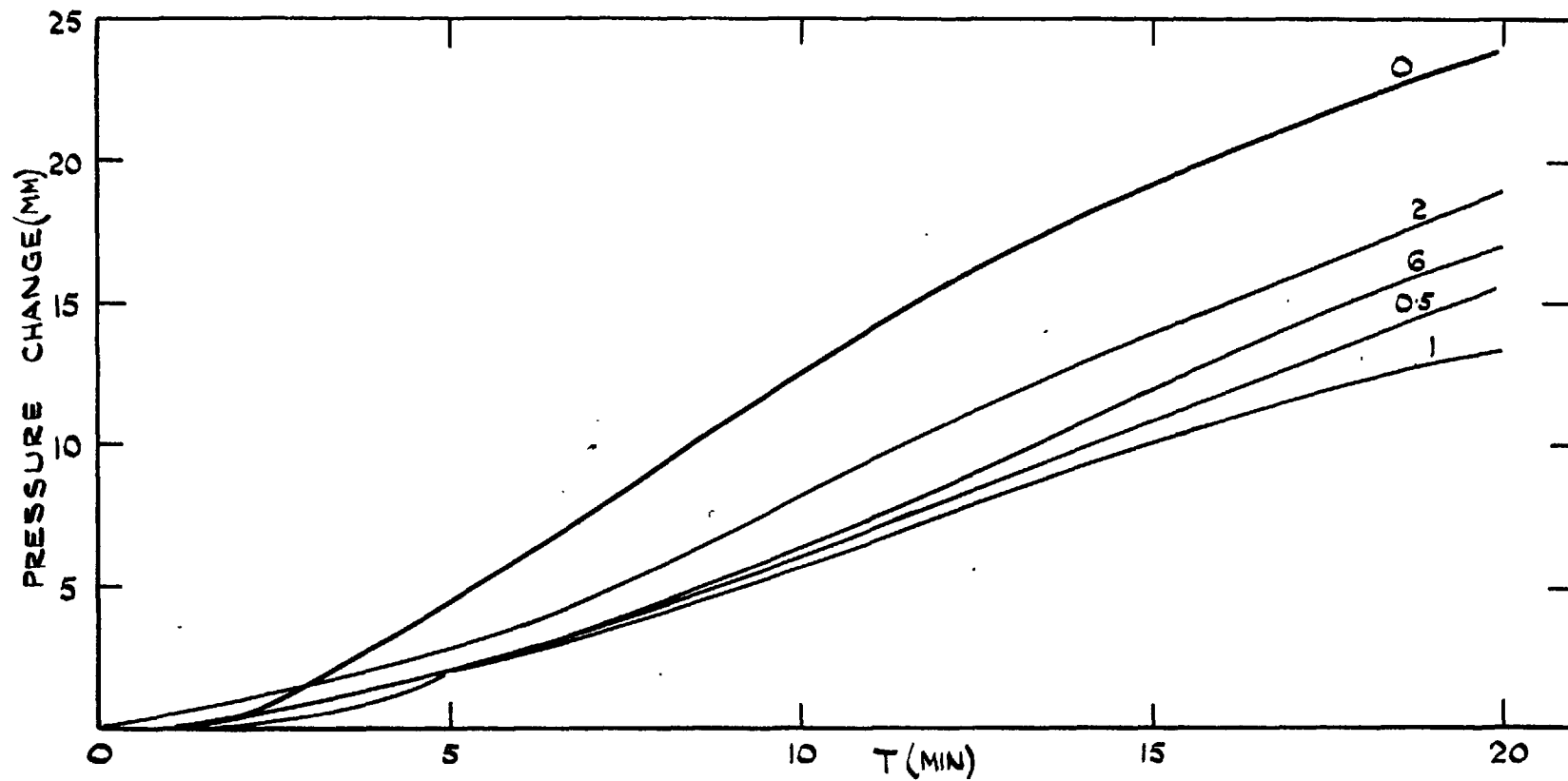
FIG. 33. THE OXIDATION OF FORMALDEHYDE IN THE PRESENCE OF DIFLUORODIBROMOMETHANE. PRESSURE-TIME CURVES. $T = 315°C.$ $H.CHO = 100MM.$ $O_2 = 100MM.$ CF_2Br_2 AS SHOWN (MM).
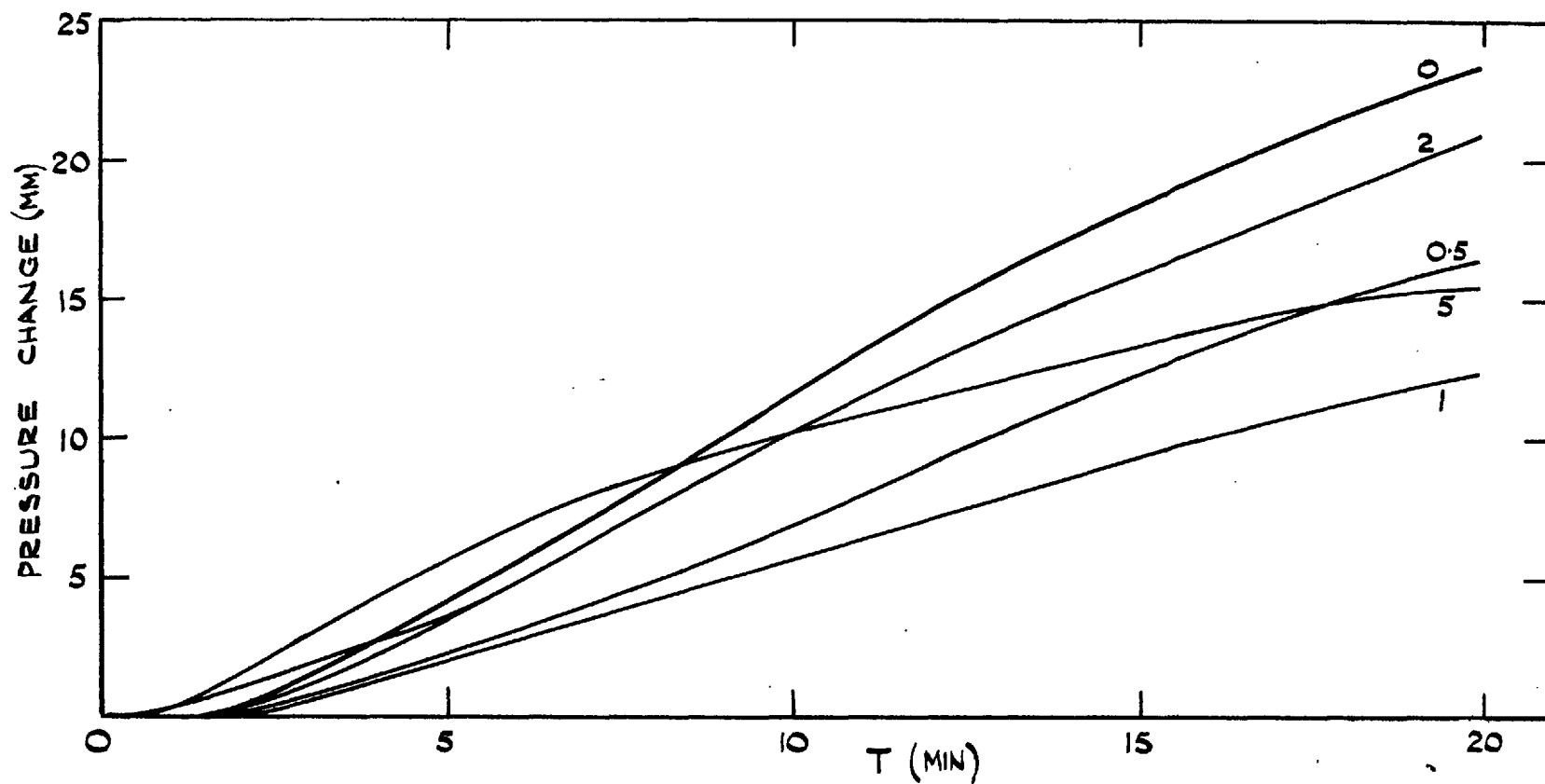
FIG.34. THE OXIDATION OF FORMALDEHYDE IN THE PRESENCE OF HYDROGEN BROMIDE. PRESSURE - TIME CURVES. T= 315°C H.CHO =100 MM. O_2 =100 MM. HBr AS SHOWN (MM)
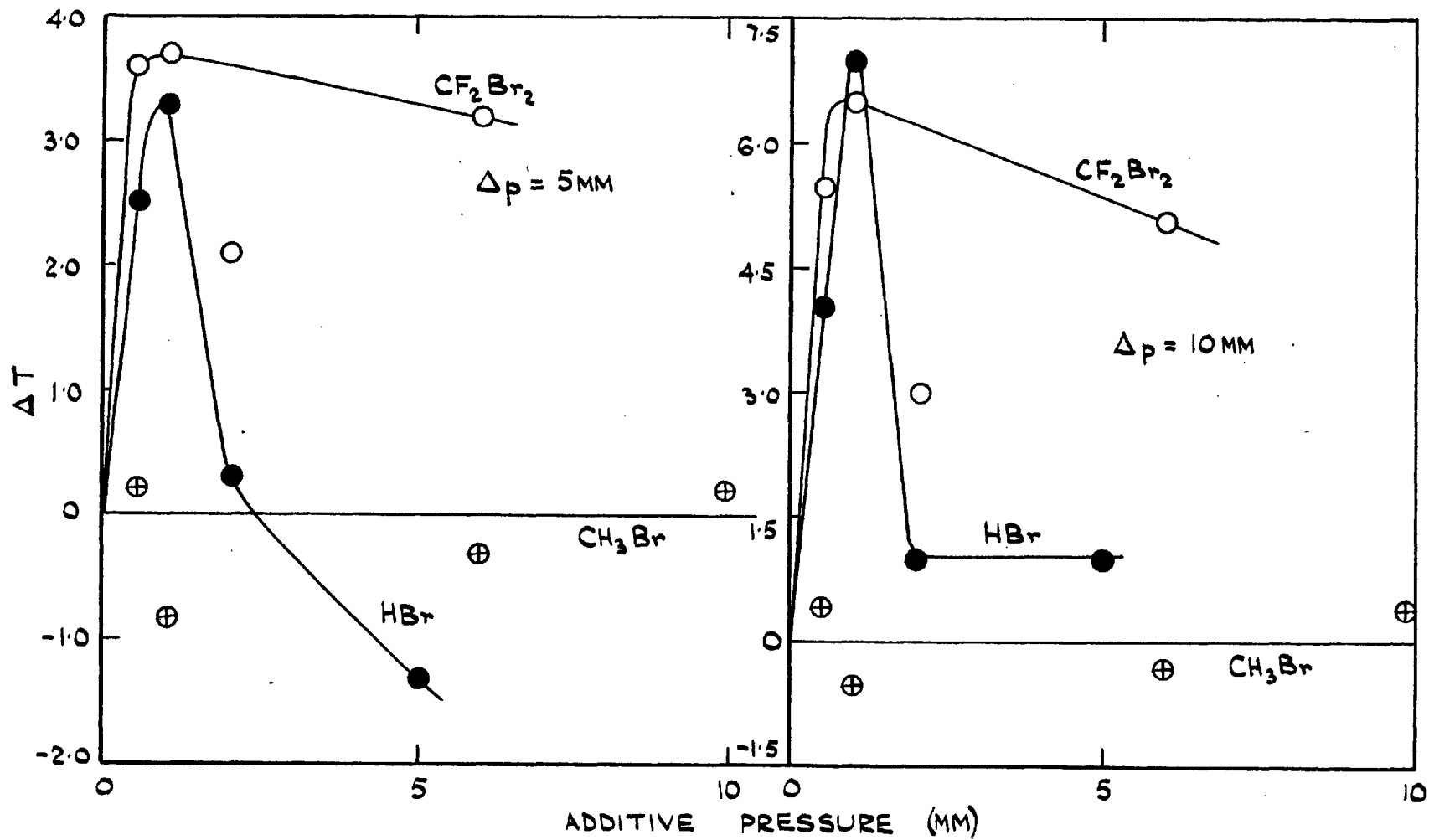
FIG. 35. THE OXIDATION OF FORMALDEHYDE IN THE PRESENCE OF VARIOUS ADDITIVES. T = 315°C. H.CHO = 100 MM. O_2 = 100 MM.
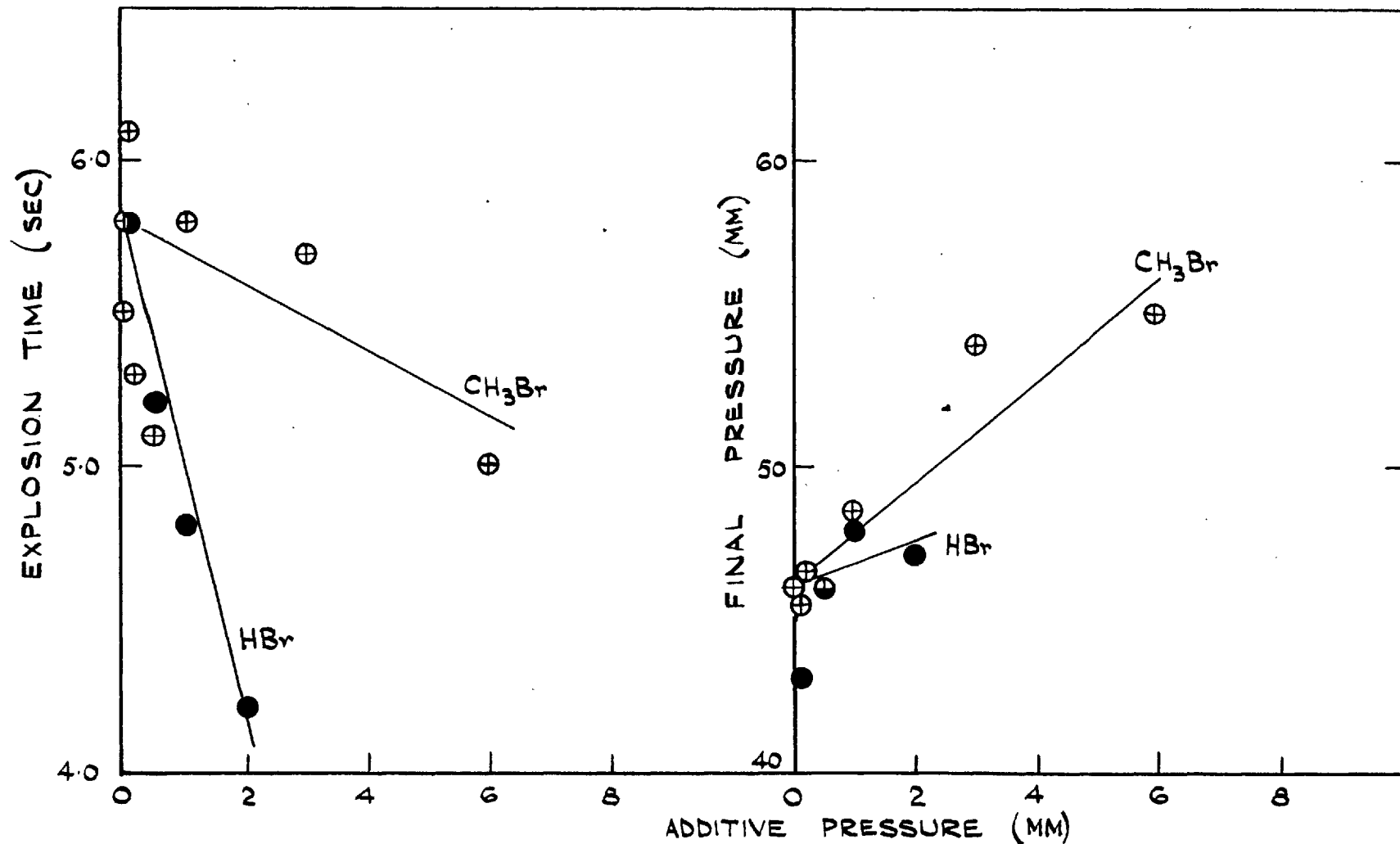
FIG.36. THE OXIDATION OF FORMALDEHYDE IN THE PRESENCE OF ADDITIVES. SPONTANEOUS IGNITION AT 515°C. THE INFLUENCE OF ADDITIVE ON THE EXPLOSION TIME AND MAXIMUM FINAL PRESSURE. HCHO=23MM. O_2=23 MM

F. THE OXIDATION OF ISOPROPANOL (at 355°C)

  1. The influence of halomethanes

The influence of methyl bromide and difluorodibromomethane on the oxidation of isopropanol at 355°C has been studied using mixtures of 100 mm. isopropanol, 100 mm. oxygen, 0.1 - 10 mm. additive. All parts of the apparatus coming into contact with isopropanol were heated to 68°C so that the desired 100 mm. pressure could be used. Some twenty fuel-oxygen runs had to be carried out before fairly reproducible pressure-time curves were obtained. The results are shown in Figs. 37, 39. The presence of methyl bromide (0.1 - 8.5 mm.) had very little effect on the reaction. Some pressures of additive accelerated the reaction slightly while others retarded it to a small extent. These effects are also shown in Fig. 40 where the time taken for a pressure change of 5 mm. to occur in the presence of additive minus the time taken for this change to occur in the normal oxidation is plotted against pressure of additive for the three additives used. Thus a negative value of $\triangle T$ means that the additive promoted the reaction and vice-versa. The values of $\triangle T$ obtained with methyl bromide are scattered about the zero line as shown. Methyl bromide thus had no well-defined effect on the reaction.

Dibromodifluoromethane (0.3 - 3.7 mm.) also had virtually no effect on the reaction, the pressure-time curves being almost identical in every case. This is also shown in Fig. 40 where $\triangle T = 0.4$ min. for the three additive pressures used. This difference is not significant in view of the observed variability in the results as a whole.

2. The influence of hydrogen bromide

The presence of hydrogen bromide (0.1 - 7.8 mm.) accelerated the reaction, the extent of the acceleration increasing steadily with additive pressure. This is seen in Figs. 38, 40. 0.1 - 2 mm. had only a very small promoting effect on the reaction but 7.8 mm. had a pronounced promoting influence. However the promoting influence per unit concentration of hydrogen bromide was greatest from 0 - 1 mm. and then fell off slightly over 1 - 8 mm. as shown in Fig. 40. The maximum rate obtained during the reaction was not appreciably affected by the presence of additive.
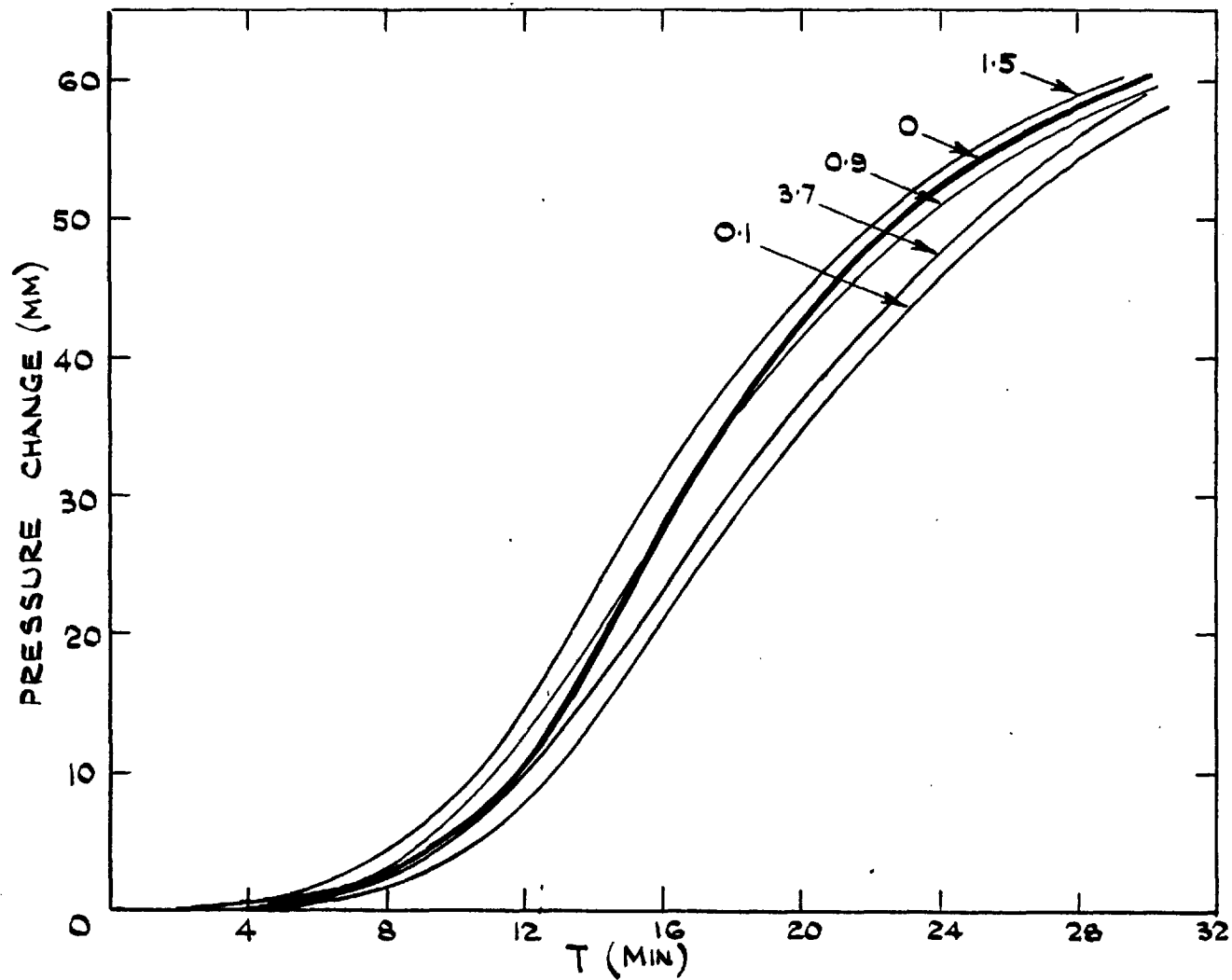
FIG. 37. THE OXIDATION OF ISOPROPANOL IN THE PRESENCE OF METHYL BROMIDE. PRESSURE - TIME CURVES.
$T = 355°C$ $(CH_3)_2 CHOH = 100$ MM. $O_2 = 100$ MM. CH_3Br AS SHOWN (MM).
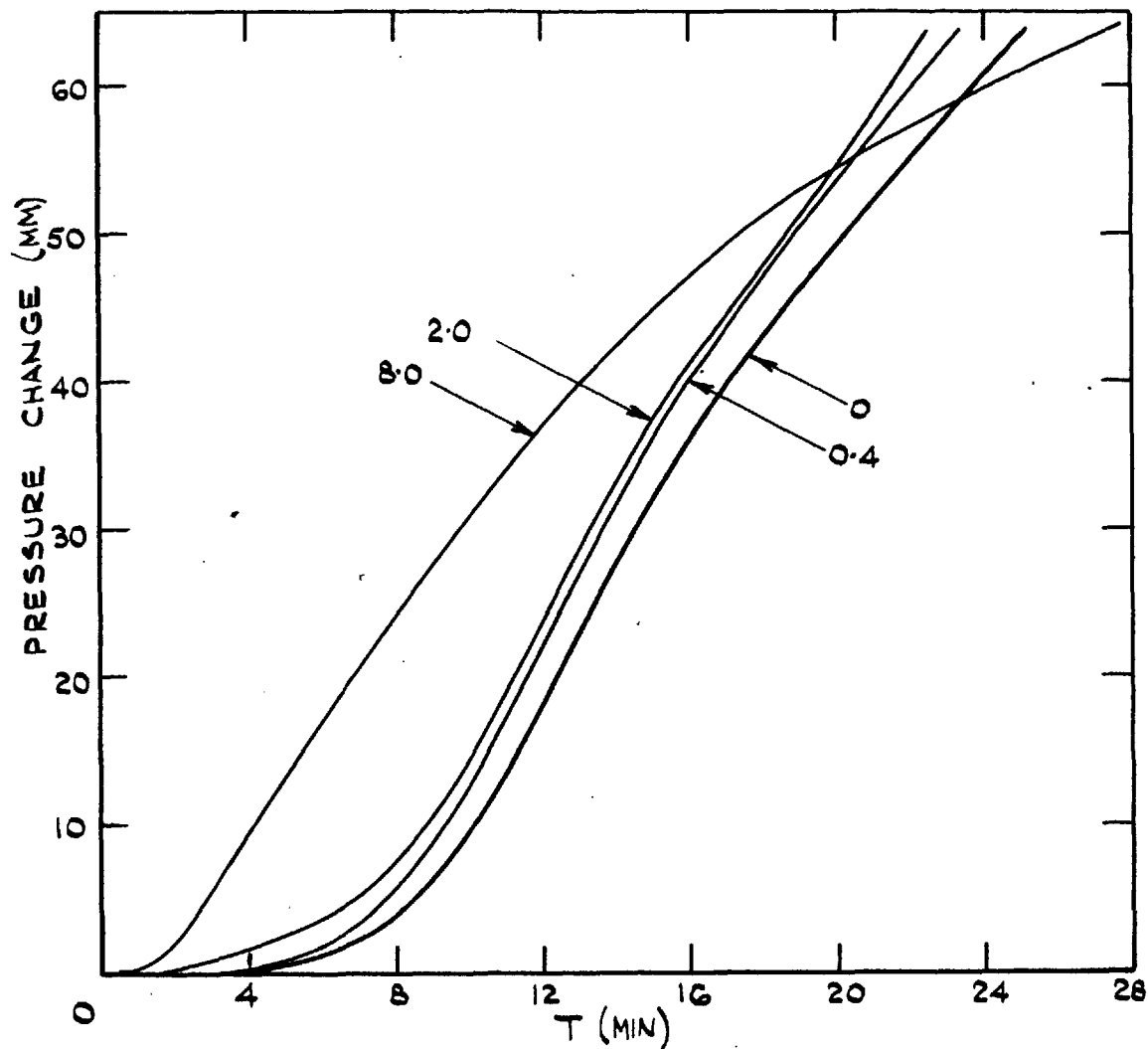
FIG. 3B. THE OXIDATION OF ISOPROPANOL IN THE PRESENCE OF
HYDROGEN BROMIDE. PRESSURE- TIME CURVES.
T = 355°C $(CH_3)_2$ CHOH = 100MM O_2 = 100MM.   HBr AS SHOWN (MM)
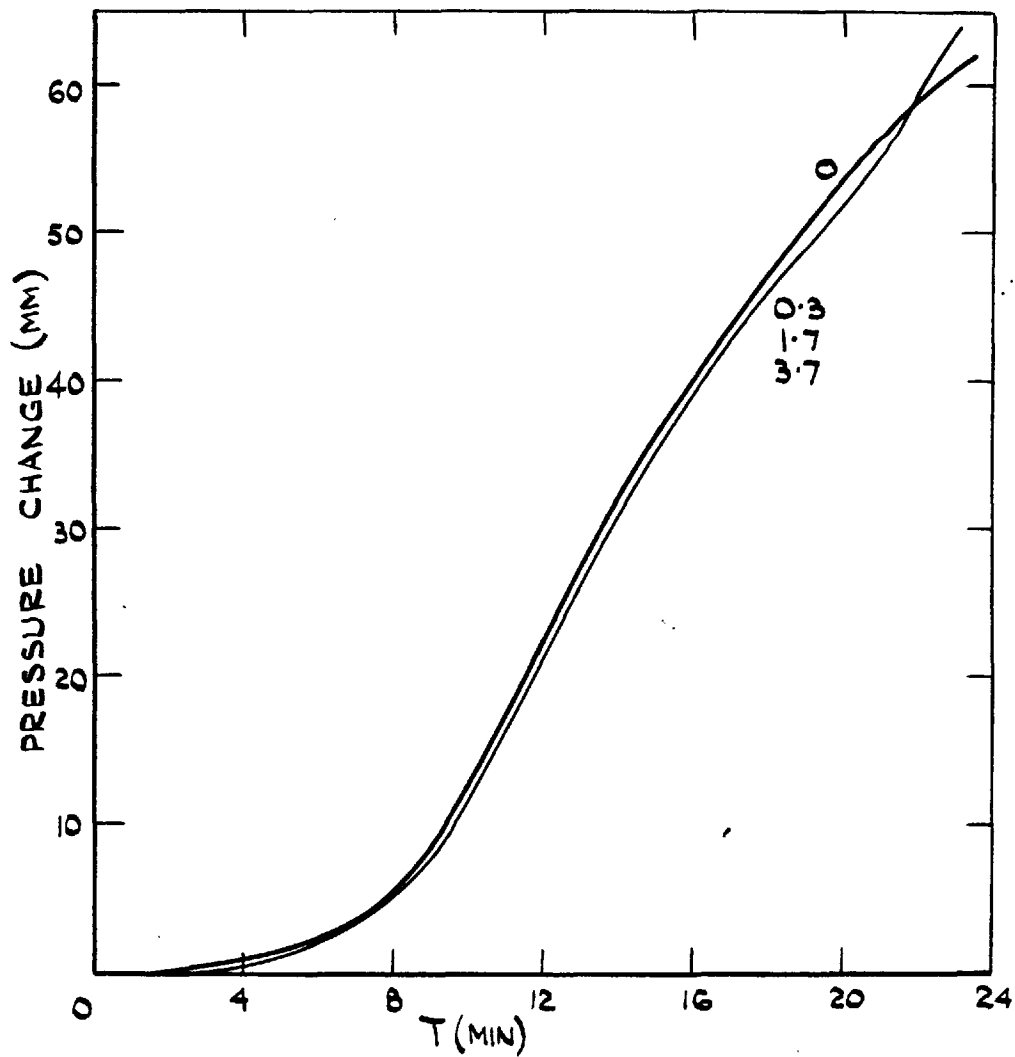
FIG. 39. THE OXIDATION OF ISOPROPANOL IN THE PRESENCE OF DIFLUORODIBROMOMETHANE. PRESSURE-TIME CURVES. T = 355°C. $(CH_3)_2$ CHOH = 100MM. O_2 = 100MM. CF_2Br_2 AS SHOWN (MM).
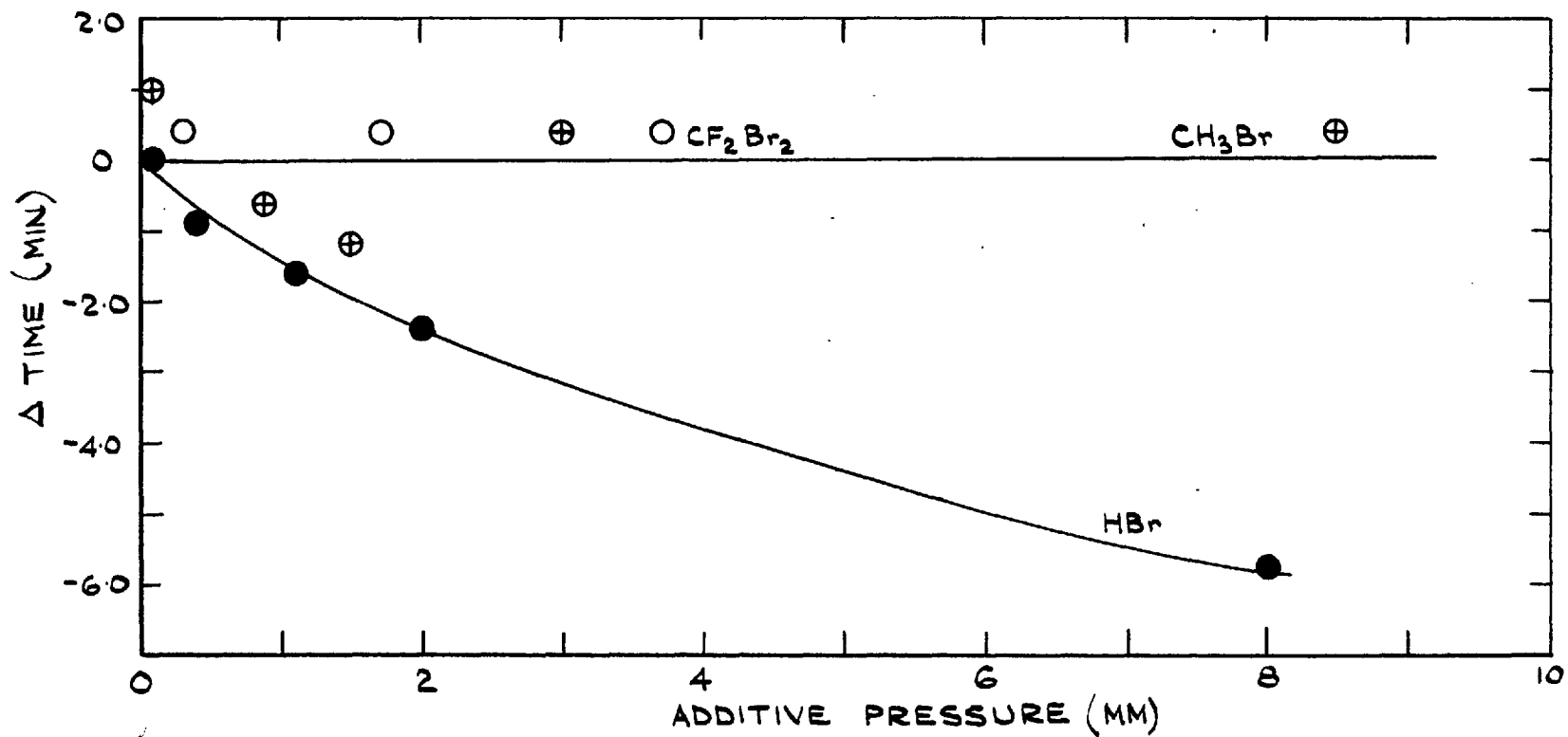
FIG.40. THE OXIDATION OF ISOPROPANOL IN THE PRESENCE OF ADDITIVES.
T= 355°C. $(CH_3)_2$ CHOH = 100 MM. O_2 = 100 MM.

