THE KINETICS OF SOME GASEOUS OXIDATION REACTIONS

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THE KINETICS OF SOME GASEOUS OXIDATION REACTIONS.

PART 1. OXIDATIONS WITH NITROUS OXIDE.

PART 2. THE OXIDATION OF ACETYLENE.

by

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INDEX

GENERAL INTRODUCTION.

The great increase during the last few years in the volume of data available on reaction-rates in gaseous systems has resulted in wide extensions in their theoretical treatment and it is now possible to give a satisfactory qualitative explanation for almost all of the results which have been obtained in that field. On the quantitative side progress has not been so marked, the calculation of reaction rates from the properties of the reactant substances apparently having been considered somewhat too hopeless a task to be attempted.

Quite recently, however, an attack has been made on the problem by the application of statistical mechanics and a reasonably good agreement between calculated and experimental rate constants seems to have been obtained for certain bimolecular association and unimolecular decomposition reactions[1]. In the case of more complicated mechanisms, such as the chain reactions with which this thesis is concerned, such a development is still far from being realized, indeed, until some general agreement is reached as to the actual courses of these reactions no detailed theoretical treatment of a quantitative nature can be given them. The present investigations were undertaken in the hope that they might help to remove some of the uncertainties in the interpretation of the data relating to gaseous oxidation reactions.

The chief point of controversy in regard to these reactions concerns whether the initial step in them is the association of the oxygen molecule as a whole with the substance being oxidized or whether it is the introduction into it of a single oxygen atom. It was thought that evidence indicating which process actually occurred might be obtained if the oxygen were replaced by some other gaseous oxidizing agent. The choice for this purpose seemed to be between ozone and nitrous oxide, the latter appearing to be the more suitable. With ozone the results obtained, whatever their nature, would probably not be conclusively in favour of either mechanism for even at room temperature the ozone molecule might break up before reaction into an atom and a molecule of oxygen, each in a highly reactive state due to the energy liberated by the decomposition, and the subsequent oxidation would therefore be more rapid than with normal oxygen. With nitrous oxide, however, unless reaction only took place at the relatively high temperatures where its decomposition was rapid, the oxidations should be slower than with oxygen itself if they involved the addition of molecular oxygen, while if they involved only one oxygen atom they might be faster since this one would not be held with so strong a force in nitrous oxide as in oxygen. With this in mind oxidation rates with nitrous oxide have been studied for a few systems for which the literature contained information concerning the corresponding reactions with oxygen with which they might be compared. The results which were obtained are discussed in detail in Part 1 of this thesis. Unfortunately they were not of such a nature as to be comparable with results from normal oxidations and since further extensions of this particular investigation seemed likely to give more negative results this study was discontinued and an investigation of the oxidation of acetylene was undertaken.

Hydrocarbon oxidations have been the subjects of a number of investigations, partly because of the great practical importance which they have as the source of power in internal combustion engines and as a possible source of valuable intermediate products and partly because of the importance to theory of a thorough knowledge of the mechanisms in so extensive a group of closely related reactions. However. although there is general agreement as to many of the experimental facts there is a wide variation in the interpretations placed on these facts. Since any final choice among the alternative theories at present in vogue must be based on further evidence from experiments, there is still need for intensive work on the subject. In the case of the oxidation of acetylene there is less information on which to draw than with any of the other simple hydrocarbons and there seems to be the closest approach to agreement as to the actual mechanism involved. It was therefore chosen as the subject of this investigation. The results are given in Part II of this thesis.

Before proceeding with the discussion of these particular reactions it appears advisable to sketch briefly those parts of the general theory which we shall have occasion to apply later. For a more comprehensive survey of the subject reference may be made to the usual texts[2].

The theoretical treatment of the kinetics of chemical change in gaseous systems is greatly simplified if the reactions are divided into the classes: simple homogeneous, chain and heterogeneous reactions. Since there will be direct experimental evidence excluding the first of these as a possibility in the reactions which are to be considered later its discussion will be omitted except where its simpler theory may serve to introduce the more complicated forms.

The significance of the term heterogeneous reactions should be apparent, it covers all those cases in which the actual chemical changes take place entirely at an interface. The concept of chain reactions, which was first introduced to explain cases of high quantum yield in photochemical reactions, is somewhat more involved. Generally speaking there are included under this heading those changes in which the products of an elementary reaction are able transitorily to bring about a renewal of that reaction, either directly or through intermediate steps. In the development of the theory two types have been suggested, the so-called "material chains" and "energy chains". In the first of these the products which carry the chain do so through chemical reaction with one or other of the reactant molecules as in the following mechanism proposed by

Nernst[3] for the photochemical reaction between hydrogen and chlorine,

$$\text{(i).}\quad Cl_2 + h\nu \longrightarrow 2Cl$$
$$\text{(ii).}\quad Cl + H_2 \longrightarrow HCl + H$$
$$\text{(iii).}\quad H + Cl_2 \longrightarrow HCl + Cl \quad .$$

Here the elementary reactions (ii) and (iii) constitute the actual chain process and the chain carriers are the hydrogen and chlorine atoms.