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G. THE OXIDATION OF ETHANE (at 416°C)

1. The influence of halomethanes

The influence of methyl bromide, methylene dibromide, chlorobromomethane, and difluorodibromomethane on the oxidation of ethane at 416°C has been investigated. Mixtures of 100 mm. ethane, 100 mm. oxygen, 0.2 - 10 mm. additive were used and the pressure-time curve was obtained on each occasion. The results are shown in Figs. 41-44. All pressures of all the additives accelerated the reaction, the major part of the pressure change occurring progressively earlier as the additive pressure was increased. These effects are also shown in Fig. 47 where the time taken for a pressure change of 5 mm. to occur in the normal reaction minus the time taken for this pressure change to occur in the reaction in the presence of additive is plotted against additive pressure. Positive values of ΔT thus denote acceleration by the additive and vice-versa. With all the halomethanes, ΔT increased steadily with additive pressure as shown. The order of effectiveness of the additives in promoting the reaction was:

$$CF_2Br_2 > CH_2Br_2 > CH_2BrCl > CH_3Br$$
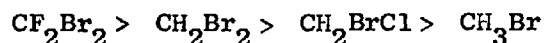
The effect of the additives on the maximum rate of pressure change observed is shown in Fig. 46. The halomethanes all reduced the maximum rate slightly at low pressures but increased the maximum rate appreciably at high pressures, the rate increasing roughly linearly with additive pressure. The order of effectiveness was the same as above.

The effect of the additives on the maximum pressure change observed is shown in Fig. 48. In all cases the pressure change increased steadily with additive pressure. Again the order of

effectiveness of the additives in increasing the maximum pressure change was the same as above.

2. <u>The influence of hydrogen bromide</u>

Hydrogen bromide (0.2 - 5 mm.) also accelerated the reaction, the major part of the pressure change occurring progressively earlier as the additive pressure was increased. However it's accelerating influence was far larger than that of the halomethanes. This is clearly shown in the pressure-time curves (Fig. 45) and in Figs. 46 - 48. Thus ΔT increased sharply with pressure of additive, 0.5 mm. additive giving a value of 9.5 min. At higher hydrogen bromide pressures, the curve flattened off close to the maximum possible value of 13.2 min. However, low pressures of hydrogen bromide (0.5 mm.) also reduced slightly the maximum rate observed but higher pressures increased the maximum rate markedly. The presence of low pressures of hydrogen bromide increased the maximum pressure change observed slightly but higher pressures had little effect on this change.
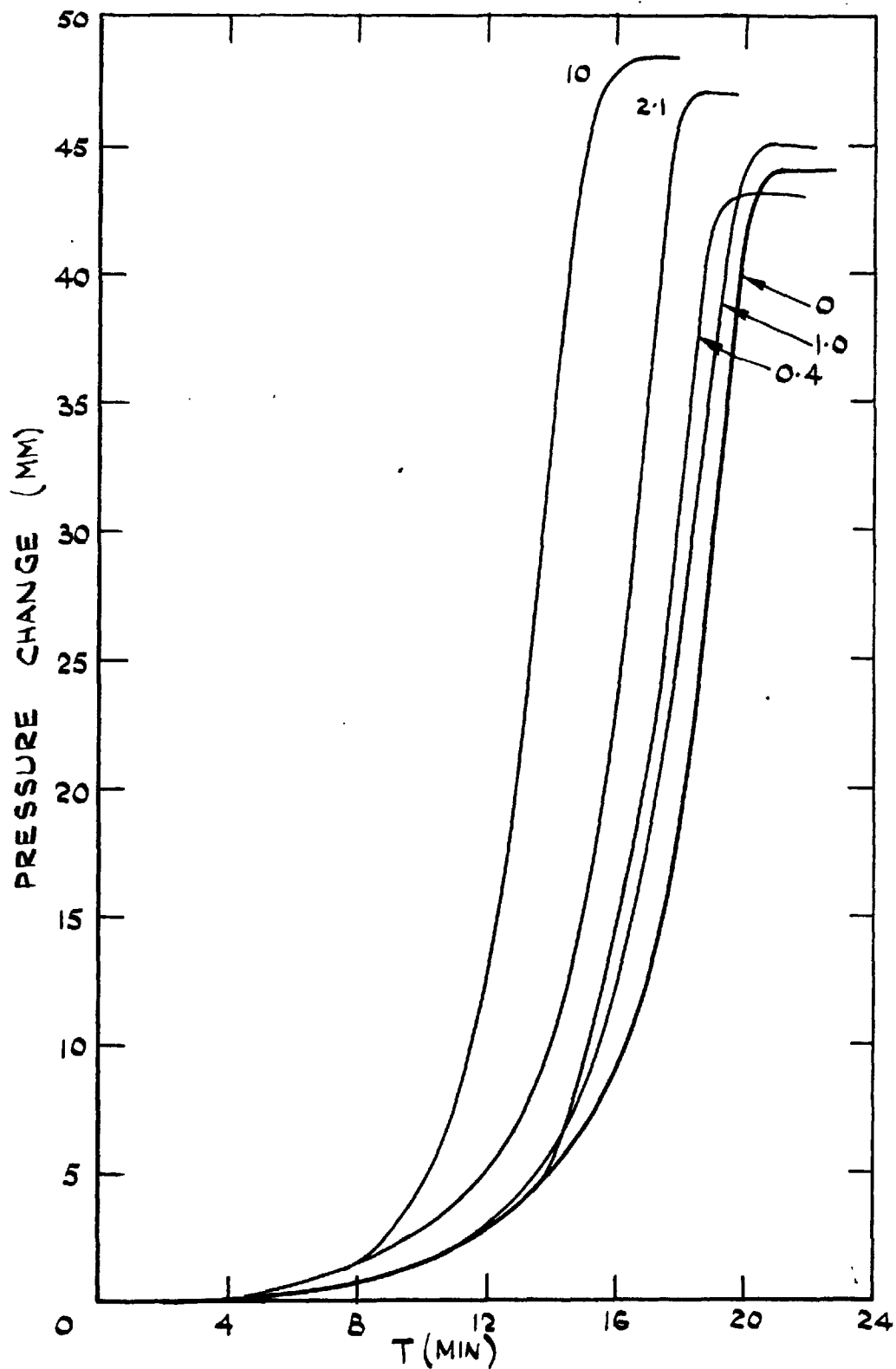
FIG. 41. THE OXIDATION OF ETHANE IN THE
PRESENCE OF METHYL BROMIDE.
PRESSURE-TIME CURVES. T=416°C.
$C_2H_6 = 100$ MM. $O_2 = 100$ MM. CH_3Br AS SHOWN (MM).
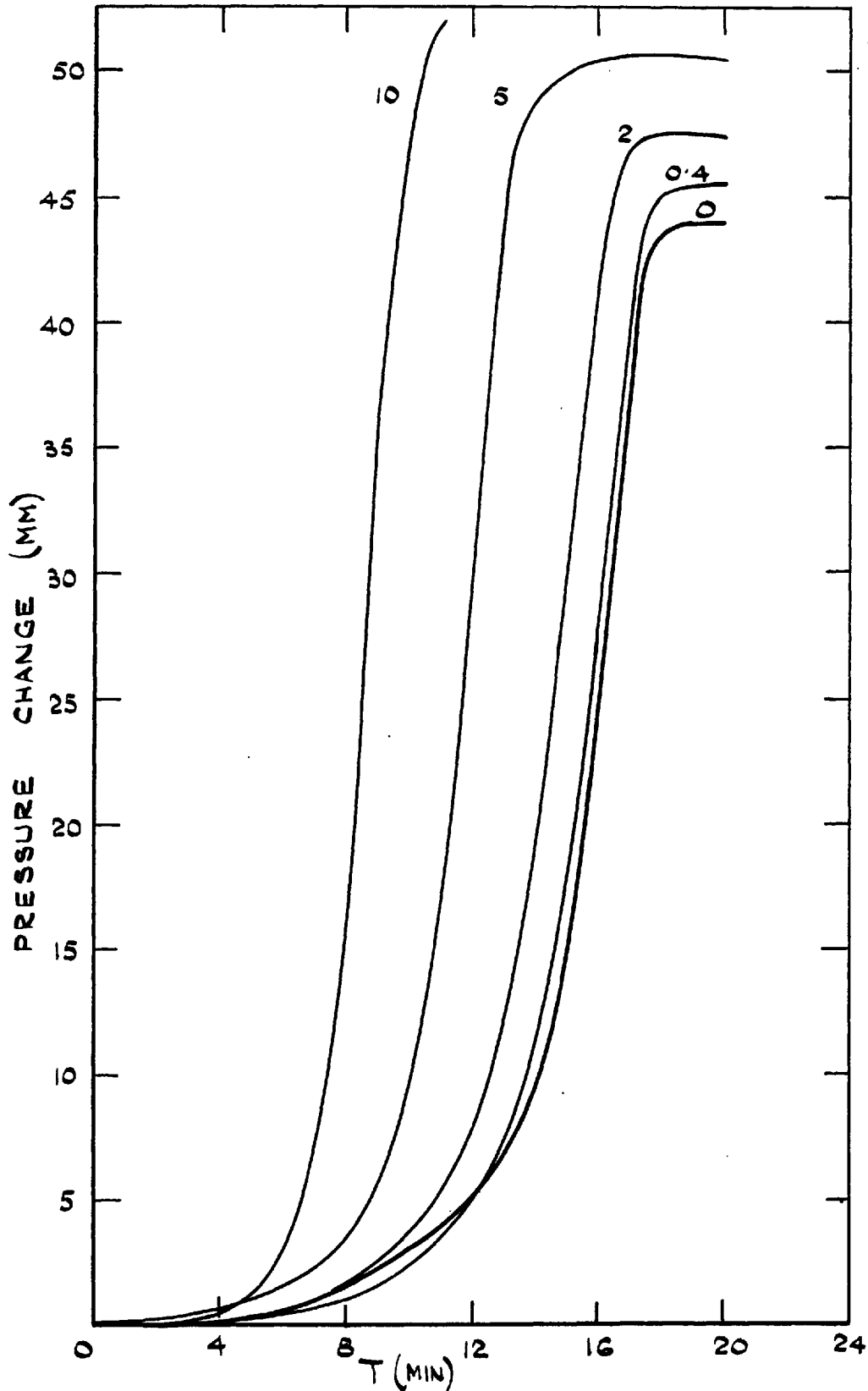
FIG.42. THE OXIDATION OF ETHANE IN THE
PRESENCE OF CHLOROBROMOMETHANE.
PRESSURE – TIME CURVES. T = 416°C.
C_2H_6 = 100 MM. O_2 = 100 MM. CH_2BrCl AS SHOWN (MM)
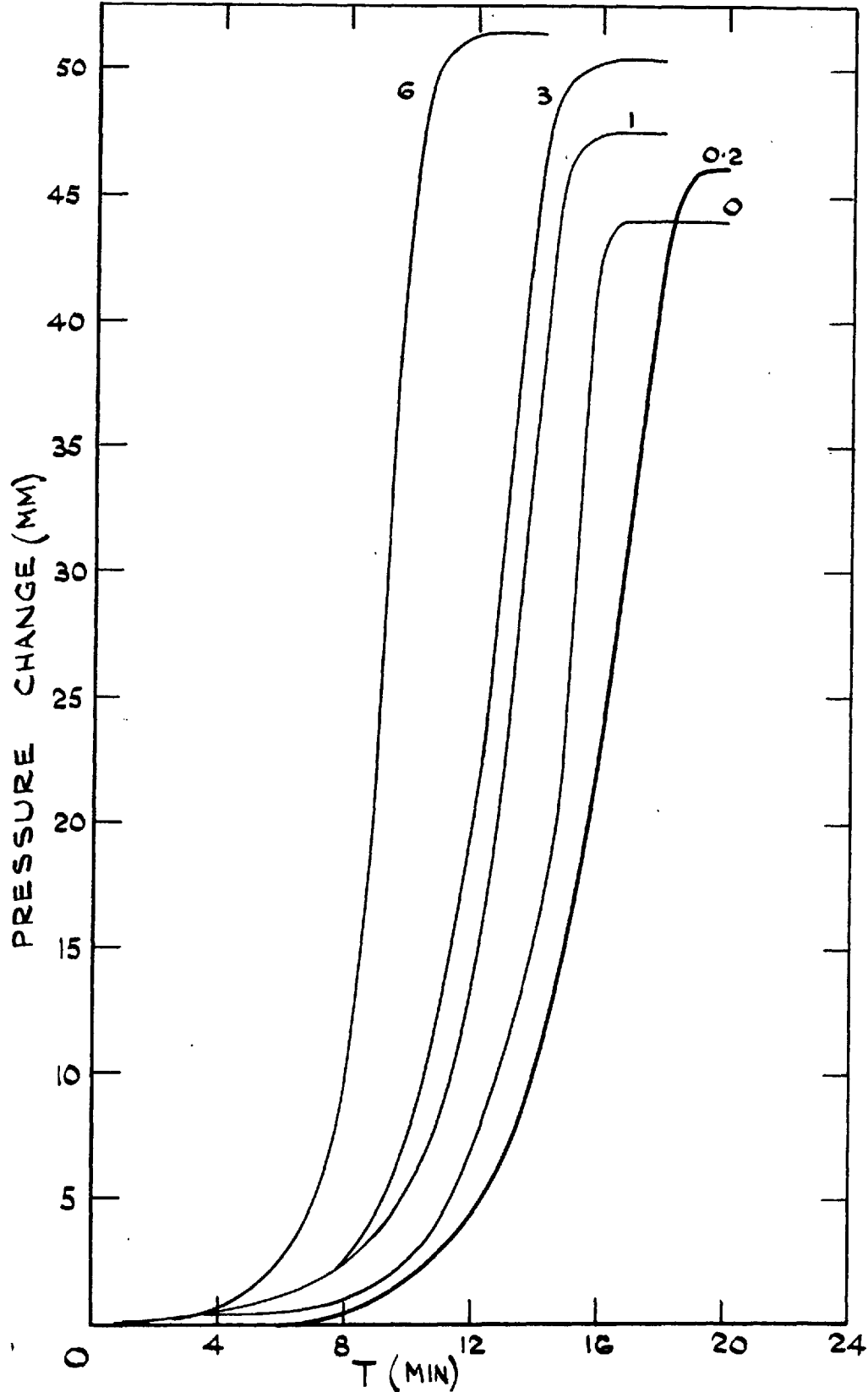
FIG. 43. THE OXIDATION OF ETHANE IN THE
PRESENCE OF METHYLENE DIBROMIDE.
PRESSURE – TIME CURVES. T = 416°C.
C_2H_6 = 100MM. O_2 = 100 MM. CH_2Br_2 AS SHOWN (MM)
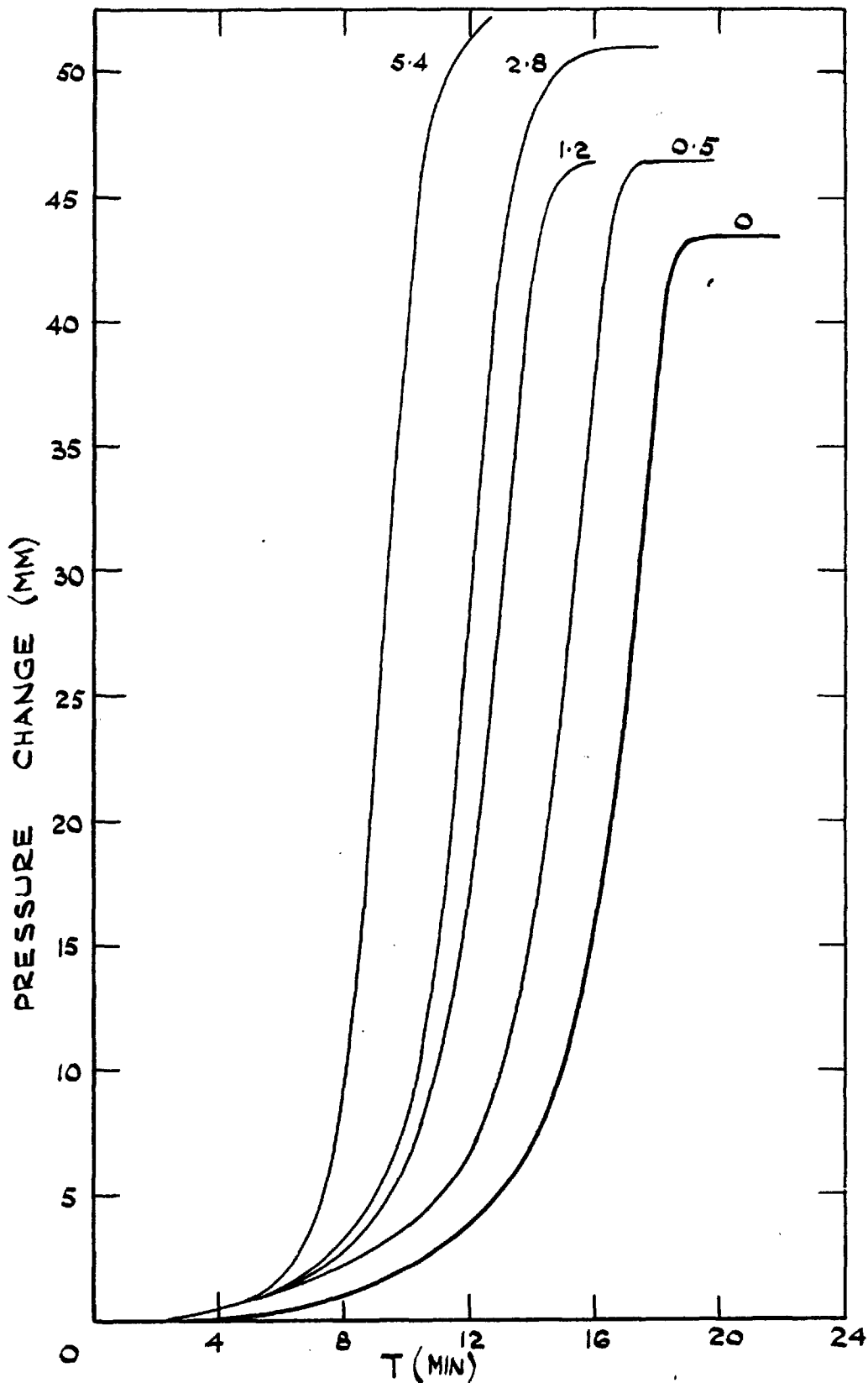
FIG. 44. THE OXIDATION OF ETHANE IN THE
PRESENCE OF DIBROMODIFLUOROMETHANE.
PRESSURE – TIME CURVES. T = 416°C.
$C_2H_6 = 100$ MM. $O_2 = 100$ MM. CF_2Br_2 AS SHOWN (MM).
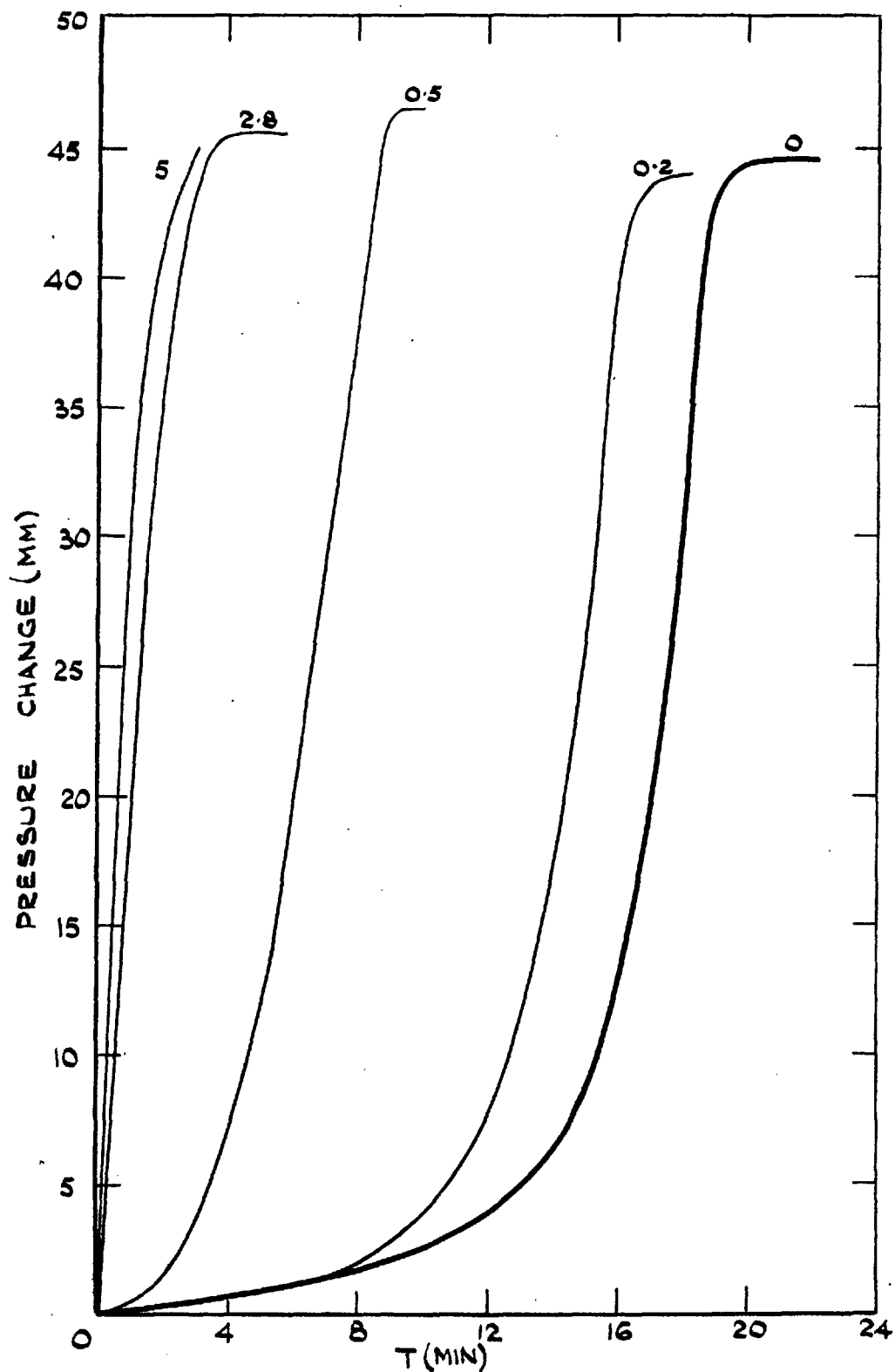
FIG.45. THE OXIDATION OF ETHANE IN THE PRESENCE OF HYDROGEN BROMIDE. PRESSURE-TIME CURVES. T = 416°C. C_2H_6 = 100MM O_2 = 100MM. HBr AS SHOWN (MM).
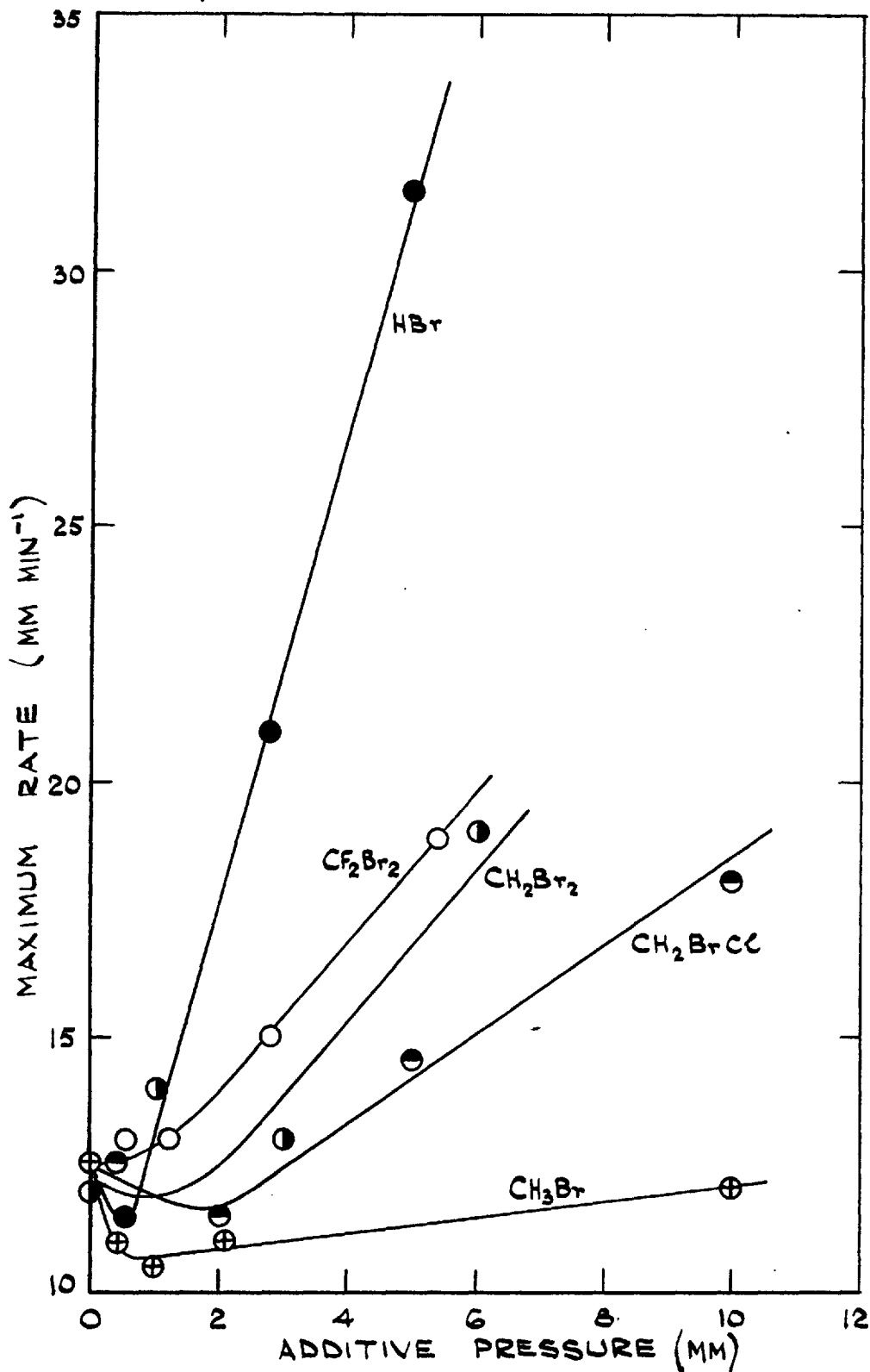
FIG.46. THE OXIDATION OF ETHANE IN THE PRESENCE OF ADDITIVES. T = 416°C. $C_2H_6 = 100$ MM. $O_2 = 100$ MM.
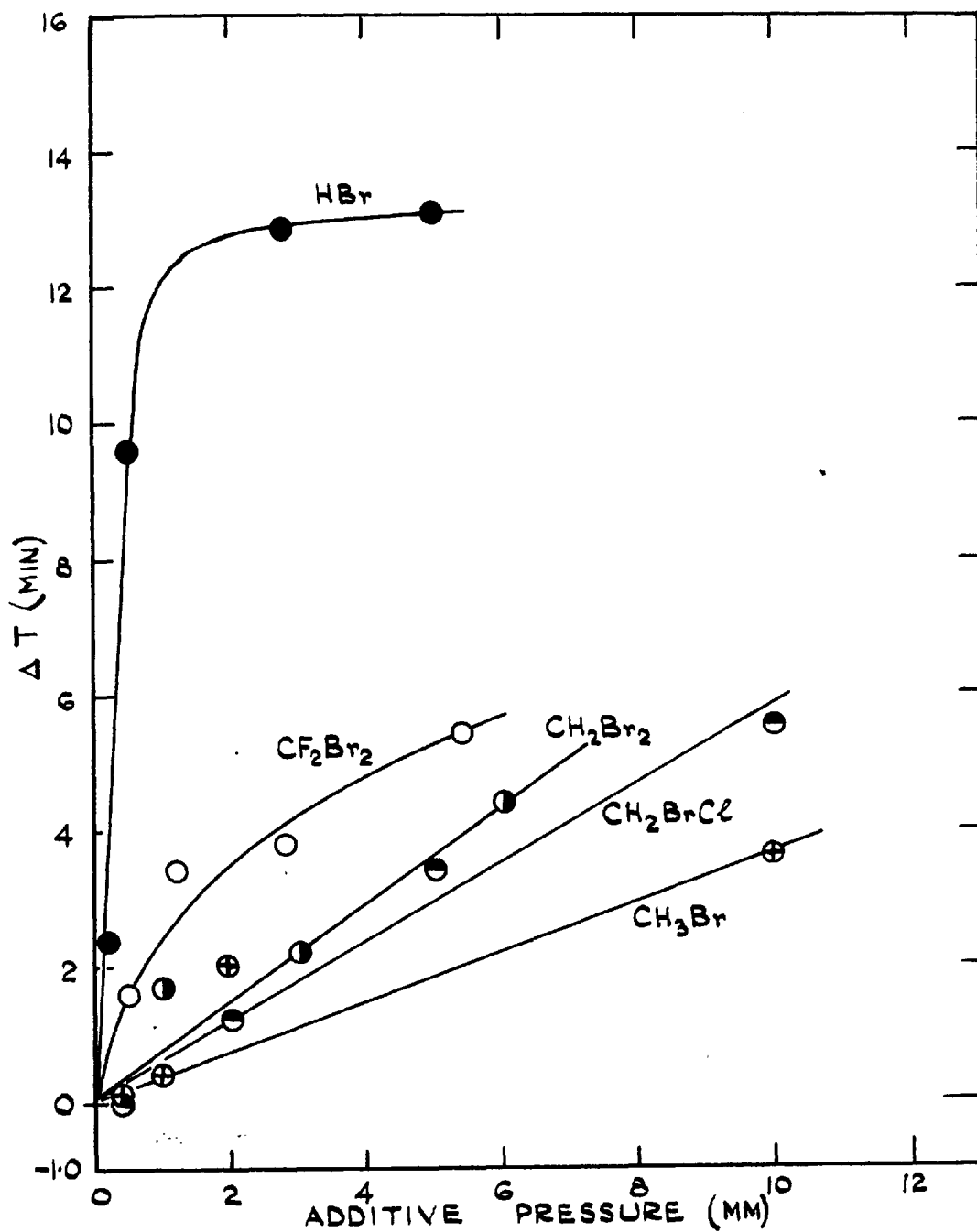
FIG. 47. THE OXIDATION OF ETHANE IN THE PRESENCE OF ADDITIVES. T = 416°C. C_2H_6 = 100 MM. O_2 = 100 MM.
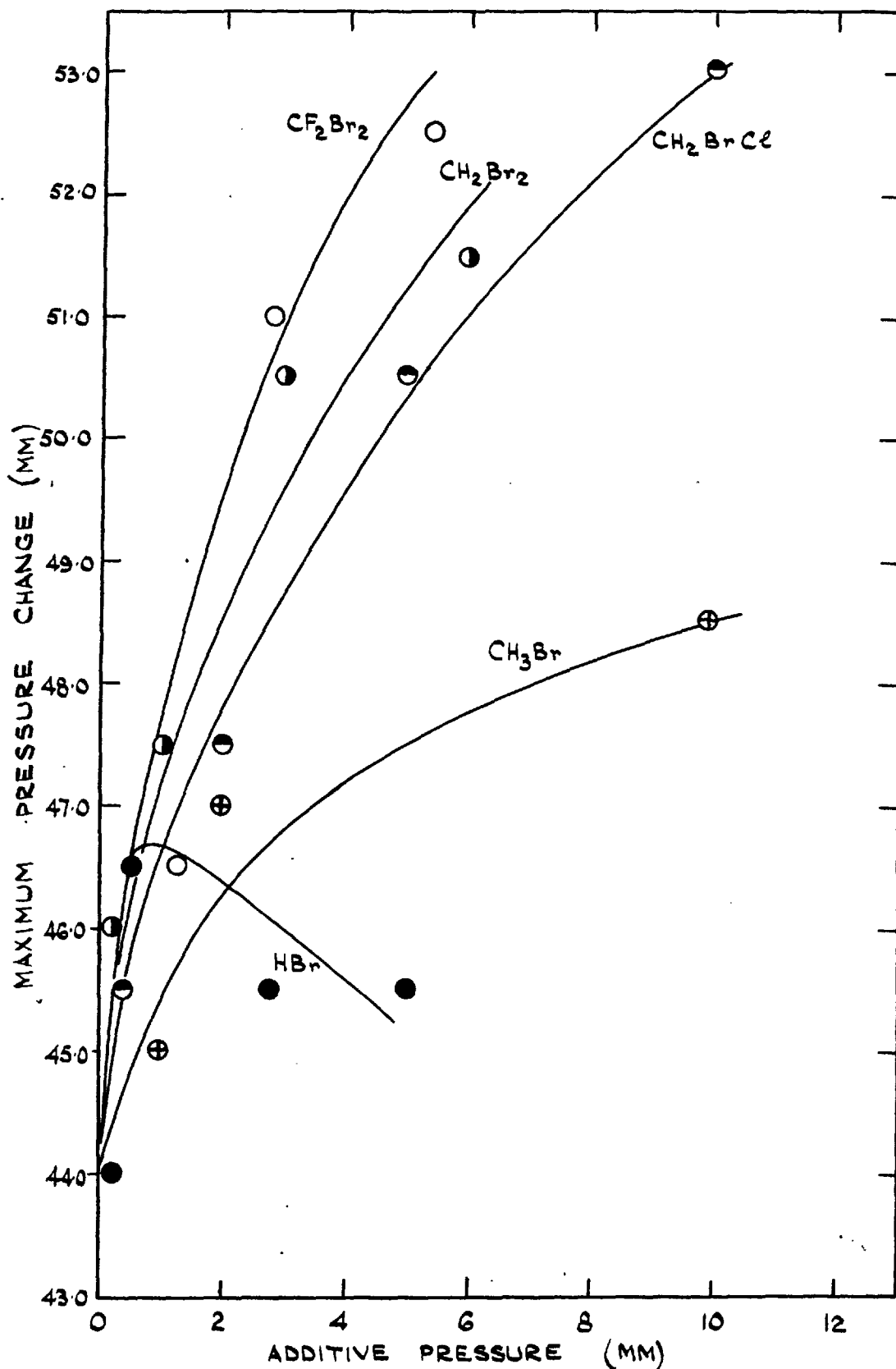
FIG.48. THE OXIDATION OF ETHANE IN THE PRESENCE
OF ADDITIVES. T = 416°C. C_2H_6 = 100MM. O_2 = 100MM.