In the second type the product is effective because of its ability to transfer its large excess energy to reactant molecules, thus making them active. This may be illustrated by the mechanism proposed by Gibson and Hinshelwood[4] for the hydrogen-oxygen reaction. The essential steps are

$$\text{(i).}\quad 2H_2 + O_2 \longrightarrow H_2O + H_2O^*$$
$$\text{(ii).}\quad H_2O^* + O_2 \longrightarrow H_2O + O_2^*$$
$$\text{(iii).}\quad 2H_2 + O_2^* \longrightarrow H_2O + H_2O^* \quad .$$

Starred symbols represent molecules of high energy content and the chain process consists of the elementary reactions (ii) and (iii), the chain carriers being O_2^* and H_2O^*. Reaction (i) only serves as the initial source of chains; its rate is much less than that of (iii).

The evidence necessary for determining which type of chain is involved in any case is difficult to obtain and it is generally considered sufficient if a proposed mechanism can be made to yield the correct rate equation. Moreover, for the purposes of this particular section, where the general theory only is to be reviewed, the two may justly be considered identical, such extensions as are necessary being made when we discuss hydrocarbon oxidations.

In homogeneous bimolecular reactions, which are the simplest ones from a theoretical standpoint, chemical change only takes place when two active reactant molecules collide in the gas phase. Its rate is therefore proportional to the total number of collisions between the reactants and so to the product of their concentrations. This may be expressed by an equation of the form

$$dx/dt = K \cdot [A] \cdot [B], \qquad (1)$$

where $[A]$ and $[B]$ represent the concentrations of the reactants and x represents that of a product. K is called the velocity constant.

In the case of more complicated mechanisms, such as those mentioned above, it is no longer possible to trace so simple a relation between the number of collisions and the rate of reaction. Nevertheless, most of the results of experiment can be expressed by giving appropriate values to the constants in the general equation

$$dx/dt = K \cdot [A]^{n_1} \cdot [B]^{n_2} \cdot \cdot \cdot \, . \qquad (2)$$

When exceptions occur they are usually due to a retarding of the reaction and the exact equation may then be of the form

$$dx/dt = K \cdot \frac{[A]^{n_1} \cdot [B]^{n_2} \cdot \cdot}{k + [C]^{n'}} \quad . \qquad (3)$$

However, even in such cases the results can often be reproduced within the experimental error if $k + [C]^{n'}$ is replaced by $[C]^{n''}$. The equation then becomes similar to (2) except that one of the powers may be negative. In these relations the sum of the indices, $n_1 + n_2 + \cdots\cdot$, is called the order of the reaction, while the individual indices are the orders with respect to the separate components.

Since the direct determination of the actual rate of reaction at any time is difficult the measurements which are actually made are of the amounts reacting over a period of time. The correct relation connecting such values is obtained by integrating the corresponding rate equations. For the case where the composition of the initial mixture is kept constant, only the total pressure being varied, it is

$$t_1 = k'/p^{n-1} \quad . \qquad (4)$$

In this equation t_1 is the time required for a certain percentage reaction, k' is a constant, dependent however on the choice of the percentage to be compared, p is the total pressure and n the order of the reaction as defined above. It follows, therefore, that the value of n may be deduced from the form of the curve obtained when t_1 is plotted against p, or may be obtained more accurately if log t_1 is plotted against log p.

The order with respect to each of the individual components can be determined from measurements in which the pressure of that component is the only variable factor. Since it is usually most convenient to express the amount of reaction in terms of one of the reactants two distinct cases are to be considered. In the one, where the pressure of the gas which is used as a measure of reaction is varied, the relation is

$$t_1 = k'_1/p_a^{n_a-1} \quad . \qquad (5)$$

In the other, where the absolute amount of reaction at t_1 does not depend on the variable pressure, it becomes

$$t_1 = k'_2/p_b^{n_b} \quad . \qquad (6)$$

These equations are, however, only approximate. The basic relations are again those connecting rates rather than elapsed times. It is evident from (2) that if all concentrations except one are constant, the initial rates will vary according to the relation

$$dx/dt = K'\cdot[A]^{n_a} \qquad \text{or} \qquad dx/dt = K'_1\cdot p_a^{n_a} \ . \ (7)$$