H. THE OXIDATION OF METHANE (at 510°C)

1. The influence of halomethanes and hydrogen bromide

The influence of methyl bromide, methylene dibromide, chlorobromomethane, difluorodibromomethane, and hydrogen bromide on the oxidation of methane at 510°C has been investigated using mixtures of 100 mm. methane, 100 mm. oxygen, 0.1 - 18 mm. additive. A pressure-time curve was obtained on each occasion and the results are shown in Figs. 49-53. The normal oxidation curve was sigmoid in shape. The additives had rather complex effects on the pressure-time curve depending upon the pressure employed. These effects can be summarized as follows:

1) Very low pressures of additive retarded the reaction at all times.

2) Rather higher pressures initiated the reaction but subsequently retarded the reaction at all stages.

3) Certain intermediate pressures of additive initiated the reaction but after a few minutes it proceeded at a slower rate than the normal reaction while later still the reaction again proceeded faster than the normal reaction.

4) High pressures of additive promoted the reaction at all stages.

The overall effect of each additive can thus be described in terms of the pressure ranges giving each of these effects, together with the additive pressure which exerted the maximum retarding effect. This data is given in Table 2.

TABLE 2

The Influence of Various Halomethanes and Hydrogen Bromide

on the Pressure-time Curve of the Oxidation of Methane

$T = 510°C.$ $CH_4 = 100$ mm., $O_2 = 100$ mm.

Pressure range of additive showing given effect (mm):					
Additive	1	Maximum retardation	2	3	4
CH_3Br	0.13 – 1.7	0.31	–	5	10 – 18
CH_2BrCl	0.1 – 0.2	0.2	0.4 – 2.0	4.5	–
CH_2Br_2	0.1	0.1	0.2 – 1.0	2	6
CF_2Br_2	–	0.5	0.5 – 2.1	–	6 – 10
HBr	0.1	0.25	0.25 – 10	–	–
Approx. range for effect	0.1 – 0.2	0.1 – 0.3	0.2 – 2.0	2.0 – 5.0	5.0–

The pressure ranges tabulated are naturally in terms of those additive pressures actually used but the actual boundary pressures will only be slightly different from these values. It is thus seen that the additives all had a rather similar effect on the oxidation of methane under these conditions. On the whole they all exerted the same type of effect over a given pressure range as shown in the table. The major exceptions to the classification given are:

1) Methyl bromide showed type 1 behaviour only in the range 0.1 - 2 mm.

2) Hydrogen bromide showed type 2 behaviour only in the range 0.2 - 10 mm.

The effects of these additives on the oxidation of methane are also shown in Figs. 54 - 56. Fig. 54 is a graph of the time taken for a pressure change of 5 mm. to occur in the reaction in the presence of additive minus the time taken for this pressure change to occur in the normal reaction plotted against the additive pressure for the five additives used. Positive values of ΔT thus mean that the additive exerted a retarding influence on the reaction. The peak on the curve for each additive corresponds to the pressure of the additive having the maximum retarding effect. These additive pressures are shown in Table 2. $\Delta T_{maximum}$ was largest for methyl bromide, -4.3 min., while the other additives all had approximately the same value of $\Delta T_{maximum}$ 1.7 - 2.1 min. The value of ΔT at an additive pressure of 0.1 mm. is a convenient measure of the retarding influence of the additive at low

concentration. The values obtained with these additives were:

TABLE 3

Values of ΔT at an Additive Pressure of 0.1 mm.

Additive	T (min.)
CH_3Br	0.2
CH_2Br_2	2.1
CH_2BrCl	0.3
HBr	0.8

Thus the order of effectiveness of the additives at low concentration in retarding the reaction was:

$$CH_2Br_2 > HBr > CH_2BrCl > CH_3Br$$
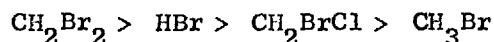
However, the retarding influence of methyl bromide was more pronounced at higher concentrations (0.2 - 0.3 mm.) where the other additives were less effective. At higher additive concentrations (0.3 - 5 mm.), the retarding influence decreased in all cases and thus ΔT also decreased and finally became negative as high pressures of all the additives promoted the reaction. At these higher pressures methylene dibromide, chlorobromomethane, and difluorodibromomethane all produced roughly the same value of ΔT for a given pressure while hydrogen bromide and methyl bromide both caused more positive values of ΔT because of their greater retarding influence in this pressure range.

The effect of additive pressure on the maximum rate of reaction is shown in Fig. 55. The maximum rate of the normal reaction was 7.5 mm. min.$^{-1}$. 0.1 - 0.3 mm. of any of the additives reduced the maximum rate to 1.0 - 1.5 mm. min.$^{-1}$. The change in the maximum rate

produced by 0.1 mm. additive is a convenient measure of the retarding influence of the additive at low concentration. The values obtained for the additives used were:

TABLE 4

Values of Δ (Maximum Rate) produced by 0.1 mm. Additive

Additive	(Max. rate) mm. min.$^{-1}$
CH_3Br	2.7
CH_2Br_2	5.5
CH_2BrCl	3.5
HBr	2.5

Thus the order of effectiveness of the additives at low concentration in decreasing the maximum rate of the reaction was:

$$CH_2Br_2 > CH_2BrCl > CH_3Br > HBr$$
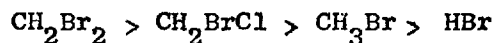
At higher additive pressures (0.3 - 5 mm.), the maximum rate increased steadily with additive pressure as shown. The rate of increase of the maximum rate with additive pressure was least with hydrogen bromide.

The effect of additive pressure on the maximum pressure change observed in the reaction is shown in Fig. 56. In the normal reaction, a pressure change of 16 mm. was observed. 0.1 - 0.3 mm. of any of the additives reduced the pressure change observed to 10.0 - 10.5 mm. The change in the maximum pressure change observed, produced by 0.1 mm. additive, is a convenient measure of the effect of low concentrations of additive on the maximum pressure change. The results obtained were:

TABLE 5

Values of the Change in the Maximum Pressure Change

observed produced by 0.1 mm. Additive

Additive	$\triangle (\triangle p \text{ max.})$ mm.
CH_3Br	4.5
CH_2Br_2	5.5
CH_2BrCl	4.5
HBr	3.0

The order of effectiveness was thus:

$$CH_2Br_2 > CH_2BrCl, CH_3Br > HBr$$
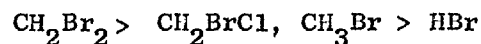
Higher pressures of additive (0.3 - 5 mm.) caused the maximum pressure change to increase steadily with additive pressure as shown. The rate of increase of the maximum pressure change with additive pressure was least with hydrogen bromide.

It is thus seen that low pressures of additive retarded the reaction and also appreciably reduced the maximum pressure change observed, while conversely, high pressures of additive accelerated the reaction and increased the maximum pressure change observed.
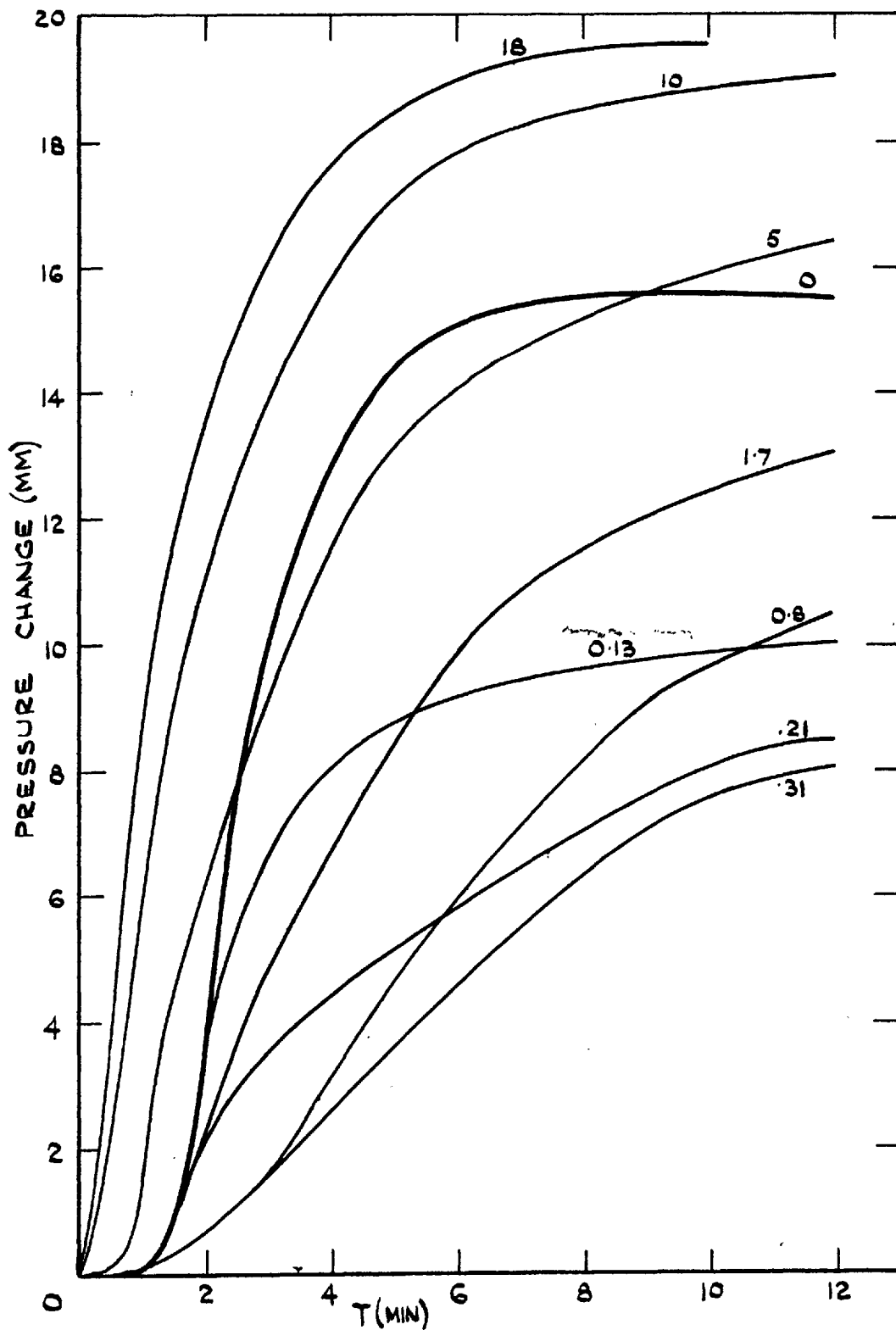
FIG.49. THE OXIDATION OF METHANE IN THE PRESENCE
OF METHYL BROMIDE. PRESSURE-TIME CURVES.
T = 510°C. CH_4 = 100MM. O_2 = 100MM. CH_3Br AS SHOWN (MM).
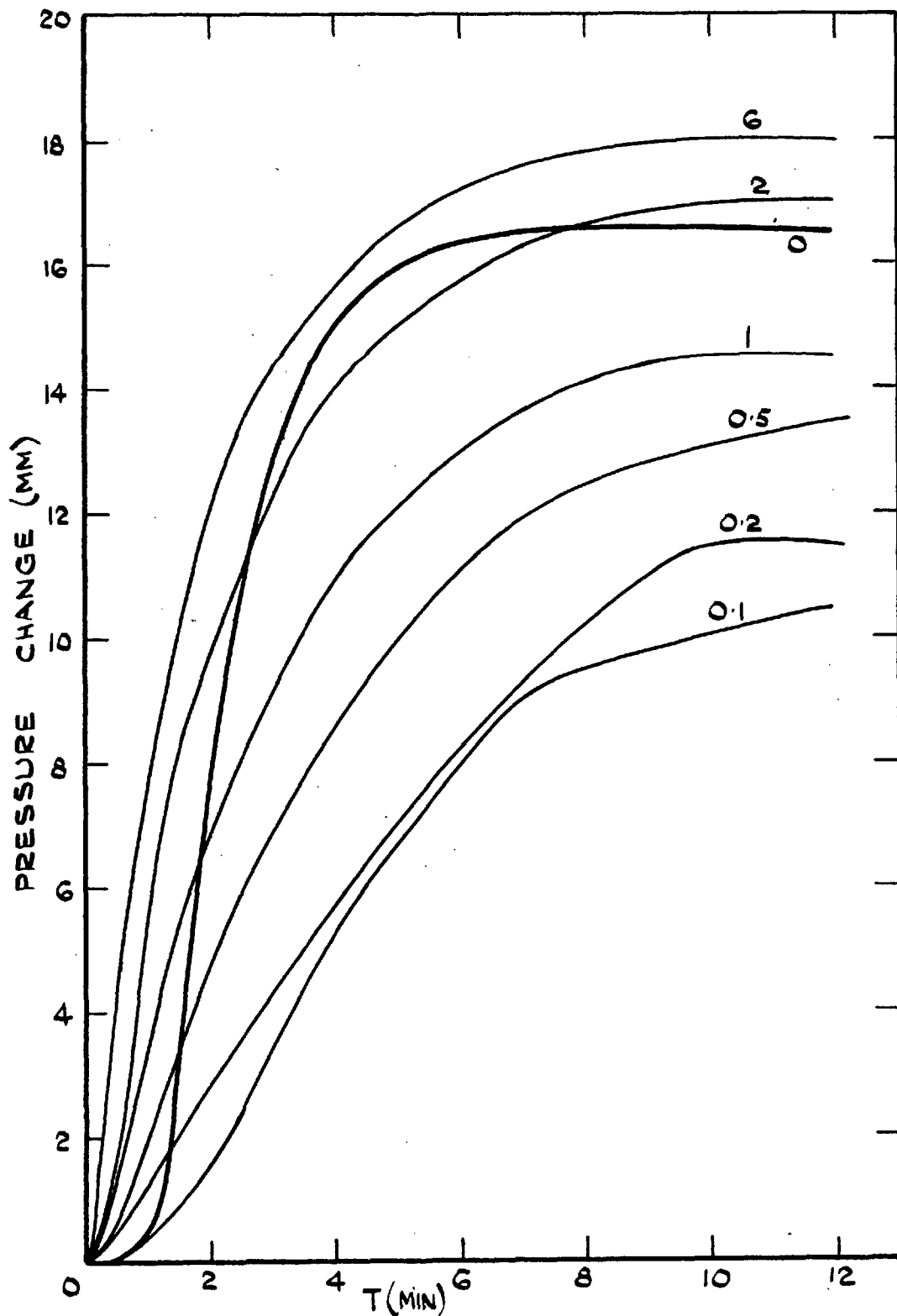
FIG.50. THE OXIDATION OF METHANE IN THE PRESENCE
OF METHYLENE DIBROMIDE. PRESSURE - TIME
CURVES. T = 510°C. CH_4 = 100MM. O_2 = 100MM.
CH_2Br_2 AS SHOWN (MM).
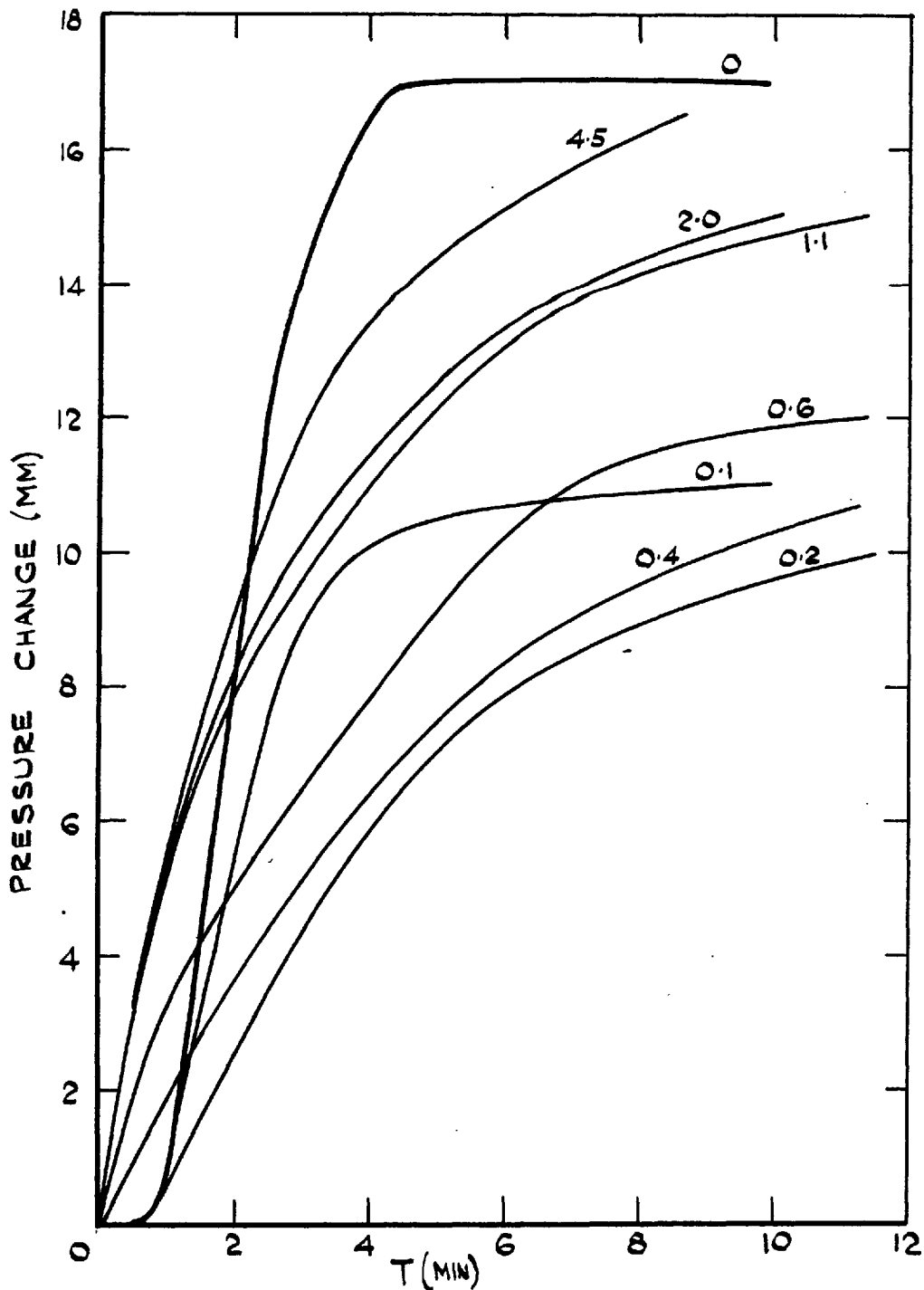
FIG.51. THE OXIDATION OF METHANE IN THE
PRESENCE OF CHLOROBROMOMETHANE.
PRESSURE-TIME CURVES.
T=510°C. CH_4 =100,MM. O_2 =100MM. CH_2BrCl AS SHOWN(MM).
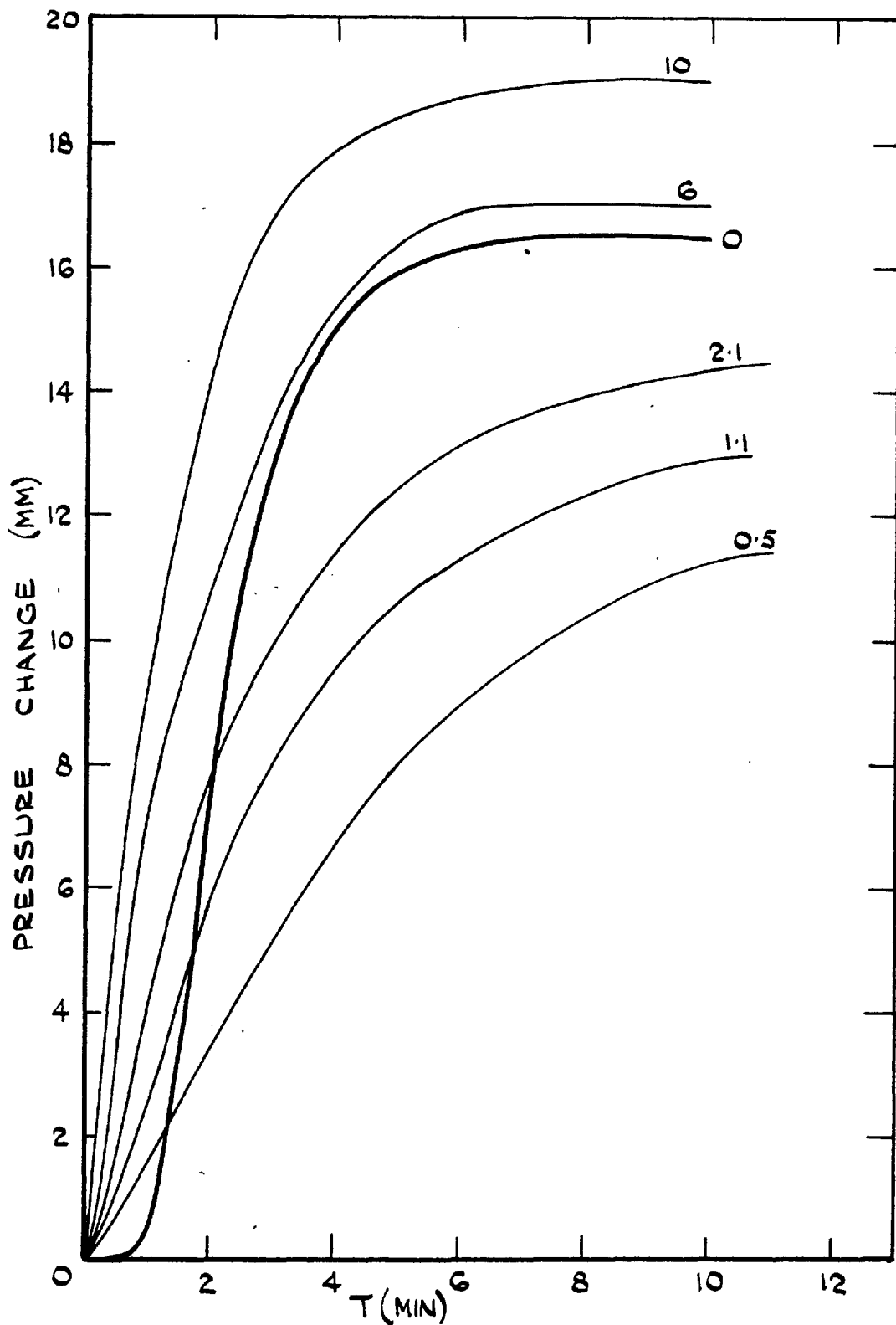
FIG. 52. THE OXIDATION OF METHANE IN THE PRESENCE OF DIFLUORODIBROMOMETHANE. PRESSURE – TIME CURVES. T = 510°C. CH_4 = 100 MM, O_2 = 100 MM. $CF_2 Br_2$ AS SHOWN (MM).
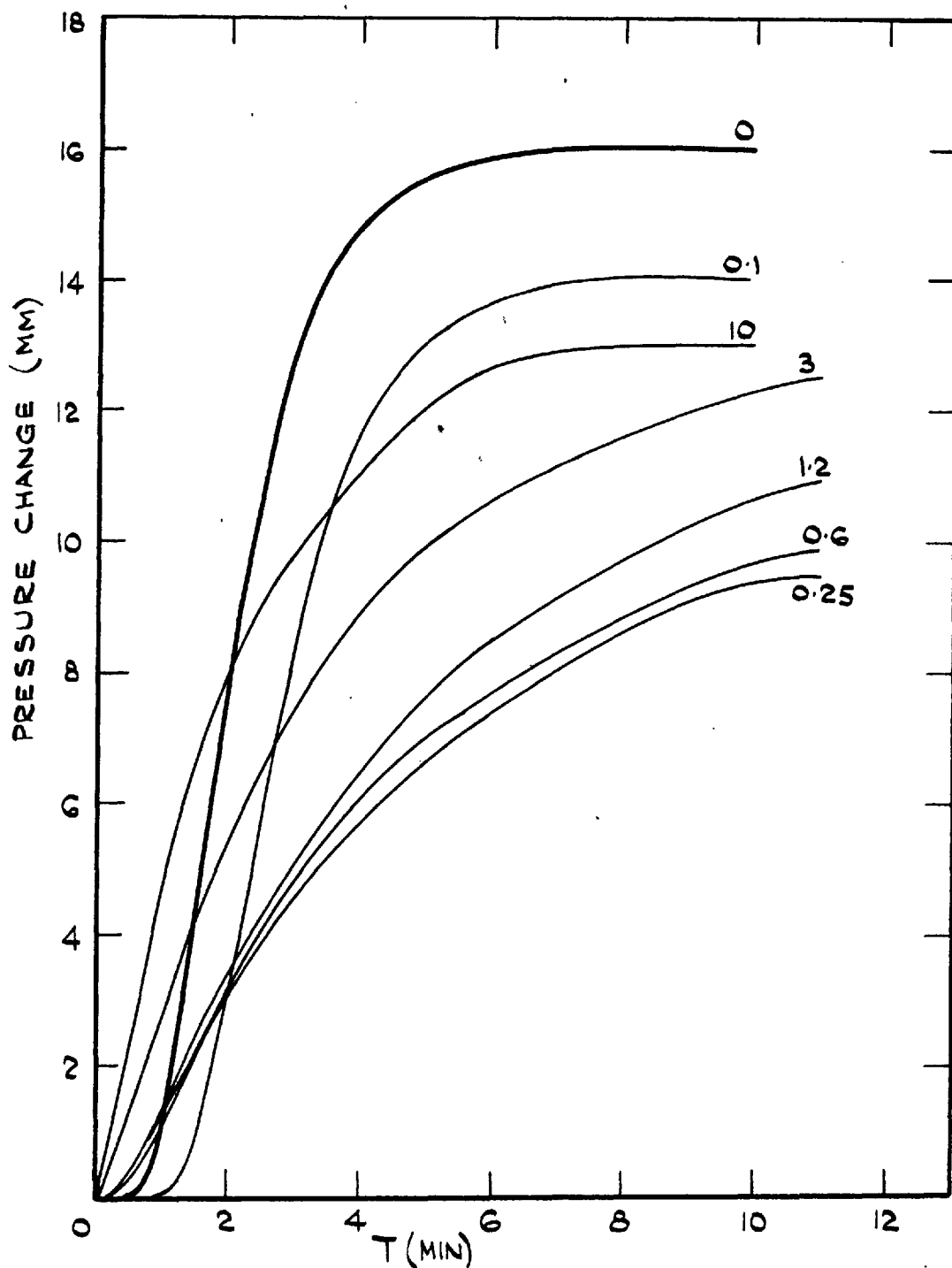
FIG.53. THE OXIDATION OF METHANE IN THE
PRESENCE OF HYDROGEN BROMIDE.
PRESSURE – TIME CURVES. T = 510°C.
CH_4 = 100 MM. O_2 = 100 MM. HBr AS SHOWN (MM).
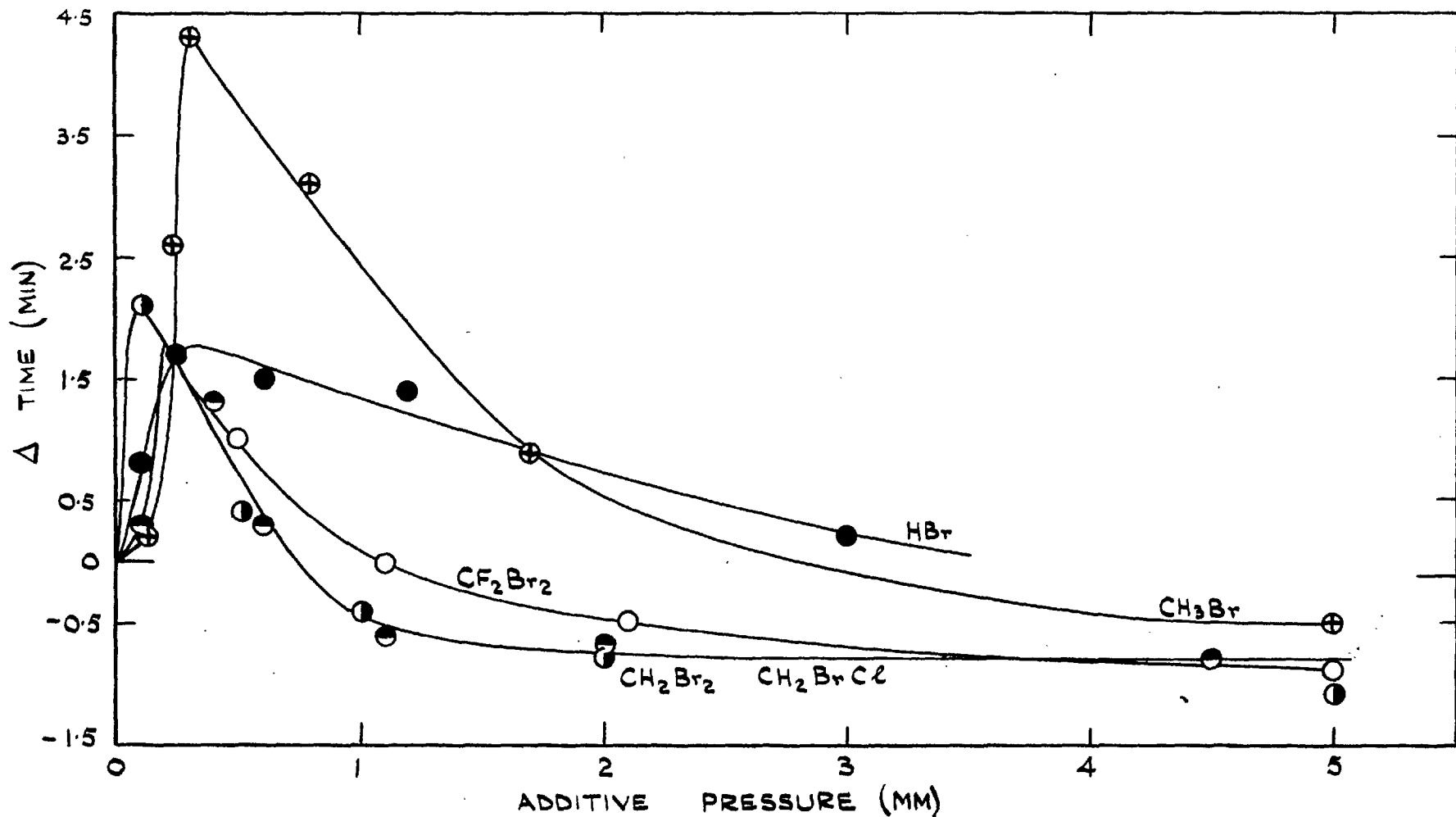
FIG. 54. THE OXIDATION OF METHANE IN THE PRESENCE OF ADDITIVES. T = 510°C.   CH₄ = 100 MM.   O₂ = 100 MM.