(5) and (6) follow from this equation but they will only hold exactly if the variation of K'_1 during the time under consideration is not affected by the relative pressures of the different reactants. That this will not be so can be shown most easily by considering an example. Suppose that one molecule of the gas A reacts with one of B, that (1) above represents the rate equation and that t_1 is defined as the time required for half of A to react. If in one experiment $[A]$ equals a, $[B]$ equals a; while in another experiment the concentrations are respectively a and 3a, the initial rate in the second case would be three times that in the first. At t_1, however, the rates would be $k\cdot a/2\cdot a/2$ and $k\cdot a/2\cdot 5a/2$, and the ratio

one to five. The value for t, in the second case therefore would not be one third that in the first, as required by equation (6), but less than that. However if the orders can be expressed by simple whole numbers the above method is exact enough to indicate their true values, while fractional orders are in any case probably an approximation.

The form of the rate equation alone will sometimes indicate the type of reaction mechanism involved in a particular case. In the gas phase the number of three-body collisions occurring in unit time is very much less than that of two-body collisions and a further increase in the number of particles involved at each collision results in a still further decrease in the rate at which they occur. It would be expected, therefore, that very few simple homogeneous reactions would have high orders. This is borne out by experiment for, while bimolecular reactions of this type are relatively common, the number of termolecular ones discovered so far is small and there are no known ones of a higher order. In heterogeneous reactions the orders are often smaller for, although the number of molecules involved is not affected, one of the reactants may be adsorbed so strongly that the amount of it on the surface is practically independent of the gas pressure over a considerable range and therefore its concentration in the gas phase does not affect the rate. With this type of mechanism, then, the order will rarely be greater than two.

The rate obtained in a chain reaction is not the result of one simple reaction but rather of the whole series which constitute the chain process. The corresponding rate equation will therefore be composite of the rate equations for each of the individual steps. The correct form for any proposed scheme may be obtained if the concentrations of the active intermediates are supposed to be so small as to remain constant after a few seconds. The time differential of these concentrations may then be equated to zero and they may be found in terms of those of the original reactant molecules. Since such a calculation will be carried out later in this thesis this point will not be discussed in any great detail here. However, some of the consequences of such a mechanism may be noted. If we consider the initiating step of the chain to be a bimolecular collision between the two reactant molecules A and B, its rate will be given by

$$-d[A]/dt = k_1 \cdot [A] \cdot [B] \quad .$$

If the product of this step is an active molecule which reacts with A to give C, is unaffected by B and is deactivated by collision with the walls, the equation for the rate of formation of C will be

$$d[C]/dt = k_2 \frac{[A]^2 \cdot [B]}{k_3[A] + k_4} \quad .$$

If k_4 is very much larger than $k_3[A]$ this will be approximately equal to

$$d[C]/dt = K \cdot [A]^2 \cdot [B] \quad .$$

If collisions with B had been the ones effective in deactivating the active molecule a term $k_5[B]$ would have appeared in the equation instead of k_4. Actually most chain processes will contain several such steps for any one of which there will be such possibilities. As a result there may be a very wide variation in the form of the rate equations for this class of reactions. In particular we may have orders which are negative with respect to one of the reactants or which are greater than two with respect to one of the reactants. Such orders when obtained in experiments are strong evidence for the chain nature of a reaction.

If a reaction proceeds by a chain mechanism its rate at any stage will be dependent on the number of chains present, and will therefore be influenced by factors which affect their starting or breaking. It happens that in a number of cases the latter process takes place almost entirely at the walls of the reaction vessel and is therefore accelerated by an increase in the ratio of its surface to its volume. As a result packing with additional material of the same composition - the test usually applied for homogeneity of the reaction - will cause a decrease in the rate of the main reaction. This is in marked contrast to the behaviour with a heterogeneous reaction where the velocity increases in almost direct proportion to the surface, and the fact that the chain theory is the only one to offer a satisfactory explanation of this well established phenomenon is a strong point in its favour. Conversely, the occurrence of such an effect may be taken as definite evidence for the presence of chains in the reaction mechanism. It should be pointed out that, so long as the chains are broken at the wall, the nature of the effect will not be affected by whether they start in the gas or at the wall, for an increase in surface will be more favourable to chain breaking than to chain initiation. This follows since the latter process will vary directly with the surface area while the former will vary with the square of the effective diameter - since the time required for active molecules to reach the surface and, therefore, the rate of their destruction is, according to the diffusion law, dependent on the square of the distance through which they have to pass. It is, however, conceivable that in some cases chains may be started at the surface and broken in the gas phase. The only effect of increasing the surface would then be to favour the initiation of chains and the resultant variation in the rate would be the same as if the reaction were a heterogeneous one. Actually it does not appear to have been necessary to invoke this explanation to account for any results in the past and it is only introduced here because we shall consider it in connection with one of the reactions which we are studying.

In the preceding discussion it has been tacitly assumed that only molecules in a certain special state react and that the difference between this state and the normal one may be only a difference in energy content. These assumptions are, in fact, the foundations upon which the modern theory of chemical kinetics is based; until they were advanced very little progress was made in the interpretation of the results of rate measurements. Their support is largely derived from two facts; first, in those reactions which proceed at a rate which can be determined the number of molecules undergoing chemical change in unit time is considerably less than would be the case if every collision between reactant molecules resulted in reaction and second, this number is very greatly influenced by the temperature. Of course the former of these by itself might be explained by such factors as orientation at collision, but in that case the proportion of effective collisions should be almost independent of temperature, that is, the rate should increase only by an amount corresponding to the increased number of collisions. This would require that the velocity constant, k, vary as the square root of the absolute temperature. The actual relation is found to be

$$\ln k = C - A/RT$$

$$\text{or} \qquad k = Ke^{-A/RT} \quad .$$

A, C and K are constants for any reaction and R is the gas constant.

The only property of a gas which changes so rapidly with temperature is the fraction of its molecules possessing energy above a certain value. From the two dimensional form of the Maxwell distribution law this may be shown to be $e^{-E/RT}$, E being the energy value considered. It follows that if the essential condition for reaction at collision be that the colliding molecules possess between them energy exceeding a certain minimum, A, the correct form for the temperature -

velocity constant equation is obtained. In simple homogeneous reactions values for A may be calculated from the number of effective collisions at any one temperature and from the temperature coefficient of the rate. Hinshelwood[2b] has shown that the two values agree quite satisfactorily. Since the two methods use quite different data this constitutes strong support for this concept of activation energy.

The value of A will be a characteristic of the actual reaction mechanism and may therefore be used to test whether this is affected by a change of temperature. For this purpose the logarithm of the rate or of the time required for a certain percentage reaction - in either case for the same gas mixture at constant concentration - is plotted against the reciprocal of the absolute temperature. If the activation energy has a constant value it can be determined from the slope of the straight line which is obtained. If, however, the reaction process changes - for example from heterogeneous to homogeneous - two straight lines joined by a curve are obtained; their slopes are dependent on the respective values of A, while that of the curve corresponds to the transition from the one value to the other.

In heterogeneous and chain reactions the value found by this method for the heat of activation has not the same significance as it has in homogeneous reactions. For heterogeneous ones the same reasoning as was used above in interpreting the temperature coefficient as due to the energy requisite to reaction would apply if the rate equation were expressed in terms of the concentrations of the actual reacting substances, that is, the adsorbed molecules. In practice, however, it is always obtained in terms of concentrations in the gas phase. While these two are related, the change from the one to the other introduces factors which vary with the temperature, generally to an unknown extent. The true heat of activation for the reaction is therefore not obtained; the slope of the curve gives an energy value which is composite of this heat of activation and those for the various processes of adsorption and desorption involved. It is generally referred to as the apparent heat of activation. By a series of calculations which need not be reproduced here Hinshelwood[2b] shows that, for cases where the product of the reaction does not affect the rate, this apparent heat of activation is less than the true one by an amount dependent on the heats of adsorption of the reactants. For such reactions the temperature coefficients are therefore smaller than those for the corresponding homogeneous ones. Where a product of the reaction is so strongly adsorbed as to exert a retarding effect the apparent heat of activation differs from the true one by an amount equal to the difference between the sum of the heats of adsorption of the reactants and the heat of adsorption of that product. The direction of the change depends, therefore, on the relative magnitudes of these quantities.

In chain reactions the rate equations which are obtained from experiment apply to an over-all reaction, each step of which has its own heat of activation. A change of temperature affects the chain length and the activation energy obtained by plotting the data, being influenced by this factor, may be either greater or smaller than that of the initiating step.

From these considerations it will be apparent that the effect of temperature on the rate of reaction is sometimes an indication of the type of reaction involved. Briefly summarized the important points are as follows: in simple homogeneous reactions the heats of activation are measures of the energy necessary at collision before reaction will occur and, as might be expected, they bear a rough relation to the temperatures at which the reactions begin; normal heterogeneous reactions in the same temperature range have lower energies of activation; retarded ones, which can always be classified on the basis of other evidence, may have values varying over a wide range; while, finally, chain reactions permit of the widest variations of all. When a value definitely does not accord with any of the first types it may therefore be considered as evidence in favour of this last one.