The figure shows Δ TIME (MIN) on the vertical axis ranging from -1.5 to 4.5, and ADDITIVE PRESSURE (MM) on the horizontal axis ranging from 0 to 5. Curves are labelled HBr, CF₂Br₂, CH₃Br, CH₂Br₂, and CH₂BrCl.
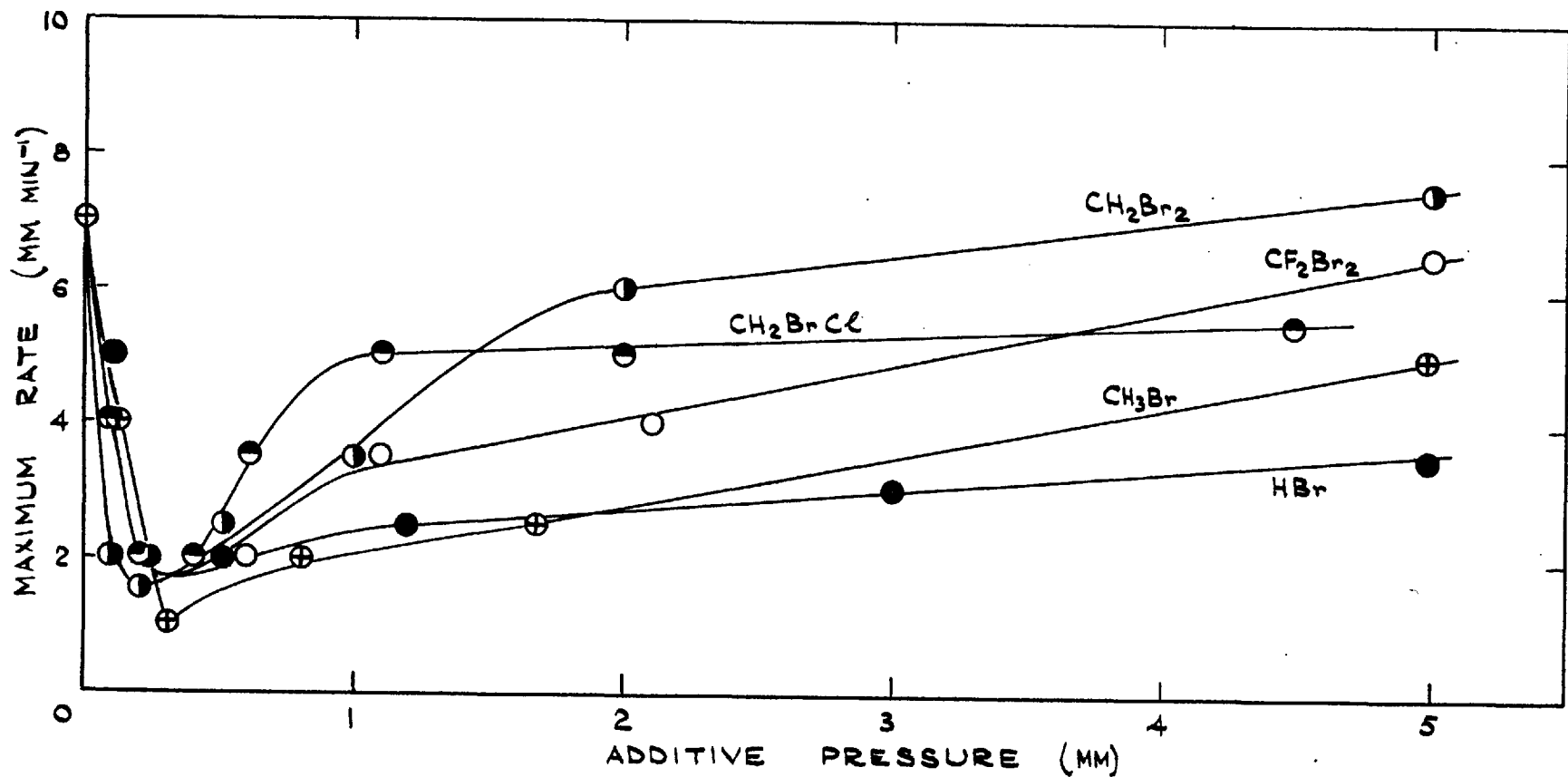
FIG. 55. THE OXIDATION OF METHANE IN THE PRESENCE OF ADDITIVES.
T = 510° C.   CH₄ = 100 MM.   O₂ = 100 MM.
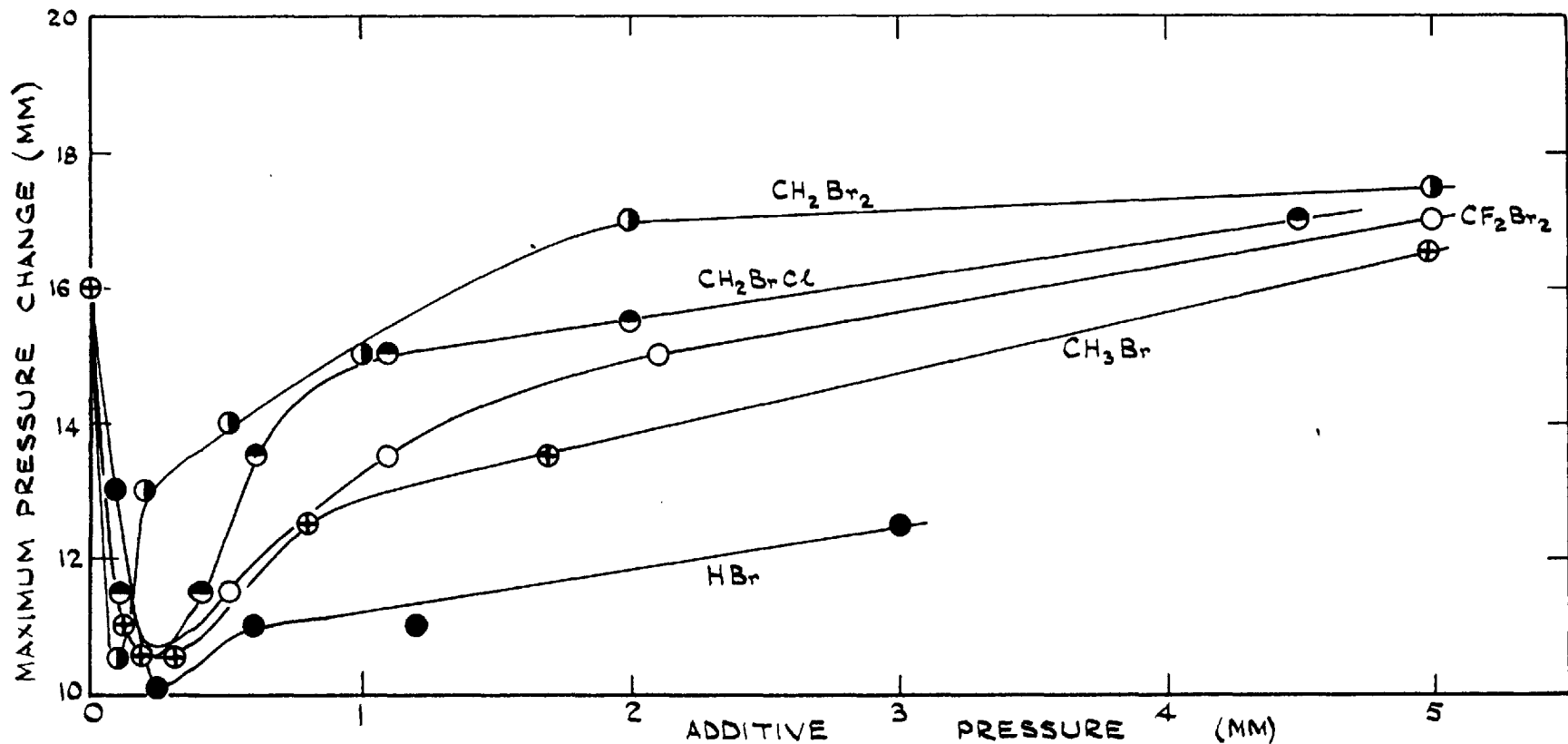
FIG. 56. THE OXIDATION OF METHANE IN THE PRESENCE OF ADDITIVES.
T = 510°C.   CH₄ = 100 MM.   O₂ = 100 MM.

I.   THE OXIDATION OF BENZENE

1.   The influence of halomethanes at 562°C

The influence of methyl bromide and difluorodibromomethane on the oxidation of benzene at 562°C has been investigated using mixtures of 50 mm. benzene, 50 mm. oxygen, 5 - 25 mm. additive.   The pressure-time curve was observed in each case and the results are shown in Figs. 57, 58.

The presence of methyl bromide (5 - 25 mm.) accelerated the reaction, the extent of the acceleration increasing steadily as the amount of additive present was increased.   The presence of difluorodibromomethane (5 - 25 mm.) also accelerated the reaction, pressures $\geqslant 10$ mm. causing the mixture to explode after a few seconds. Dibromodifluoromethane thus had a more powerful promoting influence on the reaction than methyl bromide.

2.   The influence of halomethanes and hydrogen bromide at 611°C

The influence of methyl bromide, difluorodibromomethane, and hydrogen bromide on the spontaneous ignition of benzene/oxygen mixtures at 611°C has been investigated using mixtures of 50 mm. benzene, 100 mm. oxygen, 0.1 - 5 mm. additive.   The effect of these additives on the time lag preceding explosion is shown in Fig. 59.   This time lag fell sharply in the presence of 0.1 - 1 mm. of all three additives.   Thus the benzene/oxygen mixture alone exploded after 23 sec. while the presence of 0.3 mm. hydrogen bromide caused explosion after only 3 sec. Higher pressures of additive (1 - 5 mm.) did not further reduce the explosion time.   The order of effectiveness of the additives in reducing explosion time was:

$$HBr \; > \; CF_2Br_2 \; > \; CH_3Br$$
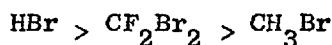
J. THE OXIDATION OF CUMENE (at 580°C)

1. The influence of halomethanes and hydrogen bromide

The influence of methyl bromide, difluorodibromomethane, and hydrogen bromide on the spontaneous ignition of cumene-oxygen mixtures at 580°C has been investigated, using mixtures of 15 mm. cumene, 50 mm. oxygen, 0.5 - 5 mm. additive. All parts of the apparatus coming into contact with cumene vapour were heated to 62°C so that the desired pressure of cumene could be employed. The influence of these additives on the time lag preceding explosion is shown in Fig. 60. The presence of 0.5 - 5 mm. of all three additives reduced this time lag slightly. The order of effectiveness was:

$$HBr > CF_2Br_2 > CH_3Br$$
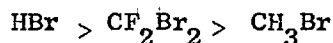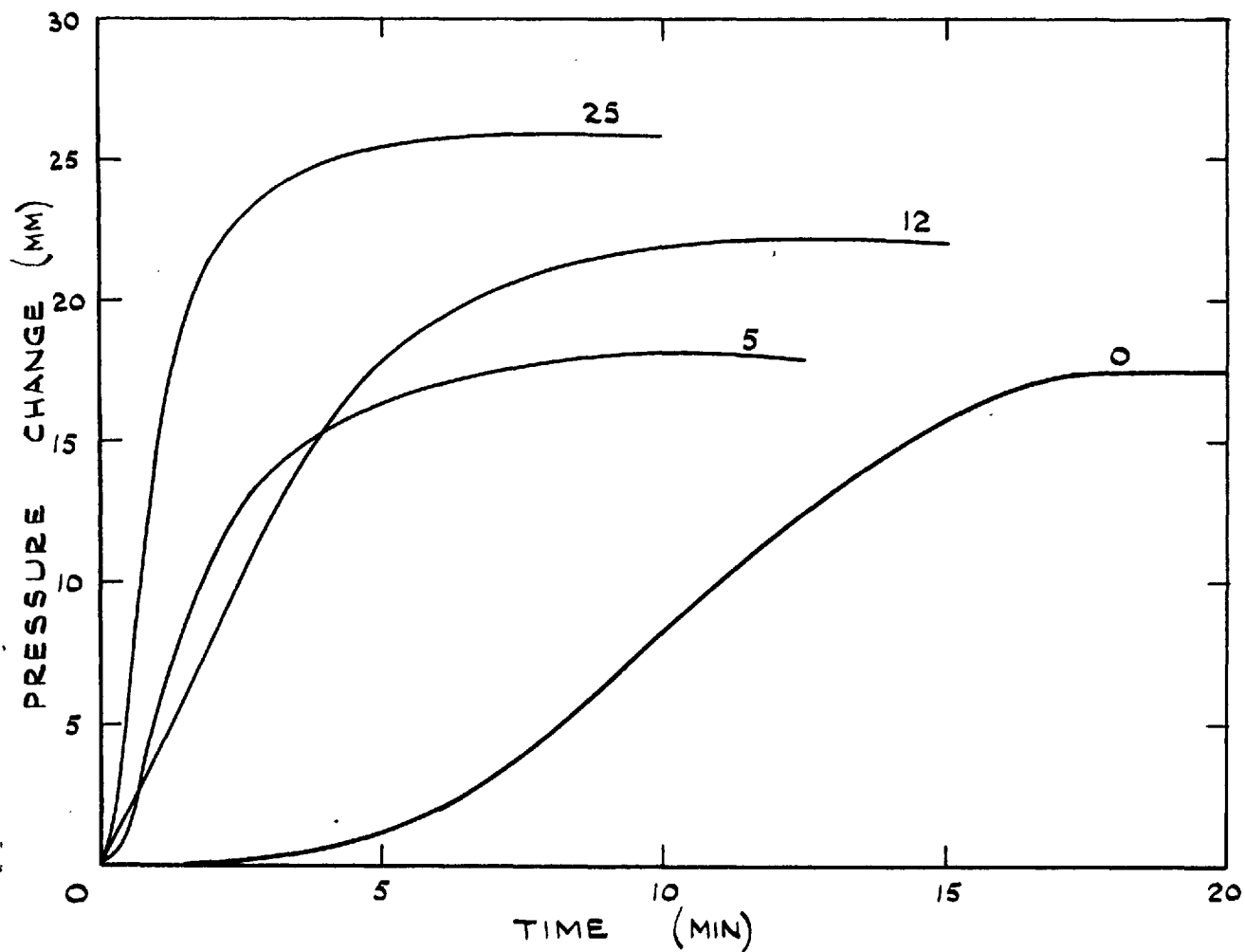
FIG. 57. THE OXIDATION OF BENZENE IN THE PRESENCE OF METHYL BROMIDE. PRESSURE — TIME CURVES. $T = 562°C$. $C_6H_6 = 50MM$. $O_2 = 50MM$. CH_3Br AS SHOWN (MM)
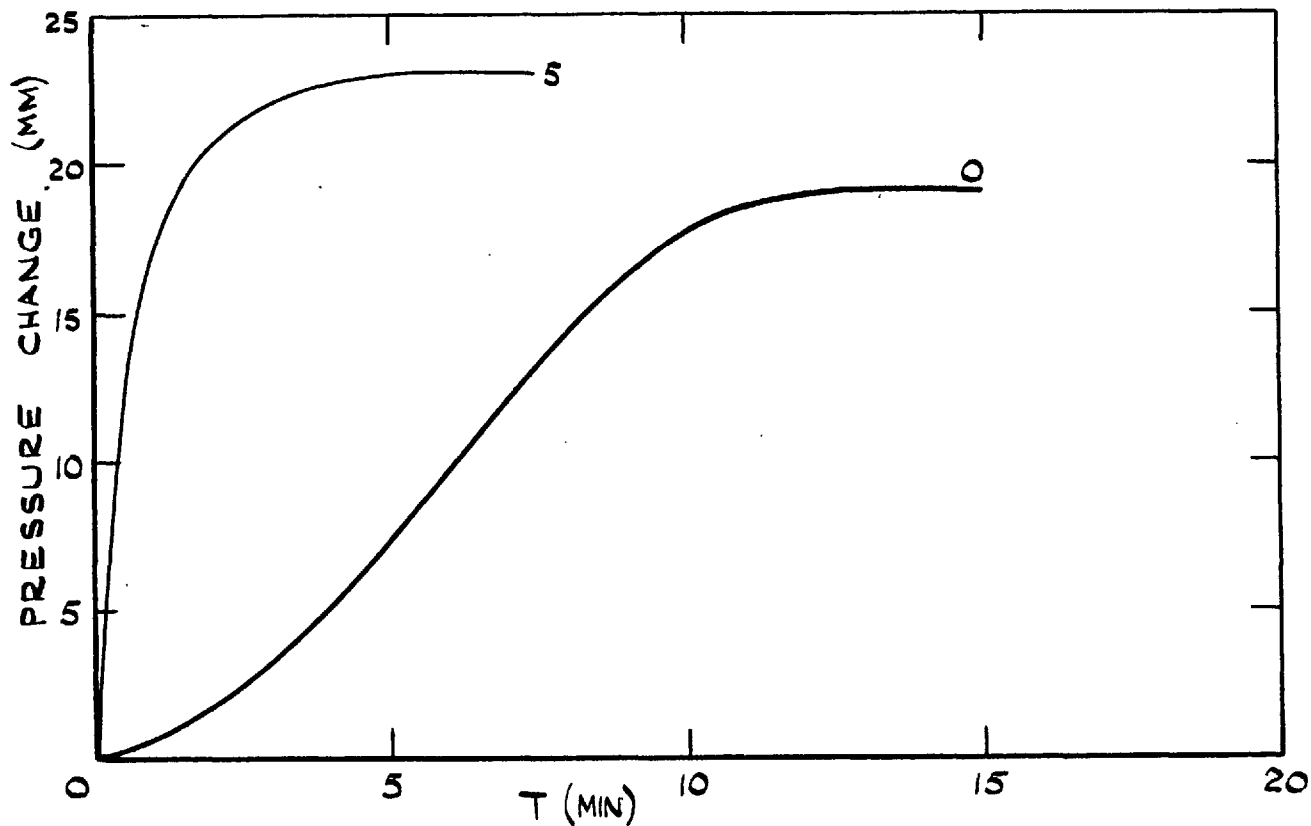
FIG. 5B. THE OXIDATION OF BENZENE IN THE PRESENCE OF
DIFLUORODIBROMOMETHANE. PRESSURE – TIME CURVES.
T = 562°C. C_6H_6 = 50 MM. O_2 = 50 MM. CF_2Br_2 AS SHOWN (MM).
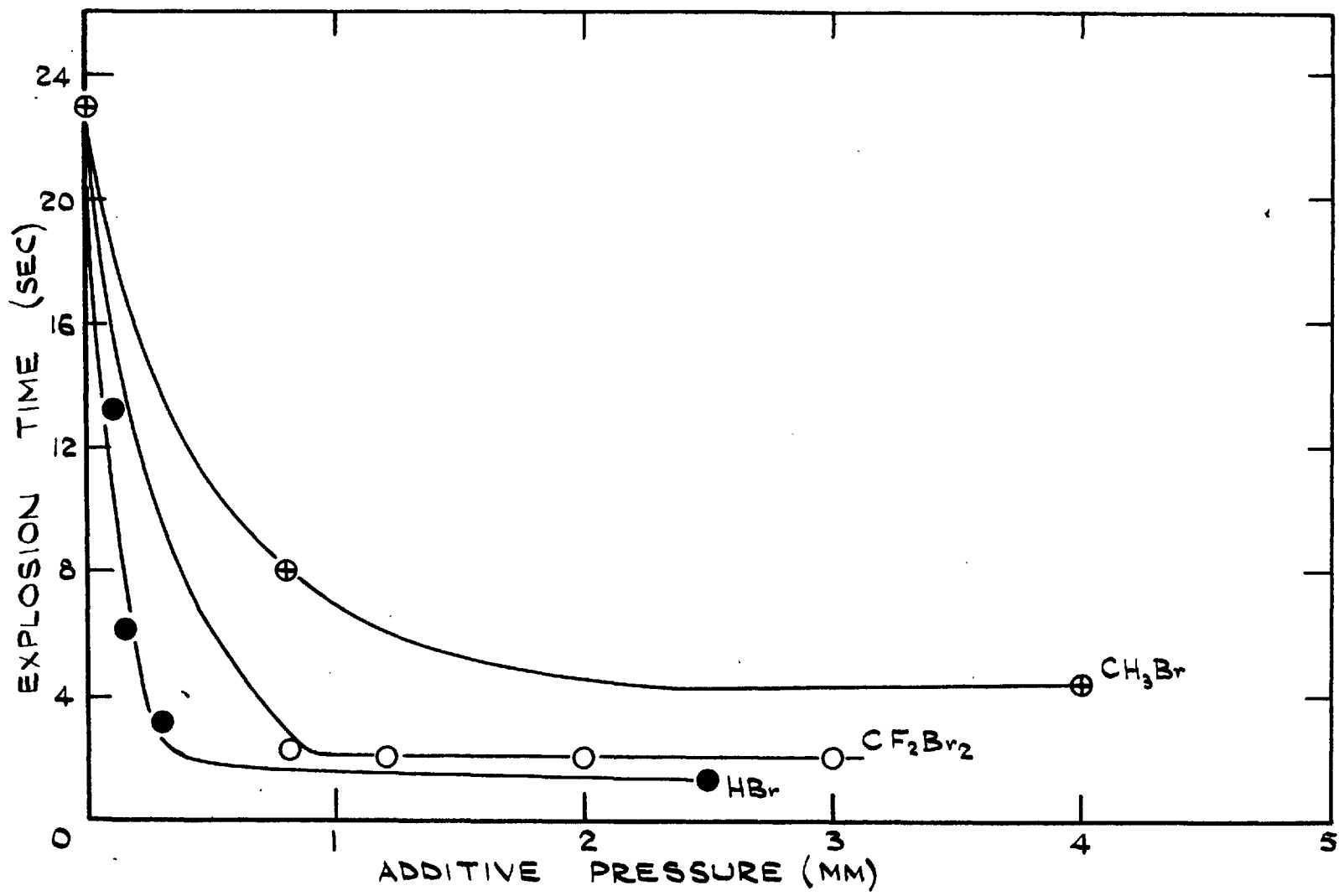
FIG. 59. THE OXIDATION OF BENZENE IN THE PRESENCE OF ADDITIVES.
T = 611°C. C_6H_6 = 50 MM. O_2 = 100 MM.
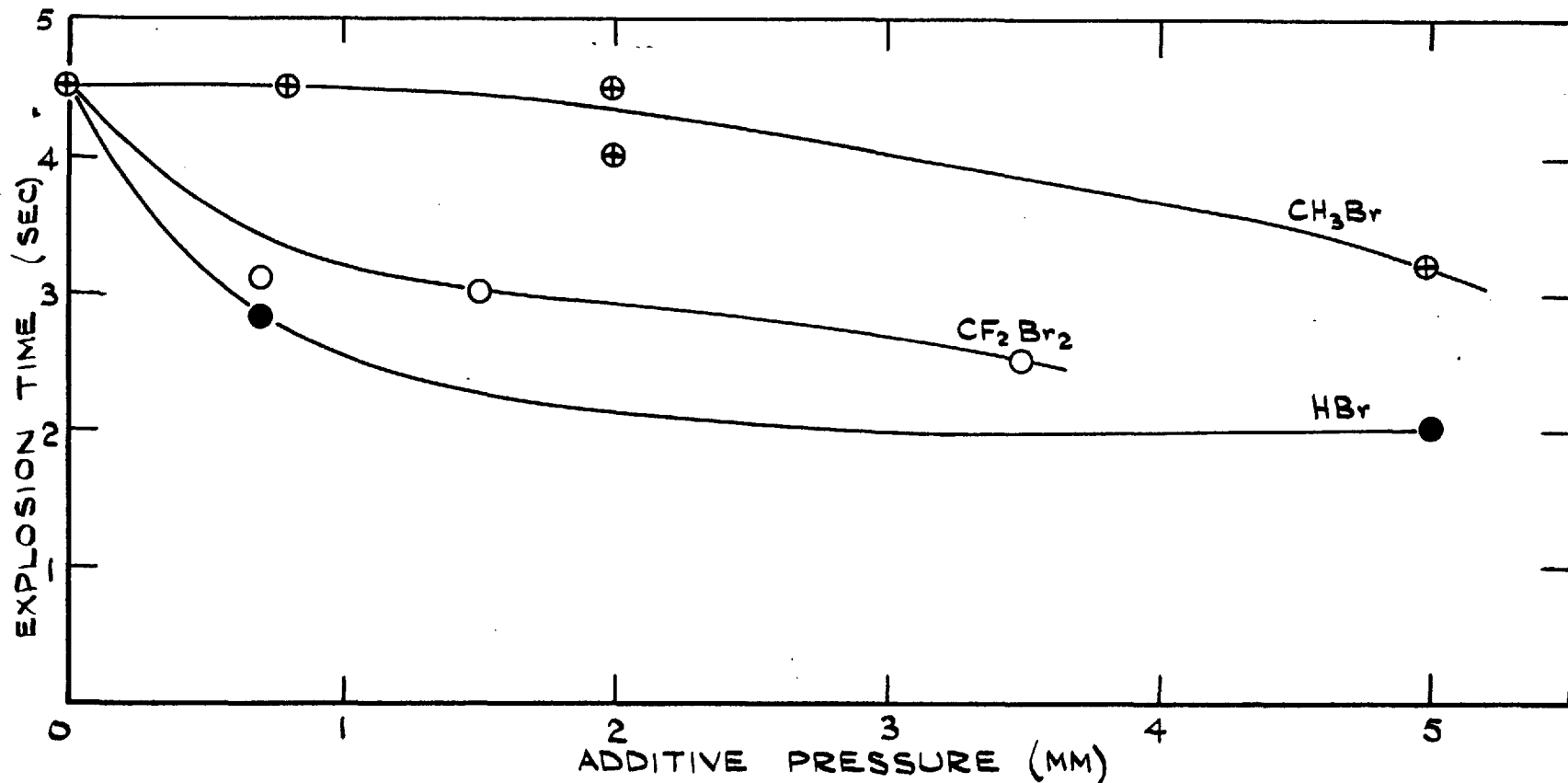
FIG. 60. THE OXIDATION OF CUMENE IN THE PRESENCE OF ADDITIVES. T = 580°C. C_9H_{12} = 15 MM. O_2 = 50 MM.

S E C T I O N 4

<u>DISCUSSION</u>

A. THE OXIDATION OF METHYL BROMIDE (at 330°C)

 1. Summary of results and deductions concerning products

From the pressure-time curves shown in Figs. 1 and 2 it is seen that, using 100 mm. methyl bromide, 50 - 300 mm. oxygen, the reaction is accompanied by an initial pressure decrease followed by an autocatalytic pressure increase. The extent of the pressure decrease increases as the oxygen pressure is increased. Using 250 mm. methyl bromide and the same range of oxygen pressures, no initial pressure decrease is observed. The maximum rate of pressure rise varies with the partial pressures of the two reactants according to the relationship:

$$\left(\frac{dp}{dt}\right) max \quad \left(P_{CH_3Br}\right)^2 \left(P_{O_2}\right)$$

This type of relationship is also observed in the oxidation of methane (42) and methylene dichloride (97).

The principal bromine-containing products are hydrogen bromide and bromine (Figs. 8 - 10). With high partial pressures of oxygen, all the bromine introduced can be accounted for as readily hydrolysable bromide, presumably unchanged methyl bromide, hydrogen bromide, and bromine, but in oxygen-deficient conditions some other bromine compound is formed which is not readily hydrolysed. This product is very probably vinyl bromide which, in contrast to alkyl and acyl bromides, exhibits great resistance to both S_N1 and S_N2 type hydrolysis (98).

Assuming that vinyl bromide is the unknown compound, some overall reactions can be considered and correlated with the total pressure change observed. For an initial mixture of 100 mm. methyl bromide, 50 mm. oxygen, the final products contain 31% vinyl bromide,

17% hydrogen bromide, 0.5% bromine. Now as more vinyl bromide
(containing 2 C atoms for every one Br atom) is formed than hydrogen
bromide and bromine, some other compound must be formed containing at
least two bromine atoms per carbon atom. The most likely compound is
methylene dibromide. The overall reaction can then be written:

$$100\ CH_3Br + 50\ O_2 \longrightarrow 31\ CH_2 = CH.Br + 17HBr + 0.5\ Br_2 + x\ CH_2Br_2$$
$$+ y\ CH_3Br + z\ H_2O + w\ O_2 + a\ CO$$
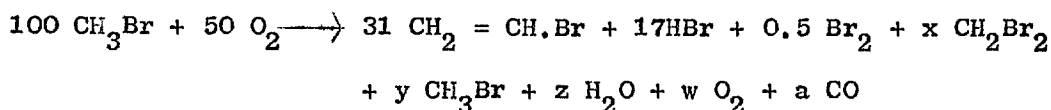
By considering the element balances for carbon, hydrogen, bromine, and
oxygen, and also the pressure change observed, the five unknowns in
this equation can be calculated. This type of calculation can be
carried out for any methyl bromide-oxygen mixture, making suitable
assumptions as to the products. Thus when the amount of vinyl bromide
produced becomes less than the amount of hydrogen bromide and bromine
produced, it is no longer necessary to postulate the formation of
methylene dibromide. Under these conditions it is assumed that
carbon dioxide is formed, as well as carbon monoxide. The results of
these calculations are shown in Table 6.

TABLE 6

The Amounts of the Various Products Formed in the Oxidation of

Methyl Bromide-Oxygen Mixtures

Reactants (mm.)								
CH_3Br	100	100	100	100	100	100	100	100
O_2	25	50	75	100	150	200	300	400
Products (mm.)								
$CH_2 = CH.Br$	19	31	27	20	12	7	0	0
CH_2Br_2	11	15	3.5	0	0	0	0	0
CH_3Br	50	21	39	45	39	33	35	30
HBr	9	17	26	33	40	44	41	40
Br_2	0	0.5	0.5	1.0	4.5	8.0	12	15
H_2O	31	48.5	34.5	36	53.5	68	77	85
CO	1	2	3.5	6	5.5	12	19	25
CO_2	0	0	0	9	31.5	41	·46	45
O_2	9	25.8	56	70	89	119	206	300
CH_3Br reacted	50	79	61	55	61	67	65	70
O_2 reacted	16	24.3	19	30	61	81	94	100
O_2/CH_3Br ratio	0.32	0.30	0.31	0.56	1.0	1.2	1.4	1.4

Although the results obtained in this way can only be semi-quantitative, they do appear to give a consistent picture of the varying amounts of the various final products formed as the oxygen pressure is increased, the methyl bromide pressure being maintained constant. Thus the methylene dibromide formed increases to a maximum of 15% in a mixture initially containing 50 mm. oxygen, and then decreases sharply to zero. In this mixture only 20% of the initial methyl bromide remains unchanged but this increases to 45% in a 100/100 mixture and then decreases gradually to 30% in mixtures containing high partial pressures of oxygen. These results are shown in Fig. 11. The amounts of oxygen reacted and of water, carbon monoxide, and carbon dioxide formed all increase fairly steadily with increasing oxygen pressure as expected. While the initial oxygen/methyl bromide ratio varies from 0.25 to 4.00, the oxygen reacted/methyl bromide reacted ratio increases from 0.32 to 1.4.

2. The reaction mechanism

The mechanism of the reaction can now be considered. In the following treatment, all bond dissociation energies are taken from Semenov (5). In the methyl bromide molecule, the bond dissociation energy of the C-Br bond is 67.5 K. cal. Also D (C-H) = 95 K. cal. Now in the reaction

$$CH_3Br + O_2 \longrightarrow \overset{\bullet}{C}H_2Br + H\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

$$\Delta H = D(H-O_2) - D(CH_2Br-H)$$
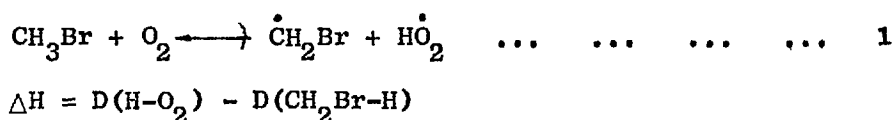
where ΔH = Heat of reaction (K. cal./mole)

D = Bond dissociation energy (K. cal./mole)

When a bond is formed, energy is evolved, while hen a bond is broken, energy is absorbed. The evolution of energy is here given a positive sign and vice-versa. Thus for the overall reaction, a positive value of ΔH denotes an exothermic reaction. In the present case

$$D(H-O_2) = 47 \text{ K. cal.}$$

$$D(C-H) = 95 \text{ K. cal.}$$

and thus $\Delta H = -48$ K. cal./mole. As the reverse reaction is a radical recombination reaction, it has only a very small activation energy. Thus the activation energy of the forward reaction is approximately equal to the heat of the reaction:

$$E_1 \simeq 48 \text{ K. cal./mole}$$

A possible alternative initiating reaction is:

$$CH_3Br + O_2 \longrightarrow \overset{\bullet}{C}H_3 + Br\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2$$
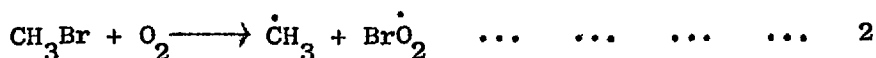
Little is known about the species $Br\overset{\bullet}{O}_2$ but its bond dissociation energy is unlikely to be greater than 5 K. cal./mole. Thus

$$H \simeq -62.5 \text{ K. cal./mole}$$

$$E \simeq 62 \text{ K. cal./mole}$$

Now the rate of a bimolecular reaction, w, is given by:

$$w = fz \; \text{expt} \; (-E/RT) \; [A] \; [B]$$

where f = Steric factor

z = Collision frequency 10^{-10} cm^3 sec^{-1}

A , B = Concentrations of the reacting species in molecules per c.c.

Thus
$$\frac{w_1}{w_2} = \frac{f_1}{f_2} \; \text{expt} \; \left(\frac{E_2 - E_1}{RT} \right)$$

$$= \frac{f_1}{f_2} \; \text{expt} \; \left(\frac{14,000}{1,200} \right)$$

$$= 1.6 \times 10^5 \frac{f_1}{f_2}$$

Now f is the fraction of the total number of collisions which involve sufficient energy for reaction to subsequently occur which actually do cause reaction. It is reasonable in this case to assume that $f_1 > f_2$ and thus reaction 1 will occur at least 10^5 times faster than reaction 2. Reaction 1 is therefore the only significant initiating reaction involving fuel and oxygen. However the methyl bromide molecule may also decompose unimolecularly:

$$CH_3Br \longrightarrow \dot{C}H_3 + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 3$$

This involves the fission of a C–Br bond and thus

$$H = -67.5 \text{ K. cal./mole}$$

$$E \doteq 67.5 \text{ K. cal./mole}$$

Then $\dfrac{w_1}{w_3} = f_1 \, 10^{-23} \, \text{expt} \left(\dfrac{20,000}{1,200} \right) [O_2]$

For 100 mm. oxygen at 600°K, $[O_2] = 1.6 \times 10^{18}$ molecules/c.c.

$$\text{Thus} \quad \frac{w_1}{w_3} = 270 \, f_1$$

Therefore, if $f_1 \doteq 1$, the oxidation reaction proceeds 270 times faster than unimolecular decomposition at 600°K. However, if $f_1 = 0.01$, which is quite possible, then the rates of the two reactions will be of the same order. Thus theory predicts that reaction 1 is the most important initiation reaction at 600°K, but reaction 3 may well also occur to an appreciable extent. In the presence of higher oxygen pressures, reaction 1 is, of course, even more important.

The $\dot{C}H_2Br$ radical produced can then react in two ways:

$$\dot{C}H_2Br + CH_3Br \longrightarrow BrCH_2CH_3 + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 4$$
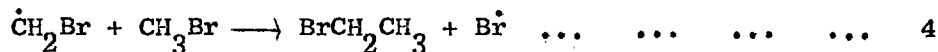
and apparently:

$$H \doteq +83-67 \doteq +16 \text{ K. cal./mole}$$

However reaction 4 also involves inversion of configuration about a carbon atom. The amount of energy required for this is unknown and thus ΔH is unknown.

$$\dot{C}H_2Br + O_2 \longrightarrow Br\,CH_2\dot{O}_2 \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 5$$

Now the reaction between an alkyl radical and oxygen is normally considered to have a very small or even zero activation energy. Thus it is reasonable to assume by analogy that $E_5 \simeq 0$. However, at the moment of formation the peroxy radical is in a highly energetic state and therefore its immediate breakdown by the reverse of 5 is quite probable. Thus by analogy with the $\dot{C}H_3\text{-}O_2$ reaction,

$$f_5 \simeq 10^{-3}$$

As E_4 is unknown, the relative importance of reactions 4 and 5 cannot be calculated. However, it is probable that these reactions occur at comparable rates and both must therefore be considered in the mechanism. The ethyl bromide produced in 4 then reacts as follows:

$$CH_3CH_2Br + O_2 \longrightarrow CH_3\dot{C}HBr + H\dot{O}_2 \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 6$$
$$E \simeq 46 \text{ K. cal./mole}$$

$$CH_3CH_2Br + HO_2 \longrightarrow CH_3\dot{C}HBr + H_2O_2 \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 7$$
$$E \simeq 14 \text{ K. cal./mole}$$
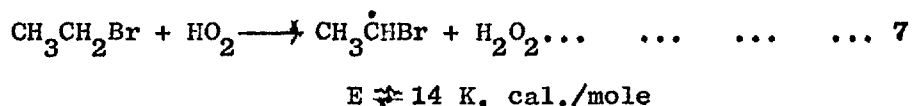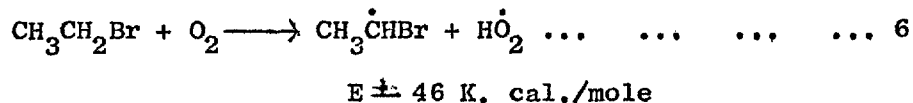
The activation energy of reaction 7, and of all subsequent reactions of this type, is calculated from the formulae:

$$E \simeq 11.5 - 0.25\,(\Delta H) \quad \text{Exothermic reaction}$$

$$E \simeq 11.5 + 0.75\,(\Delta H) \quad \text{Endothermic reaction}$$

(Semenov, 5)

$$CH_3CH_2Br + \dot{B}r \longrightarrow CH_3\dot{C}HBr + HBr \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 8$$
$$E \simeq 16 \text{ K. cal./mole}$$
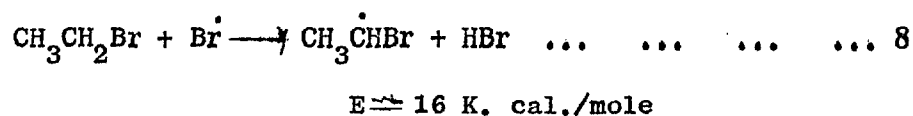
The radical produced, $CH_3\dot{C}HBr$, has the same choice as the radical, $\dot{C}H_2Br$, in that it can react with methyl bromide or oxygen. However, in this case $f \gg 10^{-3}$ for the reaction with oxygen and so this step is the preferred one:

$$CH_3CHBr + O_2 \longrightarrow CH_3.\underset{\underset{\dot{O}_2}{|}}{C}HBr \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \ 9$$
$$E \ small$$
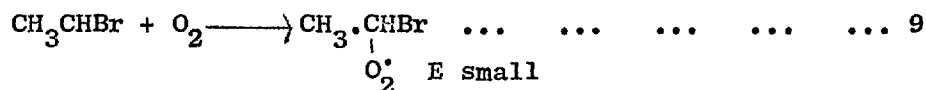
This radical can then isomerize by hydrogen atom transfer around a five-membered ring to give the radical: $\dot{C}H_2\underset{OOH}{C}HBr$. This isomerization reaction requires an activation energy of about 20 K. cal./mole. The radical formed readily breaks· down to give vinyl bromide and the $\dot{H}O_2$ radical:

$$\dot{C}H_2\underset{OOH}{C}HBr \longrightarrow CH_2 = CH.Br + \dot{H}O_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots 10$$
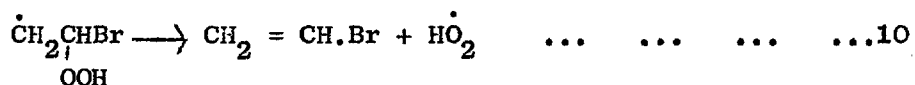
The formation of vinyl bromide in methyl bromide-rich mixtures is thus readily explained.

Methylene dibromide is formed in reactions:

$$\dot{C}H_2Br + \dot{B}r \longrightarrow CH_2Br_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots 11$$
$$E \simeq 0$$

$$\dot{C}H_2Br + CH_3Br \longrightarrow CH_2Br_2 + \dot{C}H_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots 12$$
$$E \simeq 13 \ K. \ cal./mole$$
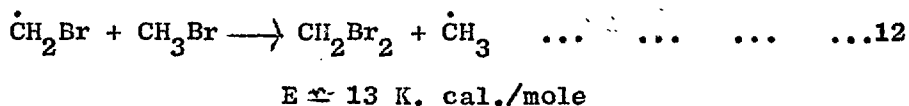
Reaction 11 is a radical-radical reaction and thus has only a very low probability of occurring in the gas phase but it may occur to a significant extent at the wall. Reaction 12 is a more probable one in the gas phase but the competing reaction, 4 is probably the predominant reaction occurring between the $\dot{C}H_2Br$ radical and methyl bromide.

The formation of the radical $Br\dot{C}H_2O_2$ as in reaction 5 presumably accounts for the initial pressure decrease observed in

oxygen-rich mixtures.   It can decompose unimolecularly as follows:

$$Br.CH_2O\dot{O} \longrightarrow Br\dot{C}HOOH \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 13$$

$$Br\dot{C}HOOH \longrightarrow BrCHO + \dot{O}H \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 14$$

The isomerization, 13, probably has an activation energy of about 20 K. cal./mole.   Alternatively the peroxy radical may abstract a hydrogen atom from a fuel molecule:

$$BrCH_2O\dot{O} \; + \; CH_3Br \longrightarrow BrCH_2OOH + \dot{C}H_2Br \quad \ldots \quad \ldots \quad \ldots \quad 15$$

This reaction is exothermic as $D(O-H) > D(C-H)$.

Therefore $E_{15} \cong 10$ K. cal./mole

and $\dfrac{W_{13}}{W_{15}} = 1.6 \times 10^3$ assuming $f_{15} = 0.1$

The unimolecular decomposition is thus the predominant reaction.

The Br.CHO produced then reacts with oxygen, giving chain-branching:

$$BrCHO + O_2 \longrightarrow Br\dot{C}O + H\dot{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 16$$

$$E \cong 28 \text{ K. cal./mole}$$

The $Br\dot{C}O$ radical can then decompose:

$$Br\dot{C}O \longrightarrow B\dot{r} + CO \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 17$$

ΔH for this reaction is unknown but it is probably about 30 K. cal./ mole exothermic.   Therefore $E_{17} \cong 5$ K. cal./mole.   Alternatively the BrCO radical can add an oxygen molecule and then abstract a hydrogen atom from a fuel molecule to give a hydroperoxide:

$$Br\dot{C}O + O_2 \longrightarrow Br\dot{C}O_3 \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 18$$

$$E \cong 0$$

$$Br\dot{C}O_3 + CH_3Br \longrightarrow BrCO_3H + \dot{C}H_2Br \quad \ldots \quad \ldots \quad \ldots \quad 19$$

$$E \cong 9.5 \text{ K. cal./mole}$$

The hydroperoxide then decomposes:

$$Br.CO.OOH \longrightarrow \dot{Br} + CO_2 + \dot{O}H \quad \dots \quad \dots \quad \dots \quad \dots \ 20$$

The production of carbon monoxide and carbon dioxide is therefore readily explained.

Bromine is produced at the walls by the recombination of bromine atoms:

$$\dot{Br} + \dot{Br} \longrightarrow Br_2 \quad \dots \quad \dots \quad \dots$$

In the gas phase, bromine atoms react largely with fuel:

$$\dot{Br} + CH_3Br \longrightarrow \dot{C}H_2Br + HBr \quad \dots \quad \dots \quad \dots \quad \dots \ 22$$
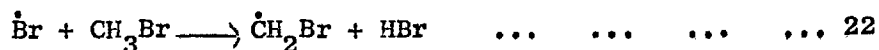
From bond energy data and the formula, $E = 11.5 + \frac{3}{4}(\Delta H)$

$$E = 18 \text{ K. cal./mole}$$

However, Kistiakowsky and Van Artsdalen (99) found that $E = 15.6$ K. cal./mole. This reaction is energetically more probable than the alternative:

$$\dot{Br} + CH_3Br \longrightarrow Br_2 + \dot{C}H_3 \quad \dots \quad \dots \quad \dots \quad \dots \ 23$$

$$E = 28 \text{ K. cal./mole}$$

Water is formed in reactions such as:

$$\dot{O}H + CH_3Br \longrightarrow H_2O + \dot{C}H_2Br \quad \dots \quad \dots \quad \dots \quad \dots \ 24$$
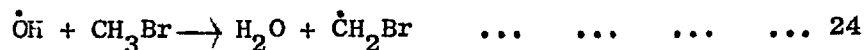
$$E = 6 \text{ K. cal./mole}$$

The $\dot{H}O_2$ radical reacts with fuel to give hydrogen peroxide:

$$\dot{H}O_2 + CH_3Br \longrightarrow H_2O_2 + \dot{C}H_2Br \quad \dots \quad \dots \quad \dots \quad \dots \ 25$$
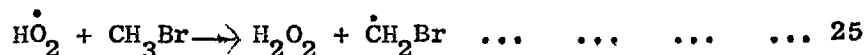
$$E = 16 \text{ K. cal./mole}$$

This then decomposes, producing $\dot{O}H$ radicals:

$$H_2O_2 \longrightarrow 2\dot{O}H \quad \dots \quad \dots \quad \dots \quad \dots \ 26$$

Hydrogen bromide is formed largely by reaction 23. Under the experimental conditions, it reacts only slowly with oxygen:

$$HBr + O_2 \longrightarrow \overset{\bullet}{Br} + H\overset{\bullet}{O}_2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad 27$$

$$E \doteq 39.5 \text{ K. cal./mole}$$

Thus the formation of all the products found in this oxidation can be explained in terms of the reaction mechanism given. The autocatalytic pressure rise is produced by the chain-branching reactions 17, 20, 26. Termination occurs through the diffusion of the less active radicals such as $\overset{\bullet}{Br}$, $H\overset{\bullet}{O}_2$, to the walls followed by recombination reactions such as 21.

About 30% of the methyl bromide remains unchanged well after the main pressure change has occurred, even in the presence of a large excess of oxygen. At this stage the rate of chain branching is no longer greater than the termination rate and thus the autocatalytic reaction ceases. The rate of chain branching falls as a result of the much decreased concentrations of the reactants. Also the product hydrogen bromide participates in reactions such as:

$$\overset{\bullet}{O}H + HBr \longrightarrow H_2O + \overset{\bullet}{Br} \quad \dots \quad \dots \quad \dots \quad \dots \quad 28$$

$$E \approx 0$$

(Bond energy data and the formula give E_{28} 4 K. cal./mole. However for $\overset{\bullet}{C}H_3 + HBr \longrightarrow CH_4 + \overset{\bullet}{Br}$
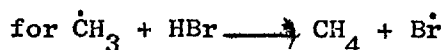
$$E = 0 \ (99)$$

and activation energies are generally lower for reactions involving $\overset{\bullet}{O}H$ radicals than for the corresponding processes involving $\overset{\bullet}{C}H_3$ radicals (100).)

$$\overset{\bullet}{C}H_2Br + HBr \longrightarrow CH_3Br + \overset{\bullet}{Br} \quad \dots \quad \dots \quad \dots \quad \dots \quad 29$$
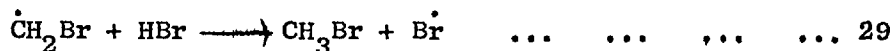
$$E = 3.6 \text{ K. cal./mole } (99)$$

These reactions have low activation energies and thus occur readily. They remove active chain carriers such as $\dot{O}H$ and $\dot{C}H_2Br$, replacing them by relatively less reactive bromine atoms. Retardation of the reaction therefore occurs. The rate of the reaction is thus reduced to a very small value even though a considerable concentration of reactants is still present.

B. THE OXIDATION MECHANISMS OF THE ADDITIVES USED IN THIS WORK

1. Methyl bromide

Methyl bromide was the only additive used whose oxidation was studied experimentally. In the methyl bromide molecule, D(C-H) = 95 K. cal., D(C-Br) = 67.5 K. cal. When methyl bromide was used as an additive, a large excess of oxygen, relative to the halomethane, was always present. The oxidation mechanism under these conditions can be summarised:

$$CH_3Br + O_2 \longrightarrow \dot{C}H_2Br + H\dot{O}_2$$
$$\dot{C}H_2Br + O_2 \longrightarrow BrCH_2\dot{O}_2$$
$$BrCH_2\dot{O}_2 \longrightarrow BrCHO + \dot{O}H$$
$$BrCHO + O_2 \longrightarrow Br\dot{C}O + H\dot{O}_2$$
$$Br\dot{C}O + O_2 \longrightarrow BrC\dot{O}_3$$
$$BrC\dot{O}_3 + CH_3Br \longrightarrow BrCO_3H + \dot{C}H_2Br$$
$$BrCO_3H \longrightarrow \dot{Br} + CO_2 + \dot{O}H$$
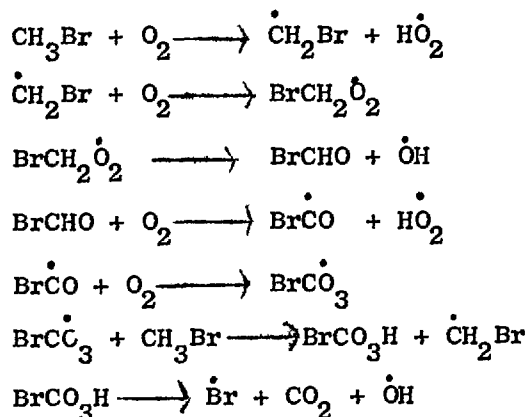
Thus when methyl bromide is introduced into an oxidation system at a sufficiently high temperature, bromine atoms are readily produced, as well as $\dot{O}H$, $H\dot{O}_2$. At high temperatures, the dissociation of the molecule also occurs to an appreciable extent. Thus at 510°C (783°K), using the nomenclature of section A,

$$\frac{w_1}{w_3} = f_1 \, 10^{-23} \, \text{expt} \left(\frac{20,000}{1,566}\right)\left[O_2\right]$$

$$= 4.5 \ f_1$$

and therefore the decomposition and the oxidation occur at comparable

rates at this temperature. The overall reaction can be written:

$$CH_3Br + O_2 \longrightarrow CO + HBr + H_2O$$

or
$$2 \ CH_3Br + 3\tfrac{1}{2}O_2 \longrightarrow 2CO_2 + 3H_2O + Br_2$$
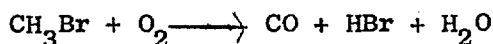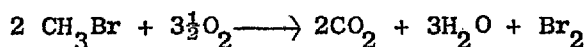
depending upon the conditions. In both cases, an overall increase in

the number of molecules present occurs. This produces an increase in

pressure under constant volume conditions.

2. <u>Methylene dibromide</u>

Although the oxidation of this compound has not been studied

experimentally, the mechanism of its oxidation can be predicted

theoretically. Thus in the CH_2Br_2 molecule, D(C–H) = 87.7 K. cal.,

D(C–Br) = 62.5 K. cal. Therefore the two possible modes of initiation

are:

$$CH_2Br_2 + O_2 \longrightarrow \overset{\centerdot}{C}HBr_2 + H\overset{\centerdot}{O}_2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \textbf{1}$$
$$E \doteq 41 \ K. \ cal./mole$$

$$CH_2Br_2 \longrightarrow \overset{\centerdot}{C}H_2Br + \overset{\centerdot}{Br} \quad \dots \quad \dots \quad \dots \quad \dots \quad \textbf{2}$$
$$E \doteq 62.5 \ K. \ cal./mole$$
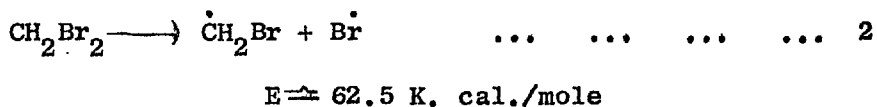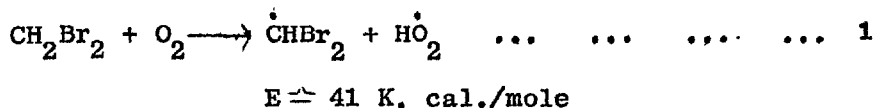
and it follows that

$$\frac{w_1}{w_2} = f_1 \ 10^{-23} \ exp \left(\frac{21,500}{2T}\right)\left[O_2\right]$$

At 600°K, $\dfrac{w_1}{w_2} = 160 \ f_1$; At 800°K, $\dfrac{w_1}{w_2} = 2 \ f_1$

Thus the oxidative mechanism is favoured at fairly low temperatures but

at higher temperatures the two modes of initiation proceed at about the

same rate.

The oxidation mechanism consists of 1 followed by:

$$\dot{C}HBr_2 + O_2 \longrightarrow Br_2CH\dot{O}_2 \quad \dots \quad \dots \quad \dots \quad \dots \qquad 3$$

$$Br_2CH\dot{O}_2 \longrightarrow Br_2CO + \dot{O}H \dots \quad \dots \quad \dots \quad \dots \qquad 4$$

$$Br_2CO \longrightarrow CO + 2\dot{Br} \dots \quad \dots \quad \dots \quad \dots \qquad 5$$
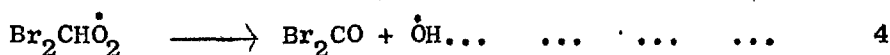
and thus bromine atoms are again introduced into the system.

The $\dot{C}H_2Br$ radical, formed by dissociation at higher temperatures, oxidises as in section 1.

The overall reaction can be written:

$$CH_2Br_2 + 1\tfrac{1}{2}O_2 \longrightarrow CO_2 + H_2O + Br_2$$
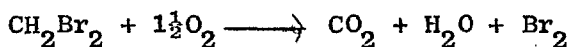
The reaction therefore occurs with an increase in the number of

molecules present.

3. Chlorobromomethane

No bond energy data is available for CH_2BrCl. However, from the known data on related compounds, it seems reasonable to assume that in this molecule, $D(C-H) = 90$ K. cal., $D(C-Br) = 65$ K. cal., $D(C-Cl) = 80$ K. cal. The two possible initiating reactions are:

$$CH_2BrCl + O_2 \longrightarrow \dot{C}HBrCl + H\dot{O}_2 \quad \dots \quad \dots \quad \dots \qquad 1$$

$$E \rightleftharpoons 43 \text{ K. cal./mole}$$

$$CH_2BrCl \longrightarrow \dot{C}H_2Cl + \dot{Br} \dots \quad \dots \quad \dots \quad \dots \qquad 2$$
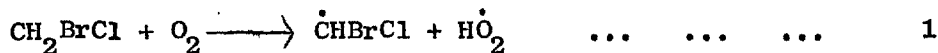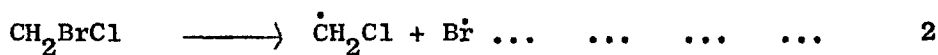
$$E \rightleftharpoons 65 \text{ K. cal./mole}$$

As the difference in activation energies of the two reactions is again about 20 K. cal./mole, the values of the ratio $\dfrac{w_1}{w_2}$ are roughly the same as for methylene dibromide. Further oxidation of the radicals $\dot{C}HBrCl$, $\dot{C}H_2Cl$, leads to the production of chlorine and bromine atoms. Again, the overall oxidation reaction occurs with an increase in the number of molecules present.

4. Dibromodifluoromethane

As this molecule contains no hydrogen atom, no conventional oxidation mechanism is possible. In the molecule, $D(C-F) = 120$ K. cal., $D(C-Br) = 65$ K. cal. The dissociation:

$$CF_2Br_2 \longrightarrow \overset{\bullet}{C}F_2Br + \overset{\bullet}{B}r \qquad E \quad 65 \text{ K. cal./mole}$$
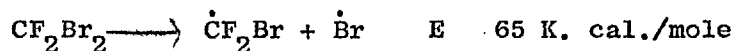
is therefore the only initiating reaction. Thus bromine atoms are again produced at a suitably elevated temperature. The overall reaction which occurs is unknown. A possible reaction is:

$$2CF_2Br_2 \longrightarrow C_2F_4 + 2Br_2$$
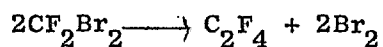
The reaction is therefore accompanied by an increase in the number of molecules present.

5. Hydrogen bromide

The oxidation of hydrogen bromide has been investigated by Rosser and Wise (55) and the mechanism proposed is given in the Introduction (Page 39). The initiation reaction is:

$$HBr + O_2 \longrightarrow H\overset{\bullet}{O}_2 + \overset{\bullet}{B}r$$
$$E = 39.5 \text{ K. cal./mole}$$

The overall reaction is:

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$
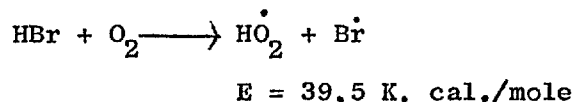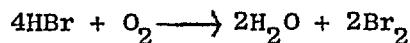
The reaction is thus accompanied by a decrease in the number of molecules present.

6. General

All five additives therefore decompose, producing bromine atoms, when introduced into an oxidation system at a suitably elevated temperature. The relative ease with which the additives decompose by an oxidative mechanism can be deduced from the bond energy data given.

It decreases in the order:

$$HBr > CH_2Br_2 > CH_2BrCl > CH_3Br$$
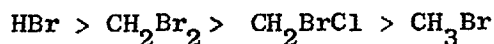
Similarly the ease with which the additives decompose by a dissociative

mechanism decreases in the order:

$$CH_2Br_2 > CH_2ClBr, \ CF_2Br_2 > CH_3Br > HBr$$
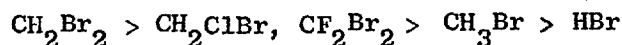
The relative importance of the two mechanisms of initial decomposition

depends on the temperature as explained previously.

The carbon and hydrogen fragments of the additives oxidise

in the normal way finally producing carbon monoxide and water. With

all four halomethanes the overall oxidation reaction (dissociation

reaction for difluorodibromomethane) produces an increase in the total

number of molecules present and consequently an increase in pressure

in a constant volume system. However, with hydrogen bromide, the

oxidation reaction produces a decrease in the number of molecules

present.

C. THE INFLUENCE OF BROMINE COMPOUNDS ON THE COMBUSTION OF VARIOUS

FUELS

1. The oxidation of acetaldehyde

a) The basic reaction

In this reaction the initiating step is:

$$CH_3CHO + O_2 \longrightarrow CH_3\overset{\bullet}{C}O + \overset{\bullet}{H}O_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$
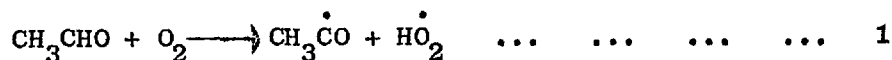
E calc = 38 K. cal./mole

E obs. = 13.8 K. cal./mole (McDowell and Thomas 40)

The calculated value of E is for the gas phase reaction. As the

observed value is much lower, it must be assumed that the initiation

reaction occurs largely on the walls. The activation energy is anyway

quite large and the initiation reaction therefore occurs relatively slowly. The chain cycle given below then follows:

$$CH_3\overset{\bullet}{C}O + O_2 \longrightarrow CH_3C\overset{\bullet}{O}_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \ 2$$

$$E \doteq 0$$

$$CH_3C\overset{\bullet}{O}_3 + CH_3CHO \longrightarrow CH_3CO_3H + CH_3\overset{\bullet}{C}O \quad \ldots \quad \ldots \quad \ldots \ 3$$

$$E \doteq 7 \text{ K. cal./mole}$$
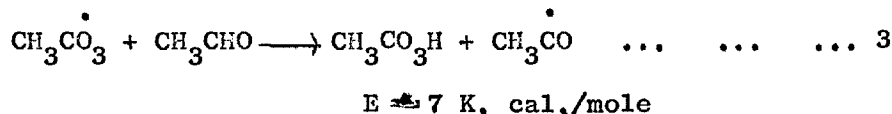
These reactions are fast and lead to the production of peracetic acid.

$$2CH_3C\overset{\bullet}{O}_3 \longrightarrow \text{inert products} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \ 4$$

The major overall reaction is:

$$CH_3CHO + O_2 \longrightarrow CH_3CO_3H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \ 5$$

1 mm. of peracetic acid is therefore formed for each 1 mm. decrease in pressure. The experimentally determined relationship is roughly in agreement with this.

Most of the $H\overset{\bullet}{O}_2$ radicals formed diffuse to the walls. However, some presumably react with fuel, forming hydrogen peroxide:

$$H\overset{\bullet}{O}_2 + CH_3CHO \longrightarrow CH_3\overset{\bullet}{C}O + H_2O_2 \quad \ldots \quad \ldots \quad \ldots \ 6$$

$$E \doteq 10.5 \text{ K. cal./mole}$$
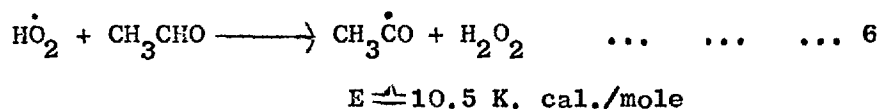
This peroxide is not estimated by the analytical method employed.

The reaction scheme given leads to the steady state equation:

$$\frac{d}{dt}\left[CH_3CO_3H\right] = K\left[CH_3CHO\right]^{3/2}\left[O_2\right]^{\frac{1}{2}} \quad \ldots \quad \ldots \quad \ldots \ 7$$

Thus the rate of peracid formation should decrease gradually with time as the reactants are consumed. However, under the conditions used in this work, the rate of peracid formation was approximately constant for the first hour of reaction (up to 40% reaction). Possibly the heat evolved in the exothermic reactions 2, 3 caused the gas temperature to rise sufficiently to maintain a constant rate of reaction.

At 122°C, the formation of peracetic acid is the major

reaction, as shown by the considerable pressure decrease in the system.

However, some decomposition of the peracid also occurs:

$$CH_3CO_3H \longrightarrow CH_3\overset{\bullet}{C}O_2 + \overset{\bullet}{O}H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 8$$

$$E \doteqdot 30 \text{ K. cal./mole}$$
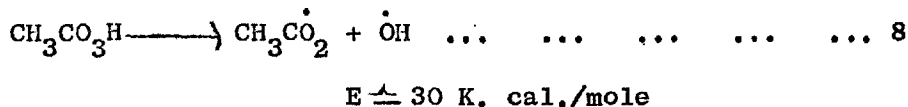
The peracid breaks up at its weakest bond, the -O-O- link (30-40 K. cal.)

giving two radicals which then react with fuel, producing acetic acid

and water:

$$CH_3\overset{\bullet}{C}O_2 + CH_3CHO \longrightarrow CH_3CO_2H + CH_3\overset{\bullet}{C}O \quad \ldots \quad \ldots \quad \ldots \quad 9$$

$$E \doteqdot 7 \text{ K. cal./mole}$$

$$\overset{\bullet}{O}H + CH_3CHO \longrightarrow CH_3\overset{\bullet}{C}O + H_2O \quad \ldots \quad \ldots \quad \ldots \quad \ldots 10$$

$$E \quad 4 \text{ K. cal./mole}$$
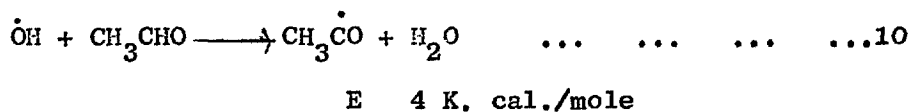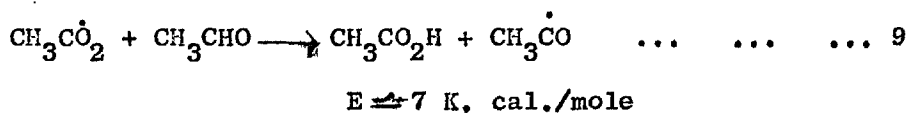
b)   The influence of hydrogen bromide (at 122°C)

The reaction:

$$HBr + O_2 \longrightarrow H\overset{\bullet}{O}_2 + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots 11$$

$$E \doteqdot 39.5 \text{ K. cal./mole}$$
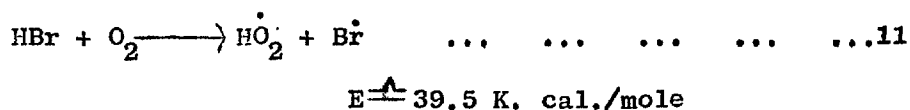
has an activation energy so much larger than 1 that it would not be

expected to occur to any significant extent in the acetaldehyde-oxygen-

hydrogen bromide system at 122°C.   However, just as 1 can probably

occur heterogeneously with a much lower activation energy, so

presumably can 11.   This supposition is supported by the experimental

results.   Thus when hydrogen bromide is admitted by itself to an

evacuated vessel, it is readily adsorbed on to the surface.   On

admitting an acetaldehyde-oxygen mixture, the additive promotes the

heterogeneous reaction immediately and initial promotion occurs.   This

was observed experimentally.   On the other hand, if the hydrogen

bromide is admitted with the oxygen and the acetaldehyde, it takes some time to diffuse to the surface and no promoting action is possible until later in the reaction, again as observed. Thus the acceleration of the reaction by hydrogen bromide is probably due to enhanced initiation through reaction 11 followed by the bromine atoms produced reacting with fuel, regenerating hydrogen bromide:

$$Br + CH_3CHO \longrightarrow CH_3\overset{\bullet}{C}O + HBr \quad \ldots \quad \ldots \quad \ldots \quad \ldots 12$$
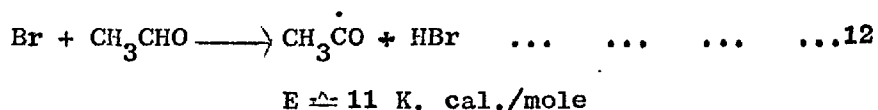
$$E \doteq 11 \text{ K. cal./mole}$$

This reaction is rather slow because of its high activation energy. The reverse reaction will not occur to any significant extent as its activation energy is 13 K. cal./mole while the acetyl radical reacts very readily with oxygen as in 2.

Further reactions are:

$$H\overset{\bullet}{O}_2 + HBr \longrightarrow H_2O_2 + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots 13$$

$$E \doteq 11 \text{ K. cal./mole}$$

$$CH_3C\overset{\bullet}{O}_3 + HBr \longrightarrow CH_3CO_3H + \overset{\bullet}{Br} \ldots \quad \ldots \quad \ldots \quad \ldots 14$$

$$E \doteq 7.5 \text{ K. cal./mole}$$

The reaction:

$$\overset{\bullet}{O}H + HBr \longrightarrow H_2O + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots 15$$

$$E \doteq 0$$
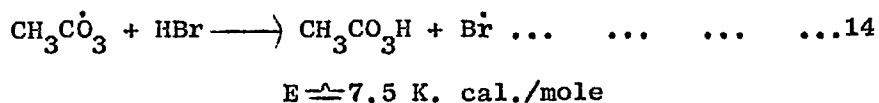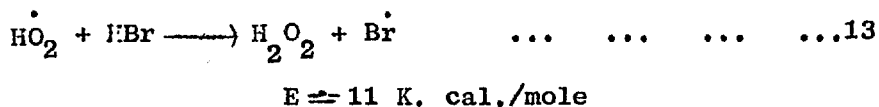
replaces the active $\overset{\bullet}{O}H$ radical by the relatively inactive bromine atom and thus has some retarding influence. However, $\overset{\bullet}{O}H$ is not a major chain carrier in this reaction and thus reaction 15 does not have an important effect on the overall reaction. In any case with the pressures of hydrogen bromide employed in this study (> 5 mm.) reactions 11, 12 would be expected to have an overriding promoting influence on the reaction.