Gaseous explosions are often of considerable importance in the study of reaction kinetics. Excluding those in which the ignition takes place from a spark or a hot wire, they may be divided into two classes, thermal explosions and explosions at a critical pressure limit. In the first type the reaction velocity increases regularly with increasing temperature or pressure until it reaches a value where the rate of heat loss through the walls becomes less than that of the liberation of heat by the reaction. At this point the temperature of the system and consequently the rate of reaction increases so rapidly that the change is complete in a fraction of a second, that is, there is an explosion. In the second type there are sharp pressure limits on one side of which the reaction is very slow - sometimes immeasurably so - while on the other an explosion occurs. The limits may be upper or lower ones, that is, the explosions may occur on decreasing the pressures below, or on increasing them above certain values. Indeed, in several cases both occur in the one system, in which there is, therefore, a definite pressure range where explosions take place, bounded on either side by regions where the slow reaction prevails. Thermal explosions might conceivably take place with any kind of reaction mechanism; the others, however, have as yet received no satisfactory explanation except on the basis of the chain theory. Their occurrence is therefore believed to indicate a chain reaction.

The limits are explained by this theory as resulting from variations in the relative efficiency of the factors controlling the breaking of chains and to a certain extent may be treated quantitatively. For our purposes it is sufficient to give the qualitative picture and to amplify it by the addition of some of the more important results from the detailed considerations. The complete derivations may be found in Hinshelwood's book[2b].

In reactions which liberate a sufficient amount of energy it is only logical to assume that, if other circumstances are favourable, more than one active product may be produced from an active reactant molecule. This branching of chains is a requisite if explosions are to occur at a sharp pressure limit. Under the conditions where the ordinary slow reaction prevails the production of additional active molecules due to this branching process must necessarily be counterbalanced by the deactivation which always occurs. Any change which affects the latter may, however, disturb the balance to such an extent that the branching becomes predominant; when that happens the number of chains existing in the gas steadily increases, becoming infinite in a fraction of a second. The result is an explosion. Expressed mathematically the above considerations take the form of the equation,

$$\text{rate of reaction} = \frac{F(c)}{f_s + f_c + A(1 - \alpha)},$$

where $F(c)$ is a function of concentration, f_s and f_c represent the factors determining chain breaking at the surface and by collisions in the gas phase, A is a constant and α is the average number of active product molecules from one molecule of activated reactant.

If branching occurs at all α is greater than one and $A(1 - \alpha)$ is therefore negative. f_s and f_c may be affected by many factors, but are certainly dependent to some extent on pressure. It may be possible, then, by varying the pressure, to change from conditions where $f_s + f_c$ is numerically greater than $A(1 - \alpha)$, and the rate has a finite value, to ones where $f_s + f_c$ is equal to $A(1 - \alpha)$. The denominator then becomes zero, the rate, accordingly, infinite and an explosion occurs. At low pressures f_s is probably the more important term and since it is decreased when the pressure increases - it is more difficult for the active molecules to reach the surface when the pressure is high - an explosion may occur on going from a low to a higher pressure, that is, there may be a lower critical limit. At high pressures the converse is sometimes true, f_c is the important term, it decreases as the pressure decreases, and an explosion may be obtained at an upper critical limit.

If this picture is essentially correct the occurrence of explosions at a lower limit is largely dependent on the ease with which the chain carriers reach the wall. Starting with this assumption Semenoff[5] derived the relation

$$p_1p_2(1 + p_i/(p_1 + p_2))d^2 = \text{constant}$$

as an expression of the conditions determining the lower limit in cylindrical reaction vessels. d is the diameter, p_1 and p_2 represent the pressures of the reactants and p_i that of any inert gas which may be present. If all of the experiments are carried out in one vessel this reduces to

$$p_1p_2(1 + p_i/(p_1 + p_2)) = \text{constant.}$$

More recently it has been pointed out that, since the important factor is diffusion of chain carriers to the wall, the effect of inert gases should depend on the diffusion coefficients of these chain carriers through the inert gas[6]. When the equation is modified to allow for this it takes the form

$$p_1p_2(1 + up_i/(p_1 + p_2)) = \text{constant}.$$

u is a constant for each inert gas in the reaction concerned, but changes when either of these factors is changed, being inversely proportional to the diffusion coefficients of the chain carriers through the gases. Both this relation and the one involving the diameter of the reaction vessel agree satisfactorily with experiment.

If, as stated above, inert gases can favour explosions because of their tendency to keep active molecules from reaching the walls, they should increase the rate of slow reaction in all cases where there is surface deactivation unless, of course, they themselves exert a specific effect in destroying chain carriers. Moreover, since the controlling factor is again diffusion, the speeding up should be related to the diffusion coefficients. In a number of reactions these conclusions have been borne out by experiment. However, such results are generally not of great importance in classifying a reaction since the retarding effect of the surface can be made much more evident by packing the vessel and the action of inert gases is actually only a manifestation of that effect.

This general discussion may be concluded by mentioning briefly three more phenomena which are satisfactorily explained by assuming chain mechanisms. They are: induction periods, where the rates of chemical change only reach their maxima after some reaction has taken place; inhibition periods, where the reactions are entirely suppressed for some time; and trace catalysis, where the rates are very greatly affected by small amounts of foreign substances.

In simple reactions the velocity of chemical change is a maximum at the moment when the process starts, but in chain reactions the greatest rate is not attained until the concentration of the chain carriers reaches its highest value. Such reactions should therefore be characterized by induction periods, but it does not necessarily follow that these will be long enough to be measured. Indeed. Semenoff[7] has expressed the opinion that if induction periods are of finite length they cannot be explained by the chain theory in its simplest form, for the active molecules in it are supposed to survive few collisions and therefore must have extremely short lives; in other words, there would not be a finite lag between successive links in the chain and the overall rate would be the same as that of the initial step. He therefore postulates a scheme involving the formation from the active molecules of relatively stable intermediate products which accumulate in the first stages of the reactions and so cause induction periods. Moreover, the same effect might even be obtained in a chemical change where the energy transfers characteristic of chain reactions did not occur, if the transition from reactants to products involved more than one step and some one of the later steps were relatively slow. The presence or absence of an induction period is therefore not a definite indication of the mechanism involved, although the very large majority of cases where one is present are chain reactions.

Inhibition periods seem to be due to the presence of small amounts of a foreign substance and so are in some respects comparable to cases of trace catalysis. To explain either phenomenon it seemed necessary at one time to assume that every foreign molecule exerted an influence over a very large number of reacting molecules in its neighbourhood, despite the fact that other evidence pointed to a range for such action not much greater than the molecular diameter. With the introduction of the concept of chain processes, however, a relatively simple explanation became possible. It follows from the earlier discussion that the rate of a chain reaction is dependent on the number of chains started in unit time and on their average length. It may be increased by increasing either of these factors or decreased by decreasing either of them. In cases of trace catalysis it is not always possible to decide which action really occurs. When the number is affected it is supposed that the catalyst is involved in the actual chemical process of chain initiation and that in its absence chains can only be started by a path less favoured by energy considerations. If it is to increase the length of the chains the catalyst must in some way hinder the destruction of the energy carriers; this may result if they are removed at the wall and if it, by adsorption, changes the nature of that surface. The converse might be true for an inhibitor. It might decrease chain initiation or it might shorten the chains. Presumably the former of these could only result if the process involved took place at the surface where adsorption of the inhibitor could have an effect; the latter, however, would only require that the inhibitor be able to remove the chain carriers. In view of their high reactivity this is quite possible. An example of these characteristics is to be found in the photochemical reaction between hydrogen and chlorine which is catalysed by traces of water and inhibited by several substances. In this case the chain length under normal conditions is of the order of 10^6 and any action which interrupts the chains at an early stage will cause an almost complete cessation of reaction.

Finally, when none of the above properties of a reacting system give a satisfactory indication of the kind of mechanism involved conclusions may sometimes be drawn from analogy with similar or related reactions. Such a method is, however, of rather doubtful value and it is questionable whether anything is to be gained in attempting a classification under such circumstances.

PART 1.

Introduction.

Shortly after he discovered nitrous oxide in 1775, Priestley recognized that it could support combustion almost as well as oxygen and noted its effect on the size and appearance of flames. It was not until recently, however, that any attempt was made to determine the actual conditions requisite for its action or to compare these with the corresponding ones for oxygen. The information available on this subject is, indeed, still very limited.

In connection with their studies on the ignition points of gases under different conditions Dixon and Higgins[8] investigated the effect of using nitrous oxide in place of oxygen or air. Their method consisted essentially in passing a combustible gas through a jet into an atmosphere of one of these three. The apparatus was heated electrically and was so arranged that the two gases were at the same temperature when they met. The combustible gas was turned on intermittently and the time required for ignition, if that took place at all, was noted. Since the recorded ignition temperatures depended on the length of this lag, it is necessary to choose some arbitrary standard for purposes of comparison and any values quoted here will refer to 0.5 seconds lag.