The powerful promoting influence of hydrogen bromide is shown by its effect on the pressure-time curves of the reaction and by the increase in the rate of production of peracetic acid in the presence of additive. However the amount of peracid produced when a given pressure change has occurred is less in the presence of hydrogen bromide. This is probably due to the additive promoting the decomposition of the peracid as well as its formation. A possible reaction is:

$$CH_3CO.OOH + HBr \longrightarrow CH_3\overset{\bullet}{C}O_2 + H_2O + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad 15$$
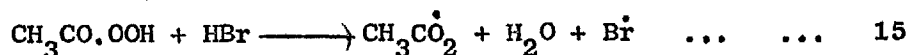
A reaction scheme for the system acetaldehyde-oxygen-hydrogen bromide can thus be formulated as follows:

$$CH_3CHO + O_2 \longrightarrow CH_3\overset{\bullet}{C}O + H\overset{\bullet}{O}_2 \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

$$E \doteq 13.8 \text{ K. cal./mole}$$

$$CH_3\overset{\bullet}{C}O + O_2 \longrightarrow CH_3\overset{\bullet}{C}O_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2$$

$$E \doteq 0$$

$$CH_3\overset{\bullet}{C}O_3 + CH_3CHO \longrightarrow CH_3CO_3H + CH_3\overset{\bullet}{C}O \quad \ldots \quad \ldots \quad \ldots \quad 3$$

$$E \rightleftharpoons -7 \text{ K. cal./mole}$$

$$HBr + O_2 \longrightarrow H\overset{\bullet}{O}_2 + \overset{\bullet}{Br} \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 11$$

$$E \text{ unknown}$$

$$\overset{\bullet}{Br} + CH_3CHO \longrightarrow HBr + CH_3\overset{\bullet}{C}O \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 12$$

$$E \doteq 11 \text{ K. cal./mole}$$

$$CH_3\overset{\bullet}{C}O_3 + HBr \longrightarrow CH_3CO_3H + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 14$$
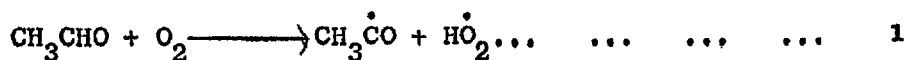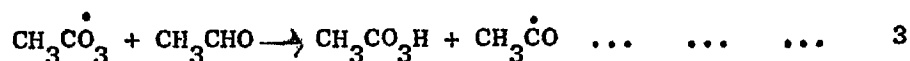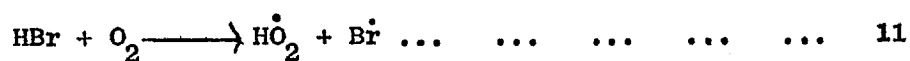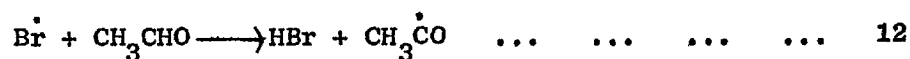
$$E \quad 7.5 \text{ K. cal./mole}$$

This is a very simplified scheme but it probably contains the most important reactions occurring. Applying the steady-state treatment to these equations, the following expression is obtained:

$$\frac{d}{dt}\left[CH_3CO_3H\right] = k_1\left[CH_3CHO\right]\left[O_2\right] + \left[k_{11} + \frac{k_{14}k_1}{k_3}\right]\left[HBr\right]\left[O_2\right]$$

$$+ \frac{k_{14}k_{11}}{k_3}\frac{\left[O_2\right]}{\left[CH_3CHO\right]}\left[HBr\right]^2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 15$$

If it is assumed that the value of $\frac{d}{dt}\left[CH_3CO_3H\right]$ at maximum rate is

proportional to the rate of maximum pressure change while the values of

$\left[CH_3CHO\right]$, $\left[O_2\right]$, $\left[HBr\right]$ at the time of maximum rate are a constant fraction

of their initial values on each occasion, then this equation can be

compared with the experimental data given in Fig. 21. Here the

maximum rate is plotted against the hydrogen bromide pressure.

Equation 15 is of the form:

$$Rate = a + bx + cx^2$$

where a, b, c are constants and

$$x = \left[HBr\right]$$

The values of the constants can be determined by inserting into the

equation the values of the rate, R, and the hydrogen bromide concentration,

x, at any three points on the experimental curve. If the values at

x = 0, x = 50, x = 90, are chosen, then a = 1.0, b = 0.13, c = 0.0020

Then, $R = 1.0 + 0.13x + 0.0020x^2$

This curve is the dotted line on Fig. 21. The theoretical line agrees

well with the experimental one for x = 50 to x = 90, but agreement is

poor for x = 0 to x = 50. However, considering the very simplified

theoretical system employed, the agreement between experiment and theory

is satisfactory.

Comparing coefficients and assuming

$$\left[CH_3CHO\right] = 100 \text{ mm.}, \left[O_2\right] = 100 \text{ mm.},$$

Then: $k_1 = 0.0001$, $k_{11} = 0.0013$, $\frac{k_{14}}{k_3} = 1.5$

Thus the k factor for reaction 11 is roughly ten times larger than the

k factor for reaction 1. Reaction 11 thus causes powerful promotion

as observed. Now

$$k = A \; \text{expt} \left(-E/RT\right)$$

As E_{11} is probably larger than E_1, A_{11} must be appreciably larger than A_1. This implies that the spatial conditions for reaction are much more favourable between hydrogen bromide and oxygen than they are between acetaldehyde and oxygen. This is quite understandable as the active hydrogen atom in the acetaldehyde molecule is considerably shielded by the rest of the molecule while in hydrogen bromide the hydrogen atom obtains appreciably less shielding from the bromine atom.

As the activation energies of 14 and 3 as calculated previously are about equal, it would be expected that $\frac{k_{14}}{k_3} \fallingdotseq 1$. As the value found was greater than one, $A_{14} > A_3$ and thus the A factor for the reaction of the peroxy radical with hydrogen bromide is larger than the A factor for the reaction of this radical with acetaldehyde. This data is in agreement with the previous deduction that $A_{10} > A_1$.

The reaction mechanism outlined above therefore satisfactorily accounts for the experimental phenomena observed in the acetaldehyde-oxygen-hydrogen bromide system at 122°C.

c) The influence of hydrogen bromide (at 225°C)

Vigorous promotion of the reaction is also observed at 225°C. Under these conditions hydrogen bromide exerts its promoting influence through enhanced initiation of the reaction as in 11 and 12.

d) The influence of methyl bromide (at 122°C)

Methyl bromide has no effect on the oxidation of acetaldehyde at 122°C. If methyl bromide participates chemically in the reaction, elementary reactions of the type:

$$\dot{R} + CH_3Br \longrightarrow RH + \dot{C}H_2Br \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$
$$H = D(R-H) -95 \text{ K. cal./mole}$$
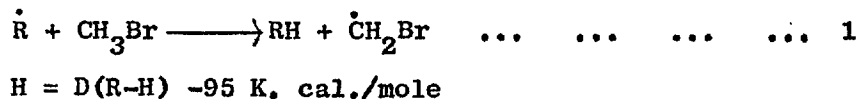
radicals R, also react with acetaldehyde:

$$\dot{R} + CH_3CHO \longrightarrow RH + CH_3\dot{C}O$$

$$\Delta H = D(R-H) -85 \text{ K. cal./mole}$$
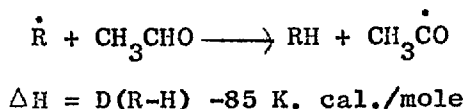
and as the CH_3CO-H bond is weaker by 10 K. cal. than the CH_2Br-H bond,

the reaction with acetaldehyde is always much faster. Further,

acetaldehyde is always present at a much higher concentration than

methyl bromide and thus, considering this mode of reaction only, a given

radical always reacts virtually entirely with acetaldehyde in preference

to methyl bromide. The acetyl radical, however, reacts preferentially

with oxygen. Another way in which methyl bromide could interact

chemically with the radicals present is:

$$\dot{R} + CH_3Br \longrightarrow RBr + \dot{C}H_3 \quad \dots \quad \dots \quad \dots \quad \dots \quad 3$$

$$\Delta H = D(R-Br) -67.5 \text{ K. cal./mole}$$
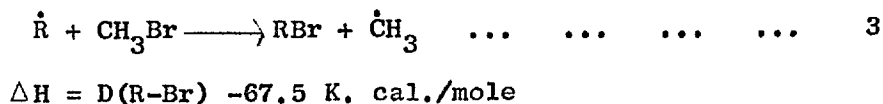
If $\dot{R} = CH_3\dot{C}O$, then $\Delta H \doteq 0$ and $E \doteq 11$ K. cal./mole. Thus the reaction

with oxygen is still much preferred. If $\dot{R} = H\dot{O}_2$, $CH_3\dot{C}O_3$, O_2, then the

reaction involves the formation of an O-Br bond. The strength of

this bond is not known but it is probably very weak. Thus reactions

of type 3 are highly endothermic and require a high activation energy

of 10 – 30 K. cal./mole. Therefore such reactions do not occur at this

temperature.

A third possible mode of interaction involves the decomposition

of the additive:

$$CH_3Br \longrightarrow \dot{C}H_3 + \dot{B}r \quad \dots \quad \dots \quad \dots \quad \dots \quad 4$$

$$E \doteq 67.5 \text{ K. cal./mole}$$
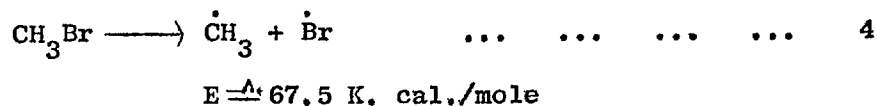
Because of the high activation energy required this reaction also does

not occur at 122°C. Thus methyl bromide cannot undergo any chemical

reaction in this system at this temperature and thus it has no effect on the reaction.

e) The influence of various halomethanes (at 154°C)

Methyl bromide, methylene dibromide, chlorobromomethane, and difluorodibromomethane all have a slight promoting influence on the oxidation of acetaldehyde at 154°C. The order of effectiveness of the additives in accelerating the maximum rate is:

$$CH_2Br_2 > CH_3Br, \quad CF_2Br_2 > CH_2BrCl \qquad .$$
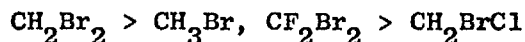
while the order of promoting effectiveness as judged from ΔT data is:

$$CH_2Br_2 > CH_2BrCl > CH_3Br > CF_2Br_2$$
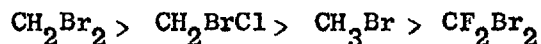
For these additives, the bond energy data is as follows:

CH_3Br D(C-H) = 95 K. cal.   D(C-Br) = 67.5 K. cal.

CH_2Br_2 D(C-H) = 87.7 K. cal.   D(C-Br) = 62.5 K. cal.

CH_2BrCl D(C-H) = 90 K. cal.   D(C-Br) = 65 K. cal.

CF_2Br_2 D(C-F) = 120 K. cal.   D(C-Br) = 65 K. cal.
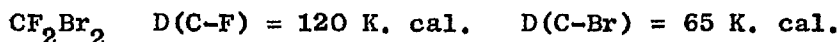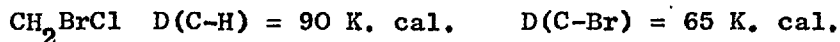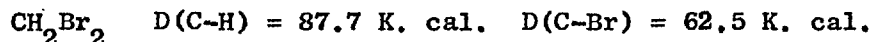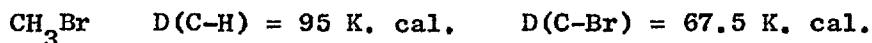
while in CH_3CHO, D(C-H) = 85 K. cal. Considering this data and the discussion of the previous section, it follows that the probability of the additive participating chemically in the reactions occurring decreases in the order:

$$CH_2Br_2 > CH_2BrCl > CH_3Br > CF_2Br_2$$
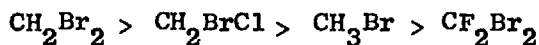
This is the observed order of activity based on ΔT data. However, it seems unlikely that these very small effects are caused by the chemical intervention of the additives in the reaction. More probably these effects are due merely to the physical presence of the additive molecules in the gas phase i.e. they are inert gas effects. The presence of nitrogen has no effect on the reaction. However, the

molecules of the halomethanes contain 1 - 4 halogen atoms and thus they have large effective collision cross-sections. They are therefore efficient in maintaining active radicals in the gas phase, thereby increasing the rates of their reactions and thus promoting the overall reaction. If the effects observed are entirely due to the increased number of gas phase collisions produced by the presence of these additives, the expected order of promoting effectiveness is:

$$CF_2Br_2 > CH_2Br_2 > CH_2BrCl > CH_3Br$$
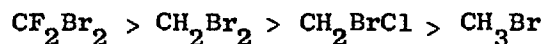
This is not the observed order of effectiveness based on either of the two criteria used. However, as the effects observed are very small, unavoidable small changes in the experimental conditions affect the results as well as the nature and pressure of the additive. It is thus not surprising that the experimental results do not agree exactly with the theoretical deductions.

As the additive concentration is increased, the number of gas-phase collisions occurring also increases, and consequently the extent of the promotion increases, as observed. Presumably, at a certain additive concentration, the number of effective gas-phase collisions reaches the maximum possible value and further additions of additive have no effect or even a retarding influence on the reaction. However, such high pressures of additive were never employed in the present work.

f) The influence of methyl bromide(at 189°C)

Methyl bromide has a slight promoting influence on the reaction at 189°C. For the reasons given previously, the effects observed are probably due merely to the physical presence of the additive molecules.

g) <u>The influence of methyl bromide(at 225°C)</u>

A mixture of 50 mm. acetaldehyde, 50 mm. oxygen ignites after ~8.5 sec. at 225°C. The pressure increase is 68 mm. Considering the reactions:

$$CH_3CHO + 2\tfrac{1}{2}O_2 \longrightarrow 2CO_2 + 2H_2O$$

20 mm.   50 mm. $\longrightarrow$ 40 mm. 40 mm.

100 mm. $\longrightarrow$ 110 mm.

$$CH_3CHO + 2O_2 \longrightarrow 2CO + 2H_2O$$

25 mm. 50 mm.   50 mm. 50 mm.

100 mm. $\longrightarrow$ 125 mm.

$$CH_3CHO + 1\tfrac{1}{2}O_2 \longrightarrow 2CO_2 + 2H_2$$

100 mm. $\longrightarrow$ 150 mm.

$$CH_3CHO + \tfrac{1}{2}O_2 \longrightarrow 2CO + 2H_2$$

100 mm. $\longrightarrow$ 225 mm.

$$CH_3CHO \longrightarrow CH_4 + CO$$

100 mm. $\longrightarrow$ 150 mm.
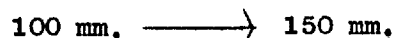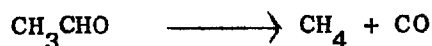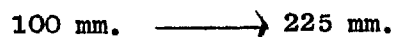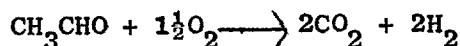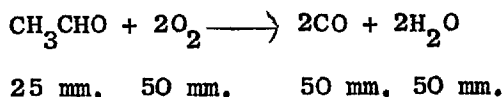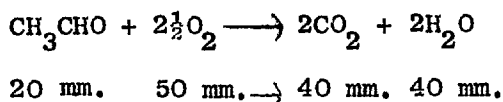
it is seen that much partial oxidation or even pyrolysis of the acetaldehyde must occur in order to account for the very large pressure change observed. The presence of methyl bromide probably promotes the ignition but any effect is small. The promotion is again probably due initially to the 'inert gas' effect of the additive. However, as the pressure increase is always larger in the presence of methyl bromide, it seems likely that the additive is decomposed to some extent at the high temperatures momentarily produced in the flame front travelling through the mixture. In the oxygen-deficient conditions of the reaction, the additive probably undergoes a pyrolysis reaction such as:

$$CH_3Br \longrightarrow C + HBr + H_2 \ .$$
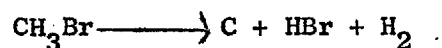
giving a pressure increase as observed.

The pressure increase observed is rather variable and appears to be largely independent of the additive pressure employed. However, with additive pressures $\leqslant 5$ mm. the value of Δp observed is always rather smaller than the mean value. These observations can be explained as follows:

If the additive initially exerts only an inert gas effect, then the energy available in the flame front on each occasion is constant, depending only on the acetaldehyde and oxygen concentrations. This energy is only capable of dissociating a given amount of methyl bromide on each occasion and thus so long as enough additive is present, the amount of additive decomposed does not depend on the amount of additive present. When only small amounts of additive are present, it is all decomposed by the flame front and thus the pressure increase observed increases linearly with additive pressure. In the present case, the energy in the flame is only capable of dissociating 5-10 mm. additive and thus little systematic variation in Δp is observed as the additive pressure is varied from 1-50 mm., especially as the random variation in Δp is large.

As methyl bromide does not react with oxygen under the experimental conditions employed, pre-heating of additive-oxygen mixtures does not affect the results.

The presence of nitrogen has virtually no effect on the reaction. This is due to the fact that its 'inert gas' effect is negligibly small in this system (cf. the effect of nitrogen on the slow combustion of acetaldehyde).

A mixture of 125 mm. oxygen, 50 mm. acetaldehyde ignites after 13 sec. The pressure increase is 9 mm. Considering the reaction:

$$CH_3CHO + 2\tfrac{1}{2}O_2 \longrightarrow 2CO_2 + 2H_2O$$

$$175 \text{ mm.} \longrightarrow 200 \text{ mm.}$$
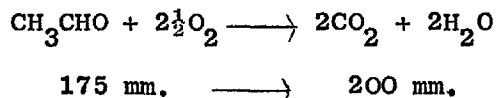
a pressure increase of 25 mm. would be expected. Thus only a small percentage of the reactants participate in the explosive reaction.

The presence of methyl bromide again promotes the reaction, the explosion time decreasing steadily as the additive pressure is increased. Again the reaction is presumably promoted initially by the 'inert gas' influence of the additive. Under these conditions this influence is sufficiently large to produce a definite decrease in explosion time as the additive pressure is increased.

The stoichiometric acetaldehyde-oxygen mixture reacts with great vigour and produces an energetic flame front which decomposes the methyl bromide present. As the pressure change observed increases steadily with the pressure of methyl bromide present, sufficient energy is presumably available to decompose all the additive present. The pressure increase is therefore linearly dependent on the additive pressure. The slope of the graph of pressure increase versus additive pressure is approximately one, suggesting that one volume of additive gives two volumes of decomposition products. The predominant decomposition reaction of methyl bromide under these conditions is probably therefore:

$$CH_3Br \longrightarrow C + HBr + H_2$$

2. The oxidation of diethyl ether (at 155°C)

a) The basic reaction

The initiation reaction is:

$$CH_3CH_2O\ C_2H_5 + O_2 \longrightarrow CH_3\overset{\bullet}{C}HOC_2H_5 + H\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad 1$$
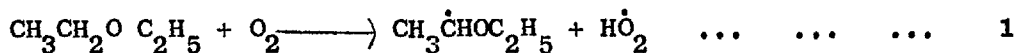
D(R-H) is not known accurately on this occasion but it is probably ~100 K. cal. Thus $E \doteqdot 50$ K. cal./mole.

However, as the oxidation proceeds readily at 155°C, the actual activation energy is probably ~20 K. cal./mole. Possibly the initiation reaction occurs largely heterogeneously.

The initiation reaction is followed by:

$$CH_3\overset{\bullet}{C}HO\ C_2H_5 \longrightarrow CH_3CHO + \overset{\bullet}{C}_2H_5 \quad \ldots\ldots\ldots\ldots \quad \ldots \quad \ldots \quad 2$$

$$E \doteqdot 25 \text{ K. cal./mole}$$

$$\text{or} \quad CH_3\overset{\bullet}{C}HOC_2H_5 + O_2 \longrightarrow \underset{\underset{\displaystyle O\overset{\bullet}{_2}}{|}}{CH_3CH.OC_2H_5} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 3$$

$$E \text{ small}$$
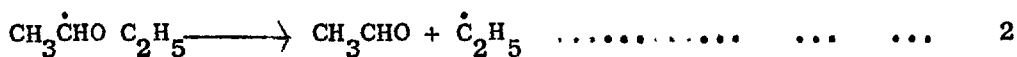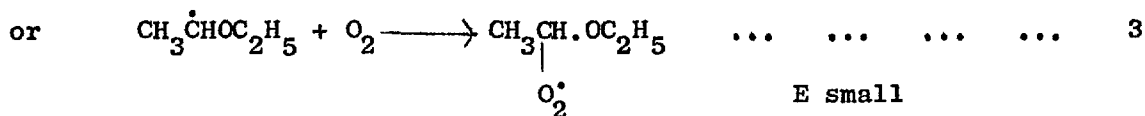
The addition of oxygen is thus the most probable reaction. This reaction also accounts for the pressure decrease initially observed in the reaction. The peroxy radical then abstracts a hydrogen atom from a fuel molecule to give a hydroperoxide:

$$\underset{\underset{\displaystyle O_2}{|}}{CH_3CHOC_2H_5} + RH \longrightarrow \underset{\underset{\displaystyle OOH}{|}}{CH_3CHOC_2H_5} + \overset{\bullet}{R} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 4$$
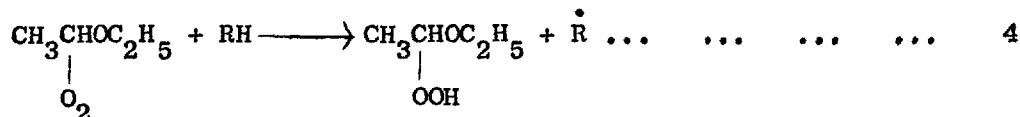
This reaction sequence is presumably the predominant one up to the point of maximum pressure decrease. The decomposition of this hydroperoxide then leads to the pressure increase observed:

$$\underset{\underset{\displaystyle OOH}{|}}{CH_3CHOC_2H_5} \longrightarrow CH_3CHO + C_2H_5\overset{\bullet}{O} + \overset{\bullet}{O}H \quad \ldots$$
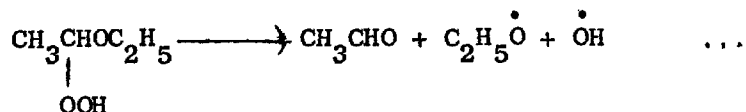
Acetaldehyde is then oxidised as previously described while the ethoxy radical abstracts a hydrogen atom from a fuel molecule, forming ethanol.

b) The influence of halomethanes

As $D(C_2H_5OCH\text{-}H)$ is not known accurately, it is not possible to
$\quad\quad\quad\quad\quad\quad\mid$
$\quad\quad\quad\quad\quad\quad CH_3$

carry out any calculations on the relative rates of radical-fuel and radical-additive reactions. However, as diethyl ether oxidises in the same temperature range as acetaldehyde, it again seems unlikely that the additives will have any chemical effect on the reaction. In this system the different additives have rather different effects. Thus methyl bromide and difluorodibromomethane retard the initial stages of the reaction while the other two additives either have little effect or they promote the reaction at this stage. All the additives promote the reaction in the later stages. The order of promoting effectiveness is:

$$CF_2Br_2 > CH_3Br > CH_2BrCl > CH_2Br_2$$
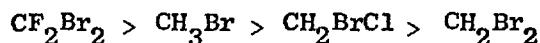
This is not the order expected if the effects are caused entirely by the 'inert gas' influence of the additives. However, although the observed differences between the effects of the various additives are fairly large, considering the observed variability of the results as a whole it still appears reasonable to attribute the effects observed merely to this 'inert gas' influence.

3. The oxidation of isopentane (at 283°C)

a) The basic reaction

The predominant initiating reaction is:

$$CH_3CHCH_2CH_3 + O_2 \longrightarrow CH_3\overset{\bullet}{C}CH_2CH_3 + H\overset{\bullet}{O_2}\ldots \quad \ldots \quad \ldots \quad 1$$
$\quad\quad\mid\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\mid$
$\quad\quad CH_3\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CH_3$

Here $D(R-H) \simeq 58$ K. cal. and thus $E \simeq 38$ K. cal./mole

The following reactions then occur:

$$CH_3\overset{\underset{CH_3}{|}}{C}.CH_2CH_3 + O_2 \longrightarrow CH_3\overset{\underset{O_2}{|}}{\underset{|}{C}}.CH_2CH_3 \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad 2$$

E small

$$CH_3\overset{\underset{CH_3}{|}}{\underset{|}{\overset{\overset{\displaystyle \overset{\bullet}{O_2}}{|}}{C}}} CH_2CH_3 \longrightarrow CH_3CO.CH_3 + CH_3CH_2\overset{\bullet}{O} \cdots \quad \cdots \quad \cdots \quad 3$$

As no initial pressure decrease is observed, the intermediate peroxy radical can only have a very short life-time and readily breaks down into various decomposition products to produce the pressure increase observed.

b) The influence of halomethanes

The oxidation is strongly promoted by methyl bromide and by difluorodibromomethane.. From the information discussed so far it would seem possible that the oxidation of the additive methyl bromide under these conditions would have a significant effect on the overall oxidation. On the other hand, difluorodibromomethane would not be expected to dissociate significantly at this temperature. However, the product chromatogram data suggests that it is unlikely that either additive participates chemically in the reactions occurring. The effects observed are again presumably due to the 'inert gas' influence of the additives. Relatively large effects are observed because the basic oxidation is carried out under conditions close to those producing ignition. Difluorodibromomethane exerts a larger promoting influence than methyl bromide because, as it is a larger, heavier molecule, it has a greater effect as an 'inert gas'.

4. The oxidation of formaldehyde

a) The basic reaction (at 315°C)

The reaction mechanism is:

$$HCHO + O_2 \longrightarrow \dot{C}HO + H\dot{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

$$E \doteq 32 \text{ K. cal./mole}$$

$$\dot{C}HO + O_2 \longrightarrow HC\dot{O}_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2$$

$$E = 0 - 5 \text{ K. cal./mole}$$

$$\dot{C}HO + O_2 \longrightarrow H\dot{O}_2 + CO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 3$$

$$E \doteq 0$$

$$H\dot{O}_2 + HCHO \longrightarrow H_2O_2 + \dot{C}HO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 4$$

$$E \doteq 9 \text{ K. cal./mole}$$

$$HC\dot{O}_3 + HCHO \longrightarrow HCO_3H + \dot{C}HO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 5$$

$$E \doteq 5 \text{ K. cal./mole}$$

$$H_2O_2 \longrightarrow wall \longrightarrow 2\dot{O}H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 6$$

$$HCO_3H \longrightarrow wall \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 7$$

$$\dot{O}H + HCHO \longrightarrow H_2O + \dot{C}HO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 8$$

$$E \doteq 2 \text{ K. cal./mole}$$
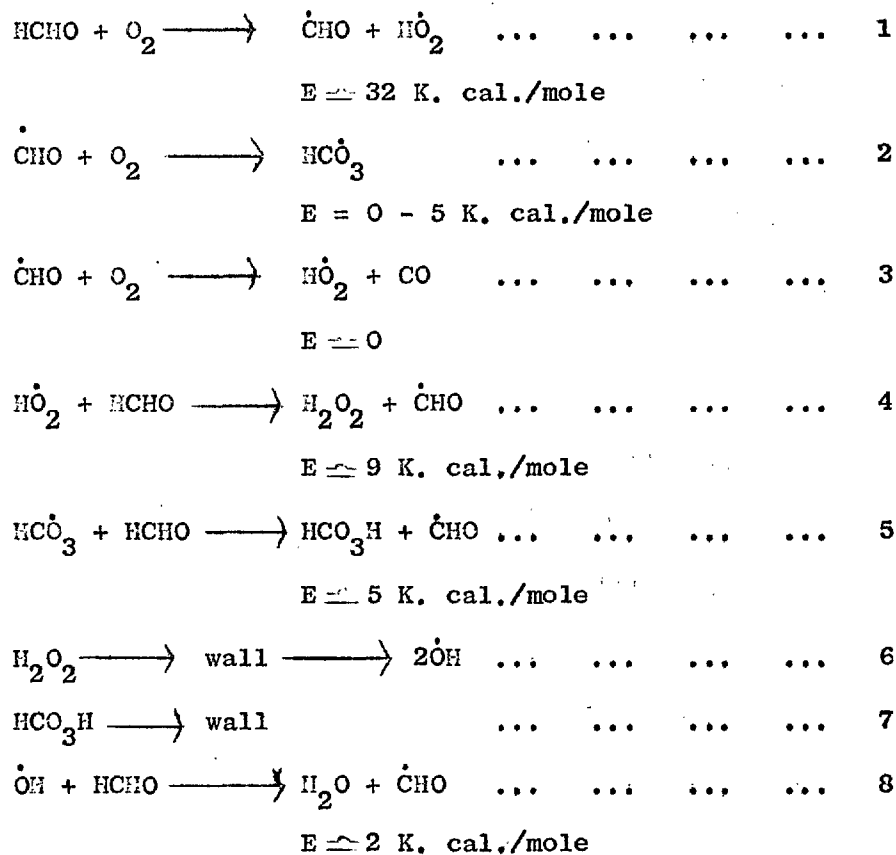
As no initial pressure decrease is observed, any performic acid formed can have only a short life-time and it breaks down readily on the walls. The pressure increase observed is due to reactions 6 and 7. The main chain carriers are $\dot{C}HO$, $H\dot{O}_2$, $\dot{O}H$.

b) The influence of hydrogen bromide (at 315°C)

Hydrogen bromide exerts a complex effect on the oxidation, low pressures of additive retarding the reaction while higher pressures promote the reaction. The maximum retarding influence is observed with 1 mm. additive. On this occasion the effects observed are certainly

chemical in origin.   The possible reactions are considered below:

$$HBr + O_2 \longrightarrow H\dot{O}_2 + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 9$$

$$E \simeq 39 \text{ K. cal./mole}$$
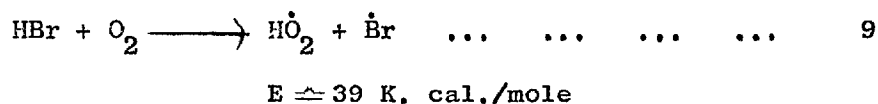
This reaction is a source of relatively active free-radicals and thus it promotes the overall reaction.   However, as its activation energy is high compared with the activation energy for 1, the reaction only occurs slowly under the reaction conditions employed.   This promoting influence is enhanced by the radicals produced in 9 attacking formaldehyde as in 4 and:

$$\dot{B}r + HCHO \longrightarrow HBr + \dot{C}HO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 10$$

$$E \simeq 10 \text{ K. cal./mole}$$
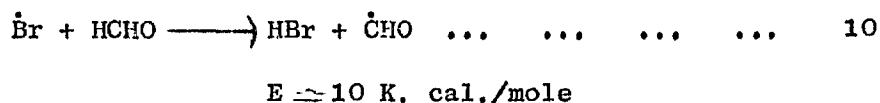
Here again the activation energy is fairly high and thus the reaction only occurs slowly.

The retarding reaction:

$$HBr + \dot{C}HO \longrightarrow HCHO + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 11$$

$$E \simeq 17 \text{ K. cal./mole}$$
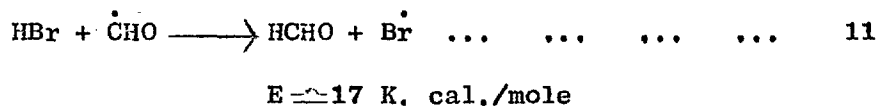
does not occur because of its high activation energy.

Further promoting reactions are:

$$H\dot{O}_2 + HBr \longrightarrow H_2O_2 + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 12$$

$$E \simeq 11 \text{ K. cal./mole}$$

$$HC\dot{O}_3 + HBr \longrightarrow HCO_3H + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 13$$

$$E \simeq 7.5 \text{ K. cal./mole}$$
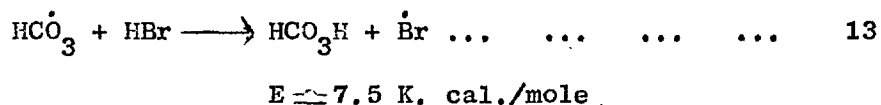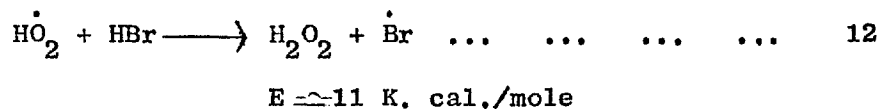
The important retarding reaction is probably:

$$\dot{O}H + HBr \longrightarrow H_2O + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 14$$

$$E \simeq 0$$
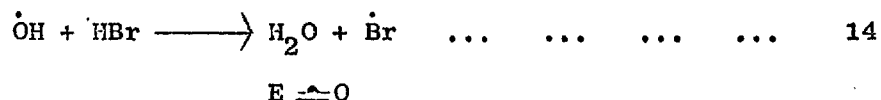
This reaction has approximately zero activation energy and thus occurs readily.   It replaces an active $\dot{O}H$ radical by a relatively less reactive

bromine atom and therefore produces retardation of the reaction.
Reaction 14 is in competition with reaction 8. It can be shown that
if the f values for the two reactions are the same, then when 1 mm.
hydrogen bromide is present, 5% of the $\dot{O}H$ radicals present react as in
14. This produces a reduction in the rate of the chain-branching
cycle:

$$\dot{O}H \xrightarrow{HCHO} \dot{C}HO \xrightarrow{O_2} H\dot{O}_2 \xrightarrow{HCHO} H_2O_2 \longrightarrow 2\dot{O}H \quad \dots \quad \dots \quad 15$$
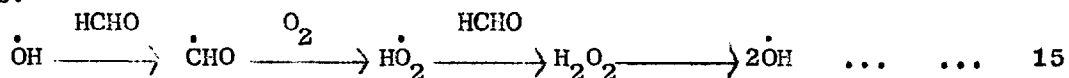
and therefore produces retardation of the reaction. The bromine atoms
produced in 14 react largely as in 10, but as $E_{10} \rightleftharpoons 10$ K. cal./mole
while $E_8 \rightleftharpoons 2$ K. cal./mole the rate of 10 is much less than that of 8
and thus overall retardation still occurs. Further, as reaction 10 is
slow, bromine atoms can diffuse to the walls and recombine rather than
react with fuel:

$$\dot{B}r + \dot{B}r \longrightarrow Br_2 \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad 16$$

E small

Alternatively the bromine atoms can react with other radicals present
at the walls e.g. $H\dot{O}_2$

$$H\dot{O}_2 + \dot{B}r \longrightarrow HBr + O_2 \dots \quad \dots \quad \dots \quad \dots \quad 17$$

E small

This reaction has a powerful retarding effect on the reaction as it not
only removes two radicals, replacing them by two molecules, but it also
regenerates hydrogen bromide which can exert further retarding action
through reaction 14. However the reverse reaction 9 also occurs tending
to promote the reaction.

The overall effect observed thus depends on the balance of all
these reactions. At additive pressures $\geqslant 1$ mm., insufficient hydrogen

bromide is present to remove a significant number of $\overset{\bullet}{O}H$ radicals and thus only a small retarding effect is observed. At additive pressures > 1 mm., the retarding influence of 14 is still important but its overall effect is much reduced by the promoting effects of reactions 9 and 10. At a pressure of 1 mm. additive these competing reactions are so balanced that the maximum retarding effect is observed.

c) The influence of halomethanes (at 315°C)

Methyl bromide has no definite effect on the oxidation at 315°C. Thus the additive probably does not participate chemically in the reaction and the small effects observed are merely 'inert gas' effects.

Considering the earlier theoretical discussion it is seen that no chemical intervention by methyl bromide in the reaction would be expected as $D(H\text{-}CHO) = 79$ K. cal. while $D(CH_2Br\text{-}H) = 95$ K. cal.