Experiments of this kind involve some uncertainty as to the conditions prevailing in the zone where ignition takes place, particularly with regard to gas composition. Moreover, the values obtained are dependent to a considerable extent on physical properties of the gases, such as specific heats and heats of reaction. The results, therefore, are not likely to be strictly comparable with those obtained by the static method. This is borne out by a study of the data contained in a recent paper by Coward[9] who, since Prof. Dixon's death, has collected and summarized the results of the latter's work, some of which were contained in a series of Reports to the Safety in Mines Research Board and so had not been generally available. A few instances may illustrate the point. With the usual method of rate measurements methane and ethane oxidize many times faster than hydrogen, yet the ignition points of hydrogen and ethane in oxygen, by this flow method, are approximately the same and that of methane is some 40° higher (H_2- 625°, C_2H_6- 628°, CH_4- 664°). The ignition point of methane in air is greatly influenced by the presence of carbon dioxide and 5% of this in the methane will raise it 45°. This effect can hardly be due to inhibition, since carbon dioxide is a normal product of the oxidation of methane and this shows no abnormalities such as would appear if the reaction produced its own inhibitor. Moreover, iodine, which is a true inhibitor, is much more effective, 0.01% raising the ignition temperatures by about 80°.

The results obtained with hydrogen, ethylene and propylene indicated that the ignition temperatures for these gases were approximately the same in nitrous oxide as in oxygen. That with the nitrous oxide was the lower in each case, but the actual differences were only one or two degrees. Ethyl ether, however, gave very different results, the values being 715° in nitrous oxide and 219° in oxygen. Abnormal results were also obtained with this compound under other conditions. Thus the use of air instead of oxygen as the atmosphere, which usually caused a change of less than 100° in the ignition temperature, with ether caused a change of over 300° (549° compared with 219°). Moreover, when pure oxygen was used the presence of nitrogen in the ether vapour itself sometimes had a considerable effect. Thus at 760 mm. pressure pure ether ignited at 219° and an equimolecular mixture of ether and nitrogen at 222°, but at 600 mm. the corresponding temperatures were 221° and 430°. These results may be summarized, then, by saying that when the ignition temperature of a gas is not greatly affected by changing the atmosphere from oxygen to air, it will not be appreciably affected by changing from oxygen to nitrous oxide, but when abnormal results are obtained in the first case they will also be obtained in the second. It is hardly justifiable, however, to base any assumptions with regard to the slow reactions on results of this kind.

The reaction

$$H_2 + N_2O \longrightarrow H_2O + N_2$$

would ordinarily not be accompanied by any change in the total pressure and so could not be followed in the apparatus commonly used in the static method since pressure changes are the important factors with it. Hinshelwood[10] investigated the reaction by sealing mixtures of nitrous oxide and hydrogen in Jena glass bulbs and determining the amount of water formed after these had been kept at 700°C. for different times. He concluded that the rate of reaction was no greater than could be accounted for by the decomposition of the nitrous oxide followed by rapid reaction of the oxygen and hydrogen.

Recently Melville[11] has made a thorough study of the reaction. By introducing a boat containing phosphorus pentoxide or calcium chloride into the cooled neck of the reaction vessel he was able to keep the water vapour in the system to a very low pressure. The reaction was then accompanied by a pressure change and its course could be followed in the usual way by measuring this on a capillary manometer. His results showed that the reaction was from 90 to 500 times faster than the nitrous oxide decomposition, the actual ratio depending on the experimental conditions, particularly the relative concentrations of the two gases and the total pressure of the mixture. The rate was directly proportional to the pressure of the nitrous oxide and nearly independent of that of the hydrogen, except when the pressure of the nitrous oxide was high. It was unaffected by nitrogen and argon. Increasing the diameter of the reaction vessel increased the velocity of the reaction. These facts are satisfactorily explained by a chain mechanism. Moreover, in the corresponding photochemical reaction, under conditions such that the light produced hydrogen atoms, each of these induced the reaction of several nitrous oxide molecules even when the temperature was more than a hundred degrees below that required for rapid thermal reaction.

This is direct evidence for the occurrence of reaction chains in the system. The addition of oxygen to the H_2 - N_2O mixtures greatly increased the rates of reaction except at low pressures where the H_2 - O_2 reaction itself would not be very rapid. This acceleration was shown to be due both to an increased rate of chain initiation and to a favourable effect on chain propagation. From this result and those obtained over a wide range of other conditions he deduced that the chain carriers were hydrogen atoms and hydroxyl radicals and that the chains were broken by recombination of the hydrogen atoms, in the gas at high pressures or on the wall at low pressures.