Difluorodibromomethane has roughly the same effect on the oxidation as hydrogen bromide. Presumably therefore, it has a chemical effect on the reaction. This is very surprising on theoretical grounds. However, the most probable mode of action of the additive is as follows:

First the additive dissociates, introducing bromine atoms into the system:

$$CF_2Br_2 \longrightarrow \overset{\bullet}{C}F_2Br + \overset{\bullet}{B}r \quad \dots \quad \dots \quad \dots \quad \dots \quad 18$$

$$E \simeq 65 \text{ K. cal./mole}$$
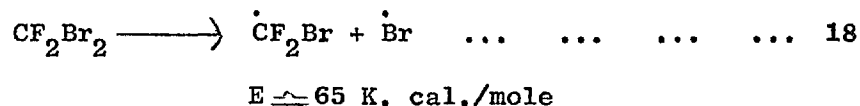
Some of the bromine atoms then react:

$$\overset{\bullet}{B}r + HCHO \longrightarrow HBr + \overset{\bullet}{C}HO \quad \dots \quad \dots \quad \dots \quad \dots \quad 10$$

$$E \simeq 10 \text{ K. cal./mole}$$
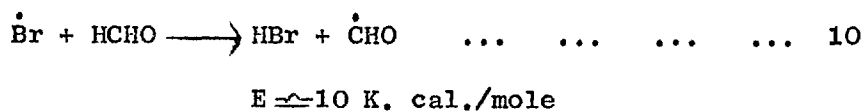
The .hydrogen bromide formed then efficiently removes $\dot{O}H$ radicals as above:

$$\dot{O}H + HBr \longrightarrow H_2O + \dot{B}r \quad \dots \quad \dots \quad \dots \quad \dots \quad 14$$

$$E \rightleftharpoons 0$$
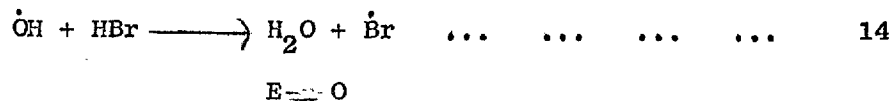
However, as 10 is slow, it alone cannot provide a sufficiently large number of hydrogen bromide molecules in the system for effective retardation of the reaction through step 14 to occur. Thus some of the bromine atoms must diffuse to the walls and react as in 17

$$\dot{H}\dot{O}_2 + \dot{B}r \longrightarrow HBr + O_2 \quad \dots \quad \dots \quad \dots \quad \dots \quad 17$$

thereby removing $H\dot{O}_2$ radicals and also forming hydrogen bromide which retards the reaction further.

As before, the overall effect observed depends on the relative importance of the various elementary steps under the differing conditions produced by the varying pressures of additive. The maximum retarding effect is again observed with 1 mm. additive. With lower pressures of additive, the rate of production of bromine atoms is not sufficient to maintain the optimum concentration of hydrogen bromide required to produce maximum retardation of the reaction through step 14. With higher pressures of additive, the rate of bromine atom production is too great for a large proportion of them to be removed by 17 and thus 10 becomes important. The resulting rate of production of hydrogen bromide is much greater than that required solely to remove all the $\dot{O}H$ radicals present and thus oxidation of the hydrogen bromide occurs to a significant extent, producing further bromine atoms to continue the cycle. Promotion at high additive pressures is therefore due to enhanced initiation of the reaction.

Retardation of the reaction at low additive pressures is due to recombination of radicals at the walls to form hydrogen bromide which then readily removes $\overset{\bullet}{O}H$ radicals, regenerating bromine atoms. These conflicting effects are balanced to give the maximum retarding effect when 1 mm. additive is present.

At high additive pressures, the promoting influence of difluorodibromomethane is considerably less than that of hydrogen bromide. However, the rate of production of radicals from hydrogen bromide by oxidation is much greater than the rate of production of radicals from difluorodibromomethane by dissociation at this temperature and thus hydrogen bromide naturally has the greater promoting influence on the reaction.

d) The influence of additives (at 515°C)

At 515°C, both methyl bromide and hydrogen bromide have a pronounced promoting influence on the reaction. At this temperature, hydrogen bromide oxidises readily and the radicals produced attack formaldehyde, causing enhanced initiation of the reaction and thereby, overall promotion:

$$HBr + O_2 \longrightarrow H\overset{\bullet}{O}_2 + \overset{\bullet}{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 9$$

$$\overset{\bullet}{B}r + HCHO \longrightarrow HBr + \overset{\bullet}{C}HO \quad \ldots \quad \ldots \quad \ldots \quad \ldots 10$$

$$H\overset{\bullet}{O}_2 + HCHO \longrightarrow H_2O_2 + \overset{\bullet}{C}HO \quad \ldots \quad \ldots \quad \ldots \quad \ldots 4$$
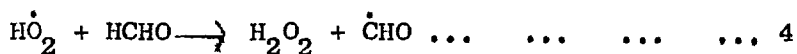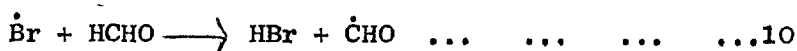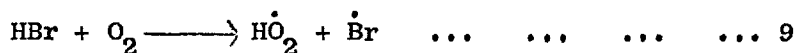
These reactions occur so readily at 515°C that the competing reactions, producing retardation, mentioned previously do not occur to a significant extent, even in the presence of only 0.1 mm. additive. The rates of these reactions, 9, 10 increase far more rapidly with temperature than the rates of 14, 17 because they have much greater

activation energies. The oxidation of hydrogen bromide proceeds with a small overall reduction in pressure at constant volume and as only small pressures of hydrogen bromide are used on this occasion, the presence of this additive has little effect on the final pressure change observed.

Methyl bromide also oxidises at 515°C, producing bromine atoms which promote the reaction as previously described through reactions 10 and 9. It oxidises far more slowly than hydrogen bromide, however, and thus it has a considerably smaller promoting influence. The overall oxidation can be written:

$$2CH_3Br + 2\tfrac{1}{2}O_2 \longrightarrow 2CO + 3H_2O + Br_2 \quad \ldots \quad \ldots \quad \ldots \quad 19$$
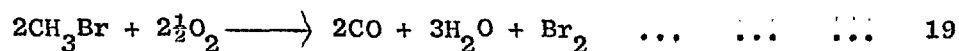
In this reaction the oxidation of 1 mm. additive produces a pressure increase of 0.75 mm. at constant volume. From Fig. 36 it is seen that the presence of 1 mm. additive produced an increase of ~1.75 mm. in the final total pressure in agreement with the requirements of equation 19. Thus this equation does represent the predominant overall oxidation reaction undergone by the additive under these conditions.

5. The oxidation of isopropanol (at 355°C)

a) The basic reaction

During the initial stages of the oxidation the predominant reaction cycle is:

$$\underset{\text{OH}}{CH_3\overset{|}{C}HCH_3} + O_2 \longrightarrow \underset{\text{OH}}{CH_3\overset{\bullet}{\underset{|}{C}}.CH_3} + \overset{\bullet}{H}O_2 \quad \ldots \quad \ldots \quad \ldots \quad 1$$

$$E \simeq 42 \text{ K. cal./mole}$$

$$\underset{\text{OH}}{CH_3\overset{\bullet}{\underset{|}{C}}CH_3} + O_2 \longrightarrow \underset{\text{OH}}{CH_3\overset{\overset{\bullet}{\underset{|}{O_2}}}{\underset{|}{C}}.CH_3} \quad \ldots \quad \ldots \quad \ldots \quad 2$$

$$E \text{ small}$$

$$CH_3\overset{\overset{\overset{\bullet}{O_2}}{|}}{\underset{|}{C}}CH_3 \longrightarrow CH_3CO.CH_3 + H\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 3$$
$$\underset{OH}{} \qquad\qquad\qquad\qquad\qquad E \rightleftharpoons 8 \text{ K. cal./mole}$$

$$CH_3\underset{|}{\overset{\bullet}{C}HCH_3} + H\overset{\bullet}{O}_2 \longrightarrow CH_3\underset{|}{\overset{\bullet}{C}}.CH_3 + H_2O_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 4$$
$$\underset{OH}{} \qquad\qquad\qquad\qquad \underset{OH}{} \quad E \rightleftharpoons 11 \text{ K. cal./mole}$$

These reactions are equivalent to the overall reaction:

$$CH_3\underset{|}{\overset{\bullet}{C}H}.CH_3 + O_2 \longrightarrow CH_3CO.CH_3 + H_2O_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 5$$
$$\underset{OH}{}$$

which produces no pressure change. The pressure increase observed is
produced by reactions such as:

$$H_2O_2 \longrightarrow 2\overset{\bullet}{O}H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 6$$

$$CH_3\underset{|}{\overset{\bullet}{C}}.CH_3 \longrightarrow CH_3CHO + \overset{\bullet}{C}H_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 7$$
$$\underset{OH}{}$$

These products then oxidise further:

$$CH_3CHO + O_2 \longrightarrow CH_3\overset{\bullet}{C}O + H\overset{\bullet}{O}_2 \ldots \quad \ldots \quad \ldots \ldots \cdot \ldots \quad \ldots \quad 8$$

$$CH_3\overset{\bullet}{C}O \longrightarrow \overset{\bullet}{C}H_3 + CO \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 9$$

$$\overset{\bullet}{C}H_3 + O_2 \longrightarrow HCHO + \overset{\bullet}{O}H \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 10$$

$$HCHO + O_2 \longrightarrow \overset{\bullet}{C}HO + H\overset{\bullet}{O}_2 \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 11$$

$$\overset{\bullet}{C}HO + O_2 \longrightarrow CO + H\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 12$$

finally producing carbon monoxide, $\overset{\bullet}{O}H$, and $H\overset{\bullet}{O}_2$ radicals. The $\overset{\bullet}{O}H$
radicals react with fuel:

$$\overset{\bullet}{O}H + CH_3\underset{|}{\overset{}{C}HCH_3} \longrightarrow CH_3\underset{|}{\overset{\bullet}{C}CH_3} + H_2O \quad \ldots \quad \ldots \quad \ldots \quad \ldots 13$$
$$\underset{OH}{} \qquad\qquad \underset{OH}{} \quad E \rightleftharpoons 5 \text{ K. cal./mole}$$

b) **The influence of hydrogen bromide**

Hydrogen bromide has a mild promoting influence on the reaction.
At 355°C, it oxidises fairly readily, promoting the reaction:

$$HBr + O_2 \longrightarrow H\overset{\bullet}{O}_2 + \overset{\bullet}{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots 14$$
$$E \rightleftharpoons 39 \text{ K. cal./mole}$$

As $E_{14} < E_1$, this promoting reaction is important even when only about 1 mm. additive is present. The bromine atoms produced then attack fuel:

$$\dot{Br} + CH_3\underset{OH}{CHCH_3} \longrightarrow CH_3\underset{OH}{\dot{C}.CH_3} + HBr \quad \dots \quad \dots \quad \dots \quad 15$$

$$E \simeq 13 \text{ K. cal./mole}$$
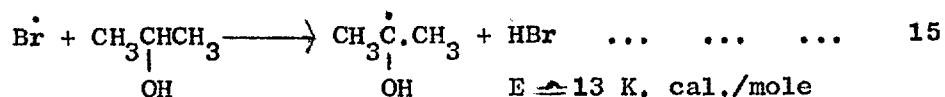
The reaction occurs slowly because of its high activation energy. The reverse reaction:

$$CH_3\underset{OH}{\dot{C}.CH_3} + HBr \longrightarrow CH_3\underset{OH}{CHCH_3} + \dot{Br} \quad \dots \quad \dots \quad \dots \quad 16$$

$$E \simeq 11 \text{ K. cal./mole}$$
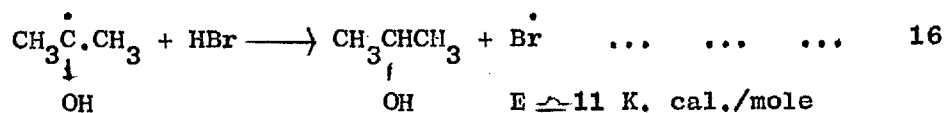
which would retard the overall reaction does not occur because the reaction of the radical with oxygen is far more favourable energetically.

Hydrogen bromide also promotes the reaction:

$$H\dot{O}_2 + HBr \longrightarrow H_2O_2 + \dot{Br} \quad \dots \quad \dots \quad \dots \quad 17$$
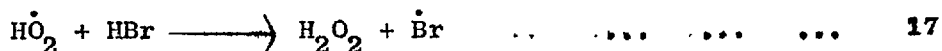
This reaction, however, is not a very important one since the $H\dot{O}_2$ radical reacts just as readily with fuel which is present at much higher concentration.

The reaction of hydrogen bromide with $\dot{O}H$ radicals again has some retarding influence on the reaction:

$$HBr + \dot{O}H \longrightarrow H_2O + \dot{Br} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad 18$$

$$E \simeq 0$$
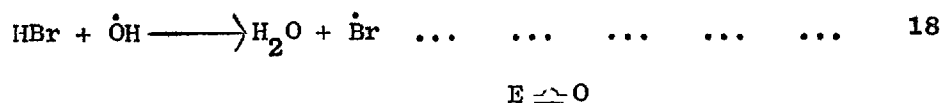
However, the regeneration of hydrogen bromide by the reverse of 14 is presumably less efficient in this system at 355°C than with formaldehyde at 315°C and thus no overall retarding effect is observed. Nevertheless, the additive does have only a mild promoting influence on the reaction and thus 18 may well be an important reaction in this system. Also, in this reaction hydrogen peroxide is produced at a relatively high

rate in a reaction cycle not involving $\dot{O}H$ radicals. The hydrogen

peroxide breaks down as in 6, producing $\dot{O}H$ radicals at an appreciable

rate. Thus it is presumably not possible to introduce a sufficiently

high concentration of hydrogen bromide to remove most of the $\dot{O}H$ radicals

by 18 without 14 occurring to a significant extent, producing promotion.

It is probable that the retarding reaction:

$$CH_3 + HBr \longrightarrow CH_4 + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 19$$

$$E \simeq 0$$
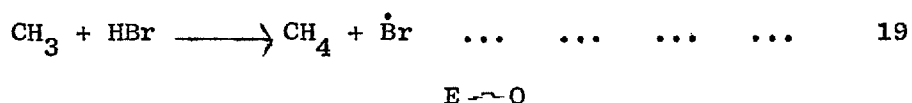
effectively competes with the chain propagating reaction:

$$\dot{C}H_3 + O_2 \longrightarrow HCHO + \dot{O}H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 20$$

$$E \simeq 0$$
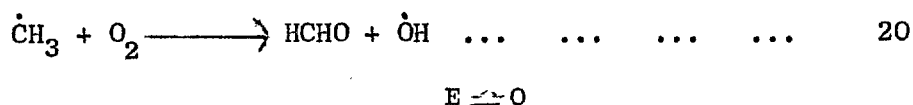
at 510°C (see Section C.7.b.).

Here the $\dot{C}H_3$ radical is an important chain carrier in the

autocatalytic phase of the reaction and thus the occurrence of 19 to

any extent would produce effective retardation of the reaction. As

this is not observed, reaction 20 must occur far more readily than

reaction 19 at 355°C. Now at 510°C, reaction 20 has an f value of

10^{-3}. Presumably the f value must be much larger under the less energetic

conditions prevailing at 355°C and thus 20 becomes the predominant

reaction.

Hydrogen bromide normally retards the slow oxidation of

formaldehyde. However, in this system hydrogen bromide is much less

effective in removing $\dot{O}H$ radicals than in the ordinary formaldehyde

system. Also at the higher temperature the reactions of formaldehyde

and additive with oxygen have a greater promoting influence and thus

hydrogen bromide does not retard the oxidation under these conditions.

Thus low pressures of additive (∼0.1 mm.) have no effect on the reaction because insufficient additive is present to participate significantly in any reaction. All higher pressures of additive promote the reaction because the promoting influence of reactions 14, 15 always outweighs the retarding influence of 18.

c) The influence of halomethanes

The presence of methyl bromide and difluorodibromomethane have no definite effect on the oxidation and thus it seems unlikely that the additives participate chemically in the reactions occurring.

The temperature is still too low for ∼10 mm. methyl bromide to oxidise significantly and radical-fuel reactions are always much faster than radical-additive reactions. No chemical interaction by methyl bromide is therefore possible and the small effects observed are thus due to the 'inert gas' influence of the additive as well as to random variations in the rate of the ordinary oxidation. With difluorodibromomethane, no oxidation reaction is possible and pyrolysis of the additive does not occur at this temperature. Thus no chemical interaction is possible and the effects are again due to the 'inert gas' influence of the additive.

6. The oxidation of ethane (at 416°C)

a) The basic reaction

The most important reactions occurring during the oxidation of ethane are:

$$CH_3CH_3 + O_2 \longrightarrow CH_3\dot{C}H_2 + H\dot{O}_2 \quad \dots \quad \dots \quad \dots \quad 1$$

$$E \doteq 51 \text{ K. cal./mole}$$

$$CH_3\dot{C}H_2 + O_2 \longrightarrow CH_3CH_2\dot{O}_2 \quad \dots \quad \dots \quad \dots \quad 2$$

$$E \text{ small}$$

$$CH_3CH_2\overset{\bullet}{O}_2 \longrightarrow \overset{\bullet}{C}H_2CH_2OOH \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 3$$
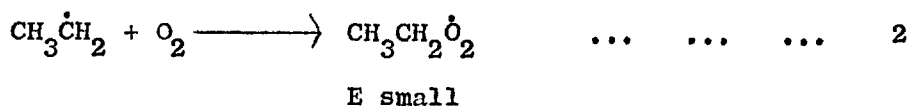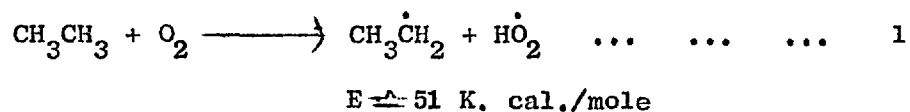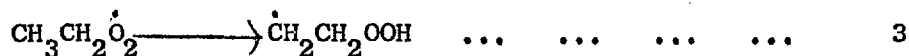
This is an internal isomerization reaction for which $E \approx 20$ K. cal./mole (Semenov, 5).

The alternative reaction is:

$$CH_3CH_2\overset{\bullet}{O}_2 + C_2H_6 \longrightarrow CH_3CH_2O_2H + \overset{\bullet}{C}_2H_5 \quad \ldots \quad \ldots \quad 4$$

$$E \approx 10 \text{ K. cal./mole}$$
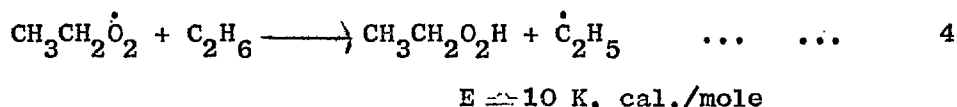
It can be shown that

$$\frac{w_3}{w_4} = \frac{50}{f_4}$$

As f_4 is probably less than 1, $w_3 \gg w_4$ and thus the isomerization is the predominant reaction. Reaction 3 is followed by:

$$\overset{\bullet}{C}H_2CH_2OOH \longrightarrow C_2H_4 + H\overset{\bullet}{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad 5$$

$$E \approx 10 \text{ K. cal./mole}$$
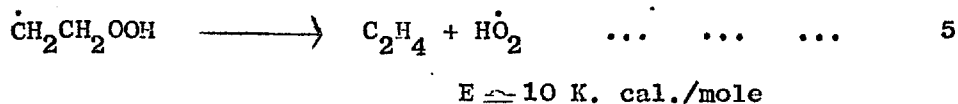
Other reactions occurring are:

$$H\overset{\bullet}{O}_2 + C_2H_6 \longrightarrow H_2O_2 + \overset{\bullet}{C}_2H_5 \quad \ldots \quad \ldots \quad \ldots \quad 6$$

$$E \approx 18 \text{ K. cal./mole}$$

$$H_2O_2 \longrightarrow 2\overset{\bullet}{C}H\ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 7$$

$$E \approx 45 \text{ K. cal./mole}$$

$$C_2H_4 + O_2 \longrightarrow \underset{O - O}{CH_2-CH_2} \longrightarrow 2HCHO \quad \ldots \quad \ldots \quad \ldots \quad 8$$
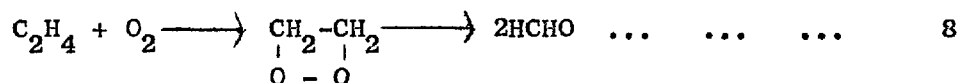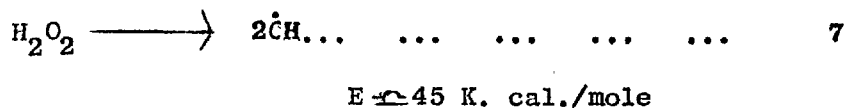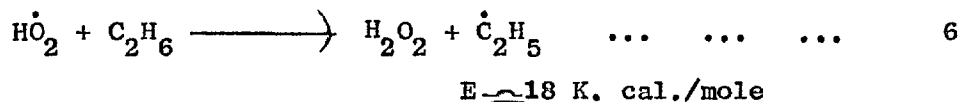
The formaldehyde then oxidises in the usual way.
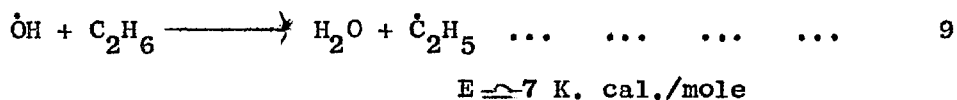
$$\overset{\bullet}{O}H + C_2H_6 \longrightarrow H_2O + \overset{\bullet}{C}_2H_5 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 9$$

$$E \approx 7 \text{ K. cal./mole}$$

b) The influence of hydrogen bromide

Hydrogen bromide has a powerful promoting influence on the reaction. At 416°C it oxidises rapidly, promoting the reaction.

$$HBr + O_2 \longrightarrow H\dot{O}_2 + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 10$$

$$E \simeq 39 \text{ K. cal./mole}$$

As $E_{10} \ll E_1$, this is an important promoting reaction even when only small quantities of additive are present. The bromine atoms produced then attack fuel:

$$\dot{Br} + C_2H_6 \longrightarrow \dot{C}_2H_5 + HBr \ldots \quad \ldots \quad \ldots \quad \ldots \quad 11$$
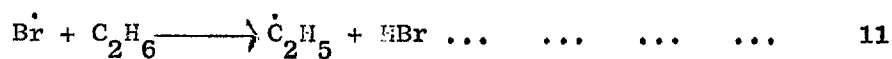
$$E \simeq 20 \text{ K. cal./mole}$$

regenerating hydrogen bromide. The reaction has a high activation energy but still occurs fairly rapidly at this temperature. The reverse reaction:

$$\dot{C}_2H_5 + HBr \longrightarrow C_2H_6 + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 12$$

$$E \simeq 8.5 \text{ K. cal./mole}$$

which would retard the overall reaction does not occur because the ethyl radical reacts far more readily with oxygen (reaction 2).

The reaction

$$CH_3CH_2O\dot{O} + HBr \longrightarrow CH_3CH_2OOH + \dot{Br} \quad \ldots \quad \ldots \quad 13$$
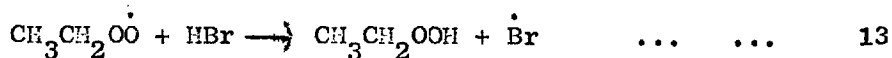
$$E \simeq 7 \text{ K. cal./mole}$$

is also unimportant as isomerization of the peroxy radical occurs far more rapidly.

Hydrogen bromide also promotes the reaction:

$$H\dot{O}_2 + HBr \longrightarrow H_2O_2 + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 14$$
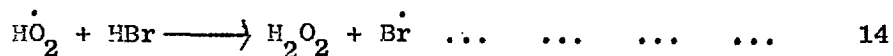
$$E \simeq 11 \text{ K. cal./mole}$$

This reaction is important as the reaction of $H\dot{O}_2$ with fuel, reaction 6, has an activation energy of 18 K. cal./mole. The two reactions therefore occur at roughly equivalent rates when the additive concentration is only one-hundredth that of the fuel. The hydrogen peroxide produced decomposes fairly readily at this temperature, giving

$\dot{O}H$ radicals.

The reaction of hydrogen bromide with $\dot{O}H$ radicals again has some retarding influence on the reaction:

$$HBr + \dot{O}H \longrightarrow H_2O + \dot{Br} \quad \dots \quad \dots \quad \dots \quad \dots \quad 15$$

$$E \simeq 0$$
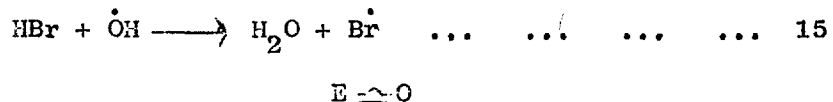
However, as the additive has a powerful promoting influence on the reaction, regeneration of hydrogen bromide by the reverse of 10 cannot occur and thus 11 is the predominant reaction for the bromine atoms produced. Therefore it is presumably impossible to introduce a sufficiently high concentration of hydrogen bromide into the system to effectively remove $\dot{O}H$ radicals by 15 without promotion through 10 and 11 occurring to an overriding extent. Promotion is thus observed under all conditions. Further, as explained previously, hydrogen bromide also promotes the oxidation of formaldehyde at this elevated temperature.

Of all the additives used, hydrogen bromide oxidises most readily and therefore it has by far the greatest promoting influence on the reaction. The oxidation occurs with a slight reduction in pressure and thus this alone has little effect on the maximum pressure change observed. As hydrogen bromide has little effect on the maximum pressure change observed it does not affect significantly the amounts of the various products formed or the extent of the reaction.

c)   The influence of halomethanes

The halomethanes all exert a powerful promoting effect on the reaction. The order of effectiveness in increasing the maximum rate is:

$$CF_2Br_2 > CH_2Br_2 > CH_2BrCl > CH_3Br$$

Neglecting difluorodibromomethane, this is also the order of decreasing
ease of oxidation of the additives.   Thus the halomethanes presumably
act by introducing bromine atoms into the system as previously described.
The rates at which the bromine atoms are introduced depends upon the
rates of oxidation of the additives.   As this rate of oxidation increases,
the rate of bromine atom production increases and consequently the
degree of promotion increases.   Difluorodibromomethane presumably
produces bromine atoms by dissociation even more readily than the other
halomethanes produce them by oxidation.   Further, difluorodibromomethane
and methylene dibromide both contain two bromine atoms per molecule and
they thus have a greater effect than the other halomethanes.   However,
as chlorobromomethane has a far greater promoting effect than methyl
bromide, the chlorine atom must also participate in the reaction,
producing promotion.

The bromine atoms produced react as follows:

$$\dot{Br} + C_2H_6 \longrightarrow HBr + \dot{C_2H_5} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 11$$
$$E \simeq 20 \text{ K. cal./mole}$$

$$HBr + O_2 \longrightarrow \dot{HO_2} + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 10$$
$$E \simeq 39 \text{ K. cal./mole}$$

The rate of initiation of the reaction is thus increased, producing the
promotion observed.

The additives all oxidise or dissociate with an overall increase
in pressure and thus the maximum pressure change observed increases as
the pressure of additive is increased.   However, the increase observed
is far larger than could be accounted for solely by the decomposition
of the additive.   Thus the additives must also cause the oxidation to

go further towards completion or alternatively they must alter the relative amounts of the various products formed in such a way as to produce a much larger pressure change.

7. The oxidation of methane (at 510°C)

a) The basic reaction

The main reactions occurring during the early stages of the oxidation of methane are as follows:

Initiation $CH_4 + O_2 \longrightarrow \overset{\bullet}{C}H_3 + H\overset{\bullet}{O}_2$ 1

$E \simeq 55$ K. cal./mole

Propagation $\overset{\bullet}{C}H_3 + O_2 \longrightarrow CH_3\overset{\bullet}{O}_2$ 2

$f \simeq 10^{-3}$ $E \simeq 0$

$CH_3\overset{\bullet}{O}_2 \longrightarrow \overset{\bullet}{C}H_2OOH$ 3

$E \simeq 20$ K. cal./mole

$\overset{\bullet}{C}H_2OOH \longrightarrow HCHO + \overset{\bullet}{O}H$ 4

$E \simeq 0$

Branching $HCHO + O_2 \longrightarrow \overset{\bullet}{C}HO + H\overset{\bullet}{O}_2$ 5

$E \simeq 32$ K. cal./mole

Propagation $\overset{\bullet}{C}HO + O_2 \longrightarrow CO + H\overset{\bullet}{O}_2$ 6

$E \simeq 0$

$H\overset{\bullet}{O}_2 + CH_4 \longrightarrow H_2O_2 + \overset{\bullet}{C}H_3$ 7

$E \simeq 20$ K. cal./mole

$\overset{\bullet}{O}H + CH_4 \longrightarrow H_2O + \overset{\bullet}{C}H_3$ 8

$E \simeq 8$ K. cal./mole

$\overset{\bullet}{O}H + HCHO \longrightarrow H_2O + \overset{\bullet}{C}HO$ 9

$E \simeq 2$ K. cal./mole

$H\overset{\bullet}{O}_2 + HCHO \longrightarrow H_2O + \overset{\bullet}{C}HO$ 10

$E \simeq 9$ K. cal./mole

Branching $\quad H_2O_2 \longrightarrow 2\dot{O}H$ 11
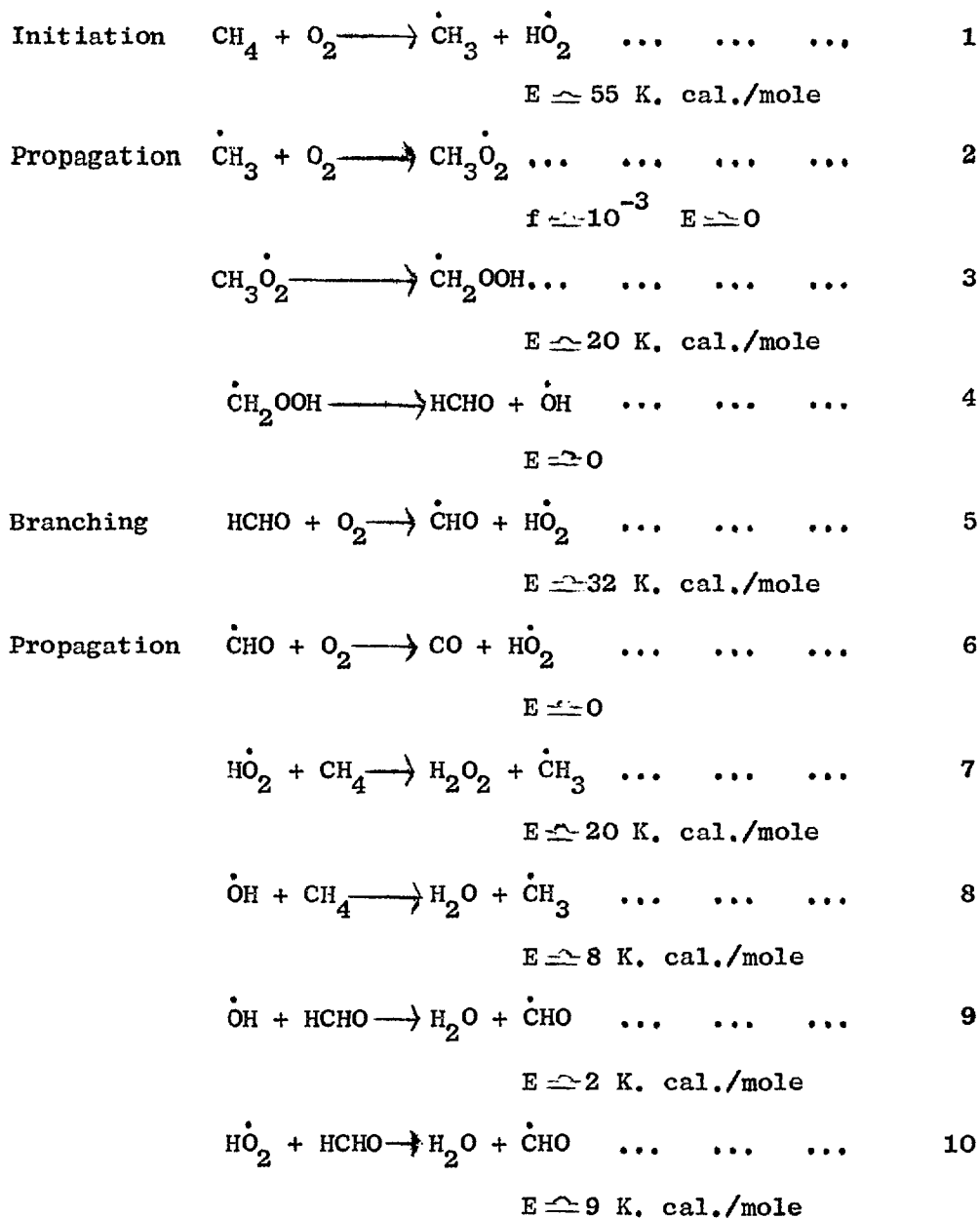
$$E \simeq 45 \text{ K. cal./mole}$$

The pressure increase observed occurs largely as a result of reaction 11.

b) The influence of hydrogen bromide

Hydrogen bromide has a complex effect on the oxidation as described previously. At 510°C it oxidises rapidly, promoting the reaction:

$$HBr + O_2 \longrightarrow H\dot{O}_2 + \dot{B}r \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad 12$$

$$E \simeq 39 \text{ K. cal./mole}$$

Then $\quad \dfrac{w_{12}}{w_1} = \dfrac{f_{12}}{f_1} \text{expt} \left(\dfrac{-39 + 55}{RT}\right) \dfrac{[HBr]}{[CH_4]}$

Assuming $f_1 = f_{12}$, it then follows that when $\left[CH_4\right]$ = 100 mm., $\left[HBr\right]$ = 0.2 mm.,

$$\dfrac{w_{12}}{w_1} = 40$$

Thus because $E_1 \gg E_{12}$ the oxidation of hydrogen bromide has a powerful promoting influence on the reaction even when only 0.2 mm. additive is present. The radicals produced attack fuel as in 7 and

$$\dot{B}r + CH_4 \longrightarrow HBr + \dot{C}H_3 \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad 13$$

$$E = 18 \text{ K. cal./mole}$$

However, on this occasion the reverse reaction is more important:

$$HBr + \dot{C}H_3 \longrightarrow CH_4 + \dot{B}r \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad 14$$

$$E = 0 \quad \text{(Ref. 99)}$$

Having zero activation energy, this reaction occurs readily. The important competing reaction is 2.

Then
$$\frac{w_{14}}{w_2} = \frac{f_{14}}{f_2}\frac{[HBr]}{[O_2]} = 2$$

assuming $f_{14} \simeq 1$, $f_2 \simeq 10^{-3}$, $[HBr] = 0.2$ mm., $[O_2] = 100$ mm.

Thus in the presence of 0.2 mm. hydrogen bromide 14 occurs at twice the rate of 2 and thus two-thirds of the methyl radicals produced by 1 react as in 14, methane being regenerated and the relatively inactive bromine atom being produced. This reaction therefore has a powerful retarding effect on the overall reaction. The remaining one-third of the methyl radicals react as in 2, eventually producing formaldehyde and $\dot{O}H$ radicals. The bromine atoms produced in 12 are thus not removed by 13. They react:

$$\dot{Br} + HCHO \longrightarrow HBr + \dot{C}HO \quad \dots \quad \dots \quad \dots \quad \dots \quad 15$$
$$E \simeq 10 \text{ K. cal./mole}$$

promoting the reaction, or otherwise diffuse to the walls where they react with other radicals present:

$$\dot{Br} + \dot{Br} \longrightarrow Br_2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad 16$$
$$E \text{ small}$$
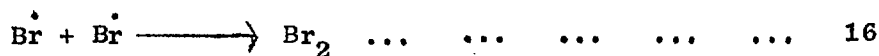
$$\dot{Br} + H\dot{O}_2 \longrightarrow HBr + O_2 \quad \dots \quad \dots \quad \dots \quad \dots \quad 17$$
$$E \text{ small}$$

The occurrence of these reactions obviously retards the overall reaction.

Hydrogen bromide also retards the reaction by reacting readily with the $\dot{O}H$ radicals present:
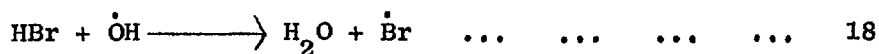
$$HBr + \dot{O}H \longrightarrow H_2O + \dot{Br} \quad \dots \quad \dots \quad \dots \quad \dots \quad 18$$
$$E \simeq 0$$

the active $\dot{O}H$ radical being replaced by the relatively inactive bromine atom. The other major reactions of the $\dot{O}H$ radical are:

$$\dot{O}H + CH_4 \longrightarrow \dot{C}H_3 + H_2O \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad 8$$

$$E \simeq 8 \text{ K. cal./mole}$$

$$\dot{O}H + HCHO \longrightarrow \dot{C}HO + H_2O \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad 9$$

$$E \simeq 2 \text{ K. cal./mole}$$
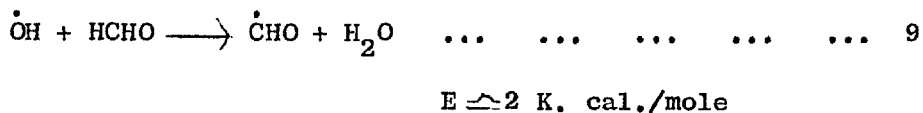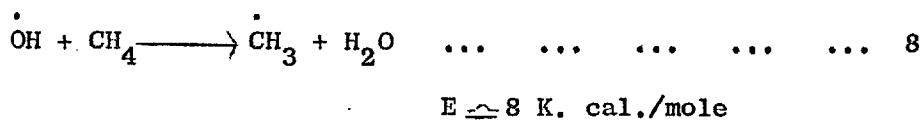
Now under the conditions employed in this work, at the time of maximum rate:

$$\left[HCHO \right] \simeq 10^{-3} \left[CH_4 \right] \quad 19 \quad (101)$$

Then, in the absence of hydrogen bromide, it can be shown that ca. 4.4% of the $\dot{O}H$ radicals react with formaldehyde at this stage of reaction. When 0.2 mm. hydrogen bromide is present, however, only ca. 3.4% of the $\dot{O}H$ radicals react in this way. The rate of reaction 9 is therefore considerably reduced. However, ca. 24% of the $\dot{O}H$ radicals react as in 18 producing bromine atoms which then react largely as in 15, but as $E_{15} \simeq 10$ K. cal./mole while $E_9 \simeq 2$ K. cal./mole, the overall reaction is still retarded. This retardation is caused by a reduction in the rate of the branching cycle:

$$\dot{O}H \xrightarrow{HCHO} \dot{C}HO \xrightarrow{O_2} H\dot{O}_2 \xrightarrow[\text{HCHO}]{CH_4 \text{ or}} H_2O_2 \longrightarrow 2\dot{O}H \quad \text{...} \quad \text{...} \quad 20$$
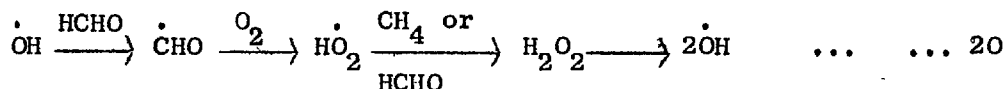
As the addition of hydrogen bromide never completely suppresses the autocatalytic development of the reaction, it is clear that it is not possible to add sufficient hydrogen bromide to remove virtually all the $\dot{O}H$ radicals through 18 without the bromine atoms produced in 12 and 18 having an important promoting influence through 15. Further, the additive does not affect the oxidation of formaldehyde, reaction 5 and thus chain-branching is never completely eliminated.

An important promoting reaction is:

$$\dot{H}O_2 + HBr \longrightarrow H_2O_2 + \dot{B}r \quad \dots \quad \dots \quad \dots \quad \dots \qquad 21$$
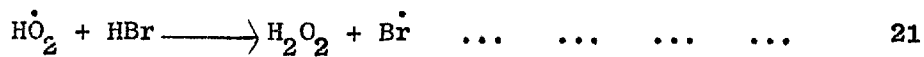
$$E \simeq 11 \text{ K. cal./mole}$$

the hydrogen peroxide formed decomposing readily to give $\dot{O}H$ radicals. This reaction occurs at a comparable rate to 7 even when only 0.2 mm. hydrogen bromide is present because $E_7 \simeq 20$ K. cal./mole.

Thus very small pressures of hydrogen bromide (<0.2 mm.) retard the reaction slightly through reactions 14 and 18, the bromine atoms produced largely diffusing to the walls as reactions 13, 15 are slow. With 0.2 mm. additive these reactions exert their maximum retarding influence on the chain-branching reactions but even at this pressure, the initiation of the reaction is promoted. With higher pressures of additive, the promoting reactions 12, 13, 15 and 21 become more important and significant promotion of the early stages of the reaction occurs.

c)   The influence of halomethanes

The halomethanes all have approximately the same effect on the reaction as hydrogen bromide, low pressures of additive retarding the propagation of the reaction while higher pressures accelerate it. At 510°C, the halomethanes all decompose readily, either by oxidation or direct dissociation, giving bromine atoms. These react:

$$\dot{B}r + CH_4 \longrightarrow \dot{C}H_3 + HBr \quad \dots \quad \dots \quad \dots \quad \dots \qquad 13$$

$$E \simeq 18 \text{ K. cal./mole}$$

$$\dot{B}r + HCHO \longrightarrow \dot{C}HO + HBr \quad \dots \quad \dots \quad \dots \quad \dots \qquad 15$$

$$E \simeq 10 \text{ K. cal./mole}$$

Reaction 13 does not occur to any significant extent except in the presence of a high concentration of bromine atoms as it is a reversible

reaction and the reverse reaction is much faster. Reaction 15 occurs only slowly as it has a high activation energy and the concentration of formaldehyde is always very small.. However, it's occurrence does promote the reaction. Most bromine atoms therefore diffuse to the walls where they react:

$$\overset{\bullet}{Br} + \overset{\bullet}{HO_2} \longrightarrow HBr + O_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 17$$

$$E \text{ small}$$

This reaction retards the overall reaction. The hydrogen bromide produced also retards the reaction as explained previously. Thus low pressures of additive retard the reaction as observed. With higher pressures of additive, the rate of bromine atom production is increased and thus reactions 13, 15 become far more important than 17. Further, the hydrogen bromide produced in reactions 13, 15 oxidises readily, regenerating bromine atoms. Promotion of the reaction therefore occurs.

d) The effects of the additives relative to one another

The order of effectiveness of the additives in producing retardation of the maximum rate at low pressures is:

$$CH_2Br_2 > CH_2BrCl > CH_3Br > HBr$$
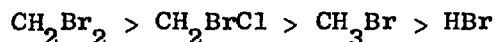
Now the ease with which these additives oxidise decreases in the order:

$$HBr > CH_2Br_2 > CH_2BrCl > CH_3Br$$

Thus for the halomethanes, the order of retarding effectiveness is related to the rate at which bromine atoms are introduced into the system, the most effective retardants producing bromine atoms at the greatest rates. These bromine atoms retard the reaction in the manner explained in the previous section. The most important function of the additive therefore is to release bromine atoms into the system.

The rest of the molecule acts as further fuel.

From the pressure-time curves it is seen that hydrogen bromide is the most effective retardant at very low pressures in the early stages of reaction. This would be expected as the molecule itself exerts a retarding effect on the reaction as explained previously. However, at the time of maximum rate it is the least effective retardant at very low pressures. Thus the bromine atoms produced in the early stages of reaction diffuse to the walls and do not participate in the later stages of reaction.

The order of effectiveness of the additives in promoting the maximum rate of the reaction at higher pressures is:

$$CH_2Br_2 > CF_2Br_2 > CH_2BrCl > CH_3Br > HBr$$
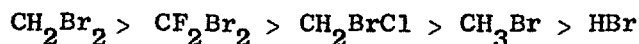
Thus again for the halomethanes, the promoting effectiveness depends upon the rate at which bromine atoms are introduced into the system, high concentrations of bromine atoms promoting the reaction as explained previously.

At high additive pressures, hydrogen bromide is the least efficient promoter. Presumably the retarding reactions of the additive itself are still important under these conditions and the retarding effects thus produced offset the promoting effects caused by the oxidation of the additive.

These verying effects are also related to the maximum pressure change observed. Thus the additives also reduce the final extent of reaction when retarding the reaction and vice-versa.

8. The oxidation of benzene (at 562°C and 611°C)

a) The basic reaction

The main reactions occurring in the early stages of reaction are:

Initiation $\quad C_6H_6 + O_2 \longrightarrow \dot{C}_6H_5 + H\dot{O}_2$ 1

$$E \simeq 57 \text{ K. cal./mole}$$

Propagation $\quad \dot{C}_6H_5 + O_2 \longrightarrow C_6H_5\dot{O}_2$ 2

$$E \simeq 13 \text{ K. cal./mole (102)}$$

$$C_6H_5\dot{O}_2 + C_6H_6 \longrightarrow \dot{C}_6H_5O_2H + C_6H_5 \quad ... \quad ... \quad 3$$

$$E \simeq 11 \text{ K. cal./mole}$$

Branching $\quad C_6H_5O_2H \longrightarrow C_6H_5\dot{O} + \dot{O}H$ 4

$$E \simeq 40 \text{ K. cal./mole}$$

Propagation $\quad C_6H_5\dot{O} + C_6H_6 \longrightarrow C_6H_5OH + \dot{C}_6H_5 \quad ... \quad ... \quad 5$

$$E \simeq 11 \text{ K. cal./mole}$$
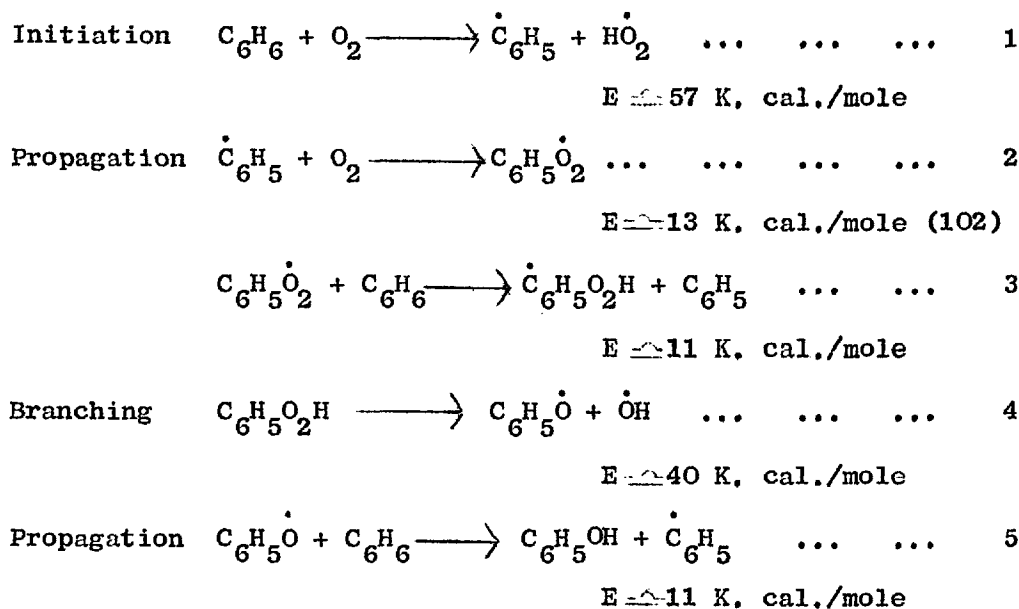
b) The influence of halomethanes (at 562°C)

Both methyl bromide and difluorodibromomethane vigorously promote the reaction at 562°C. At this temperature both additives decompose readily:

$$CH_3Br \longrightarrow \dot{C}H_3 + \dot{B}r \quad ... \quad ... \quad ... \quad ... \quad 6$$

$$E \simeq 67.5 \text{ K. cal./mole}$$

$$CH_3Br + O_2 \longrightarrow \text{Radicals including} \quad ... \quad ... \quad 7$$

$$\dot{B}r, \ H\dot{O}_2 \qquad E \simeq 48 \text{ K. cal./mole}$$

$$CF_2Br_2 \longrightarrow \dot{C}F_2Br + \dot{B}r \quad ... \quad ... \quad ... \quad ... \quad 8$$

$$E \simeq 65 \text{ K. cal./mole}$$
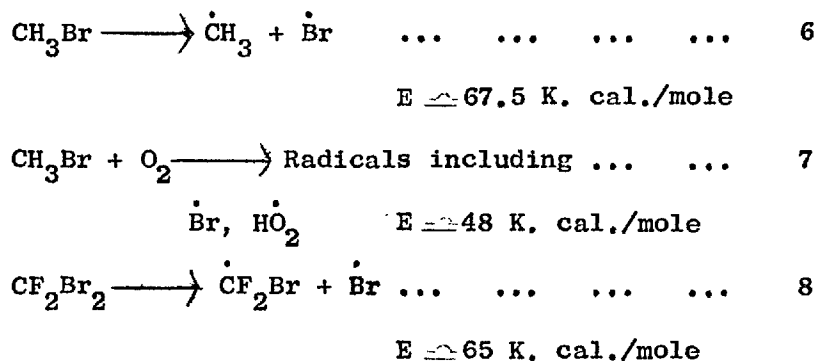
As reactions 6 – 8 all occur far more rapidly than reaction 1, they are important sources of free radicals and thus have a powerful promoting

influence on the reaction. The radicals formed attack benzene:

$$\dot{Br} + C_6H_6 \longrightarrow \dot{C}_6H_5 + HBr \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 9$$

$$E \backsimeq 25 \text{ K. cal./mole}$$

$$H\dot{O}_2 + C_6H_6 \longrightarrow H_2O_2 + \dot{C}_6H_5 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 10$$

$$E \backsimeq 22 \text{ K. cal./mole}$$

The products then react:

$$H_2O_2 \longrightarrow 2\dot{O}H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 11$$

$$E \backsimeq 45 \text{ K. cal./mole}$$

$$HBr + O_2 \longrightarrow H\dot{O}_2 + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 12$$

$$E \backsimeq 39 \text{ K. cal./mole}$$
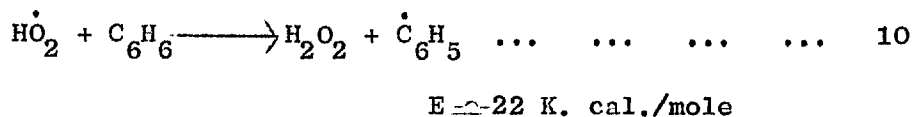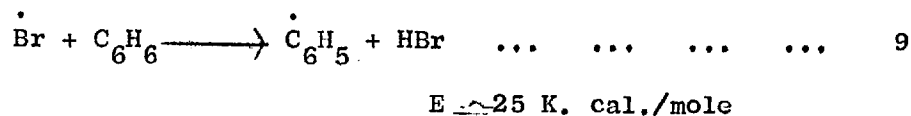
These reactions all produce further promotion of the reaction. Possible retarding reactions of hydrogen bromide e.g.

$$HBr + \dot{O}H \longrightarrow H_2O + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 13$$

$$E \backsimeq 0$$

$$HBr + \dot{C}_6H_5 \longrightarrow C_6H_6 + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 14$$

$$E \backsimeq 7 \text{ K. cal./mole}$$
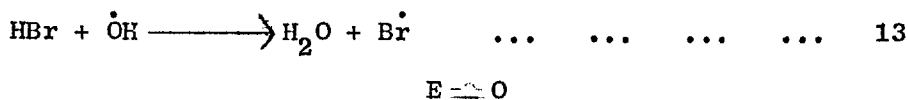
do not occur to any significant extent because hydrogen bromide is so readily oxidised at this temperature. Thus the additives vigorously promote the reaction. Difluorodibromomethane has a greater effect than methyl bromide because it contains two bromine atoms per molecule, and thus a given pressure of this additive produces twice as many bromine atoms as the same pressure of methyl bromide.

   c)   The influence of halomethanes and hydrogen bromide(at 611°C)

      Methyl bromide, difluorodibromomethane, and hydrogen bromide all vigorously promote the reaction. The reasons for this behaviour are the same as those set out in b. Hydrogen bromide is the most

powerful promoter because 12 is a more rapid reaction than 6, 7 or 8 and thus it introduces radicals into the system at the greatest rate.

9. The oxidation of cumene (at 580°C)

a) The basic reaction

The main reactions occurring in the early stages of the oxidation are:

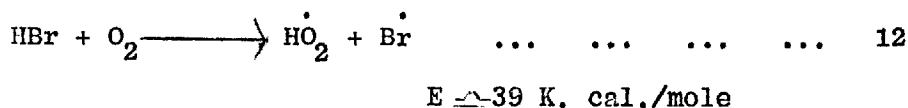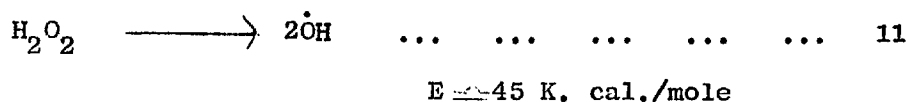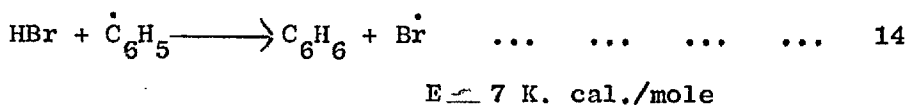Initiation $\quad C_6H_5CH(CH_3)_2 + O_2 \longrightarrow C_6H_5\overset{\bullet}{C}(CH_3)_2 + H\overset{\bullet}{O}_2 \quad \ldots \quad 1$

$$E \lesssim 42 \text{ K. cal./mole}$$

Propagation $\quad C_6H_5\overset{\bullet}{C}(CH_3)_2 + O_2 \longrightarrow \underset{\underset{\overset{|}{\overset{\bullet}{O}_2}}{}}{C_6H_5C(CH_3)_2} \quad \ldots \quad \ldots \quad 2$

E small

$$\underset{\underset{\overset{|}{\overset{\bullet}{O}_2}}{}}{C_6H_5C(CH_3)_2} \longrightarrow CH_3CO.CH_3 + C_6H_5\overset{\bullet}{O} \quad \ldots \quad 3$$

$$C_6H_5\overset{\bullet}{O} + C_6H_5CH(CH_3)_2 \longrightarrow C_6H_5OH + C_6H_5\overset{\bullet}{C}(CH_3)_2 \quad \ldots \quad 4$$

The products, acetone and phenol, are then further oxidised.

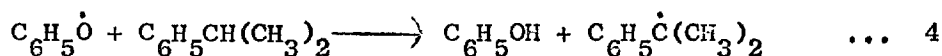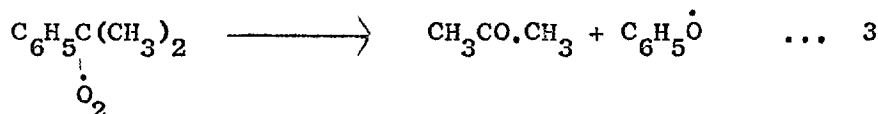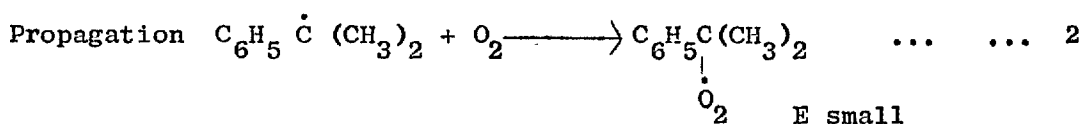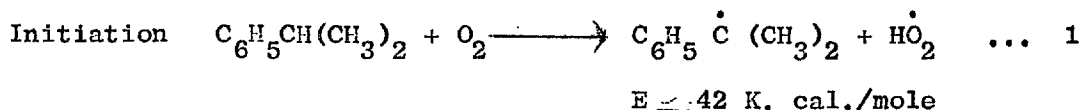b) The influence of halomethanes and hydrogen bromide

Methyl bromide, difluorodibromomethane, and hydrogen bromide all vigorously promote the reaction. The reasons for this behaviour are the same as those given in section 8, b and c. Although E_1 is considerably less on this occasion, the rapid decomposition of the additives at this temperature is still a most important source of free radicals and thus the initiation of the reaction is much enhanced, producing the promotion observed.

10. General discussion

a) Survey of results

The results as a whole show clearly that, whereas hydrogen bromide exerts a marked, usually promoting, influence on the slow
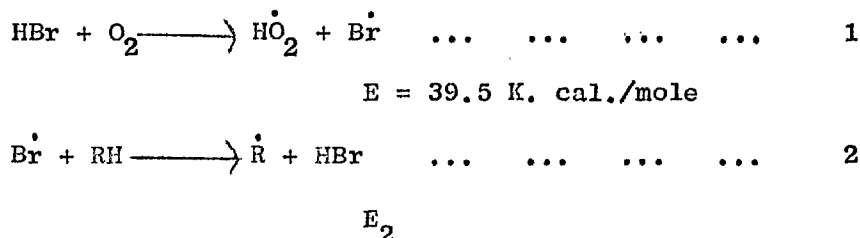
oxidation and spontaneous ignition of all the fuels studied, the halomethanes only have a well-defined effect as additives where oxidation of the fuel takes place above ca. 400°C. Furthermore, when the organic compounds do exert an appreciable influence on combustion, their effect is qualitatively similar to that of hydrogen bromide. The effect of the different halomethanes relative to that of hydrogen bromide increases with increasing reaction temperature and with methane, the halomethanes have a greater effect than hydrogen bromide. However, with benzene and cumene, hydrogen bromide again has the greatest effect. In general the dibromo compounds have a greater effect than the monobromo compounds.

These findings suggest that the halomethanes themselves do not affect appreciably the slow combustion or spontaneous ignition of the fuels studied and it is only their oxidation or pyrolysis products, such as bromine atoms, which exert a definite influence on these reactions. In agreement with this theory, methyl bromide (100 mm.) starts to react with oxygen (100 mm.) at ca. 280°C and it is only on combustion processes which take place well above this temperature that additions of this compound have a considerable effect.

No experimental studies have been made of the slow combustion of the other halomethanes used but from the theoretical considerations outlined previously it is seen that they too will decompose to give halogen atoms at a suitably elevated temperature, rather more readily than methyl bromide. The influence of halomethanes on combustion processes can therefore be largely explained in terms of the reactions of bromine atoms and hydrogen bromide.

b)   The influence of hydrogen bromide

The promoting action of hydrogen bromide is largely due to the enhanced rate of initiation of the oxidation reaction resulting from the reaction cycle:

$$HBr + O_2 \longrightarrow H\dot{O}_2 + \dot{B}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

$$E = 39.5 \text{ K. cal./mole}$$

$$\dot{B}r + RH \longrightarrow \dot{R} + HBr \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2$$

$$E_2$$

where RH is the fuel undergoing oxidation.   This sequence of reactions provides an extra mode of chain-initiation in addition to the normal reaction:
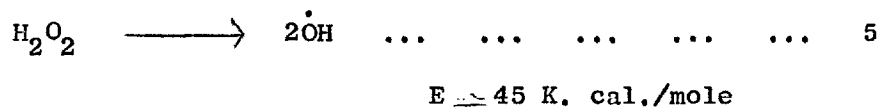
$$RH + O_2 \longrightarrow \dot{R} + H\dot{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 3$$

$$E_3$$

The importance of this additional mode of initiation depends on E_3. If $E_3 < 39$ K. cal./mole, i.e. with acetaldehyde, formaldehyde, then reaction 3 occurs much faster than reaction 1 and thus 1 should not be an important promoting step.   However, in practice it appears that 1 is an important reaction in both systems for $p_{HBr} \geqslant 5$ mm. and thus the actual value of $E_1 - E_3$ is probably not as large as that calculated. Alternatively, reaction 1 may not be very important in these systems, the additive exerting its promoting influence largely by its interaction with intermediate peroxides (103) giving rise to enhanced chain-branching in the later stages of reaction.

On the other hand, if $E_3 > 39$ K. cal./mole, i.e. with methane, ethane, benzene, etc., then reaction 1 occurs faster than reaction 3 even when hydrogen bromide is present at a much lower concentration

than the fuel. Reaction 1 is then an important source of free radicals and it thus produces appreciable promotion of the reaction. However, in all cases, reaction 2 requires a considerable activation energy, 10 - 25 K. cal./mole, and it is therefore slow. Thus, on the whole, the importance of reactions 1, 2 increases as the reaction temperature increases.

Hydrogen bromide also affects the reaction by reacting with intermediate peroxy radicals, i.e:

$$H\overset{\bullet}{O}_2 + HBr \longrightarrow H_2O_2 + \overset{\bullet}{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 4$$

$$E \simeq 11 \text{ K. cal./mole}$$

$$H_2O_2 \longrightarrow 2\overset{\bullet}{O}H \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 5$$

$$E \simeq 45 \text{ K. cal./mole}$$
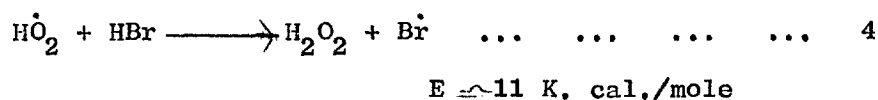
The importance of reaction 4 depends on several factors. Below about 300°C, reaction 5 occurs only very slowly and thus reaction 4 merely replaces the rather inactive $H\overset{\bullet}{O}_2$ radical by the relatively inactive bromine atom. Reaction 4 thus has little effect on the overall reaction below about 300°C. However, at higher temperatures, reaction 5 occurs fairly rapidly, producing active $\overset{\bullet}{O}H$ radicals and thus reaction 4 leads to promotion of the reaction. Further, reaction 4 is in competition with the reaction:

$$H\overset{\bullet}{O}_2 + RH \longrightarrow H_2O_2 + \overset{\bullet}{R} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 6$$

However, as D(H-Br) > D(R-H) in most cases, reaction 4 is usually important even though the concentration of hydrogen bromide is always far less than the concentration of fuel.

With methane and formaldehyde as fuels, low pressures of hydrogen bromide produce retardation of the reaction. This retarding

influence must naturally be ascribed to the replacement of reactive
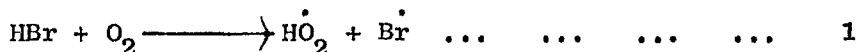chain-carriers by less active species. A possible retarding reaction
is:

$$\dot{R} + HBr \longrightarrow RH + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 7$$

the reactive, chain-carrying radical R being replaced by the relatively
inactive Br atom. The important competing reaction is:

$$\dot{R} + O_2 \longrightarrow R\dot{O}_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 8$$

It has been shown that 7 is competitive with 8 only when R = CH_3 and
thus reaction 7 is an important retarding reaction in this system. As
the gas-phase reactions of bromine atoms are all slow, at low
concentrations most of these radicals diffuse to the walls and possibly
react:

$$\dot{Br} + H\dot{O}_2 \longrightarrow HBr + O_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 9$$
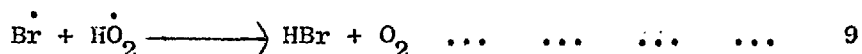
thereby removing radicals from the system and producing retardation of
the overall reaction. With higher concentrations of bromine atoms,
however, the gas phase reactions:

$$\dot{Br} + RH \longrightarrow \dot{R} + HBr \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2$$

$$HBr + O_2 \longrightarrow H\dot{O}_2 + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

become important, producing promotion. Reaction 9 is important in the
formaldehyde system but not in the isopropanol and ethane systems,
presumably because the increased temperature favours reactions 2 and
1 even at low concentrations of bromine atoms. Reaction 9 is again
important in the methane system because reaction 2 does not occur readily.

The reaction

$$\dot{OH} + HBr \longrightarrow H_2O + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 10$$
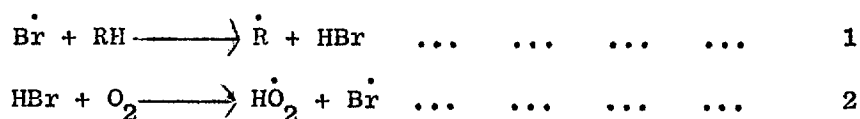
E ≒ O
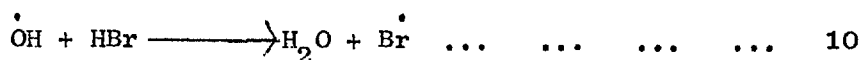
produces some retardation in all the systems. With formaldehyde as fuel, this reaction is the important retarding step in conjunction with 9. In the isopropanol and ethane systems, the rate of $\dot{O}H$ radical production is much greater than in the formaldehyde system and thus the added hydrogen bromide is unable to remove a significantly high percentage of them to cause efficient retardation without reactions 2, 1 occurring to an overriding extent. In the methane system, although the temperature is higher still, the rate of $\dot{O}H$ radical production is much decreased as a result of 7 and thus efficient retardation through 10 is also possible.

The overall effect of hydrogen bromide on the oxidation system thus depends on the relative importance of all these reactions. This relative importance alters as the additive pressure is varied and produces the variety of effects observed.
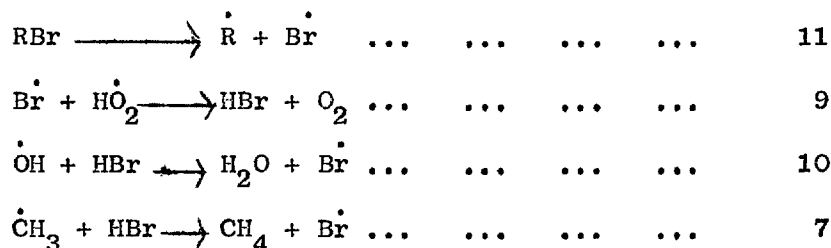
c) The influence of halomethanes

Below about 400°C the halomethanes have no well-defined influence on the oxidation reactions studied. Presumably the additives do not decompose under these conditions and exert only an 'inert gas' effect on the reactions.

At higher temperatures, the additives oxidise, producing bromine atoms. These promote the reaction in the normal way:

$$\dot{Br} + RH \longrightarrow \dot{R} + HBr \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 1$$

$$HBr + O_2 \longrightarrow H\dot{O}_2 + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2$$

The importance of this additional mode of chain-initiation again depends on the relative ease of oxidation of the fuel and the additive and thus it increases as the reaction temperature increases. The

reaction is also promoted by the normal combustion of the carbon and hydrogen fragments of the additive molecule. The halomethanes retard only the oxidation of methane. The retardation mechanism involves the same reactions as for hydrogen bromide, e.g.

$$RBr \longrightarrow \dot{R} + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 11$$

$$\dot{Br} + \dot{HO_2} \longrightarrow HBr + O_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 9$$

$$\dot{OH} + HBr \longrightarrow H_2O + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 10$$

$$\dot{CH_3} + HBr \longrightarrow CH_4 + \dot{Br} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 7$$

Again the overall effect observed depends on the relative importance of all these reactions under the particular conditions used.

d) Flame studies

The fact that bromine compounds exert an exclusively retarding influence on the reactions occurring in oxygen-supported flames suggests that the processes which are inhibited in flames may well bear a close chemical relation to those reactions which are retarded during the slow combustion of methane. It is of interest to note in this connection that a recently postulated mechanism of flame inhibition by bromine compounds (78) involves the removal of active radicals, such as $\dot{OH}$, by a cycle involving bromine atoms and hydrogen bromide.

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