The H_2 - O_2 reaction probably involves as its first step the formation of a molecule of hydrogen peroxide[12] or two hydroxyl radicals[13] from a molecule of hydrogen and one of oxygen. According to the latter scheme, which is the more generally accepted, the chains which are started by this initial step have the same carriers and are broken in the same way as those which Melville postulates for the H_2 - N_2O reaction. Such close similarity in these two cases would encourage one to expect that interesting results could be obtained with gases other than hydrogen. This is especially so since those with the latter are in accord with the hypothesis advanced in the general introduction, namely, that oxidations would proceed more rapidly with oxygen than with nitrous oxide if the initial step in presence of the former involved combination of the oxygen molecule as a whole.

The choice of the gases to be used should be guided by the following conditions: they should be relatively easily oxidized, so that the reactions can be studied in a range where nitrous oxide decomposition is negligble, they should not decompose until fairly high temperatures are reached, they should be as simple as possible and their oxidations with molecular oxygen should have been studied. These conditions appear to be satisfied by methyl alcohol. The CH_3OH - O_2 reaction has been studied in some detail by Fort and Hinshelwood[14]. They found that its rate was measurable above 400°, depended on the cube of the methyl alcohol concentration and on the total pressure and was considerably decreased by a reduction in the diameter of the reaction vessel. They concluded that the reaction was a chain process and were able to develop an approximately quantitative treatment for it. Unfortunately the CH_3OH - N_2O reaction was not readily measurable below about 530° and at such temperatures the decomposition of methyl alcohol began to take place. Moreover, the results from different phases of the investigation were not always easily reconciled and no clear indication of the reaction mechanism was obtained. It was therefore impossible to make so close a comparison between these two reactions as was made between the corresponding ones with hydrogen.

Since some of the difficulties might have been due to the decompositions of the individual components, the investigation was continued using phosphine and then carbon disulphide instead of the methyl alcohol. Each of these substances is very easily oxidized and quite stable to heat but from the point of view of our original purpose have the disadvantage that the mechanisms of their slow oxidations are not fully known. The PH_3 - O_2 reaction is characterized by explosion limits and these have been studied in detail[15]. There are both upper and lower pressure limits at room temperature so that the two gases cannot be mixed without giving an explosion unless very special precautions are taken. The CS_2 - O_2 system is somewhat similar. Here, however, no reaction occurs below 140° with a mixture containing three parts of oxygen to one of carbon disulphide. At this temperature the explosion limits appear[16]. Slightly above 210° the upper limit disappears, at least over the range of pressures investigated. It would seem, therefore, that conditions in the two corresponding systems with nitrous oxide should be as favourable for homogeneous reaction as could be obtained with that gas.

Actually, however, the results obtained were less satisfactory than those with methyl alcohol. With phosphine reaction did not begin much below 600° and was only accompanied by a very small pressure change. With carbon disulphide the temperatures required were even somewhat higher and the pressure change was not much greater than that given by nitrous oxide alone. In the meantime Dr. Steacie[17] had made a short study of the ethylene - nitrous oxide and acetaldehyde - nitrous oxide reactions which showed that they were equally unsatisfactory. It did not appear advisable. therefore, to devote any further time to this particular problem.

Experimental.

All of the reactions were followed by measuring the pressure changes at constant volume.

The apparatus was of the type commonly used in experiments of this kind[18]. When both reactants were gaseous at room temperature it was of the form shown in Figure 1. When one of them was a liquid the large gas storage bulb, H, was replaced by a small tube containing about 10 cc. of the liquid.

In the former case the gases were introduced into the apparatus through taps 9 and 10 and stored in the bulbs G and H. In the latter the liquid was placed in the small tube before it was sealed to the apparatus. The desired amounts of the separate reactants could then be admitted from these stock supplies into the mixing bulb E. The partial pressures in the mixture were read on the manometer F, one side of which was kept evacuated through the tap 6. The reaction bulb A was of pyrex and had a volume of about 200 cc. It was sealed to pyrex capillary which was joined to the rest of the system by a DeKhotinsky joint. The dead space outside the furnace was not greater than 2%. The capillary manometer D and the tubing joining it to the reaction bulb were wound with resistance wire and kept at 60°C. The one side of the manometer was fitted with a mercury reservoir of large diameter relative to the capillary so that each pressure measurement involved reading only one arm. This side was also kept evacuated through tap 1. The zero reading was taken with both sides evacuated and since only relative pressures

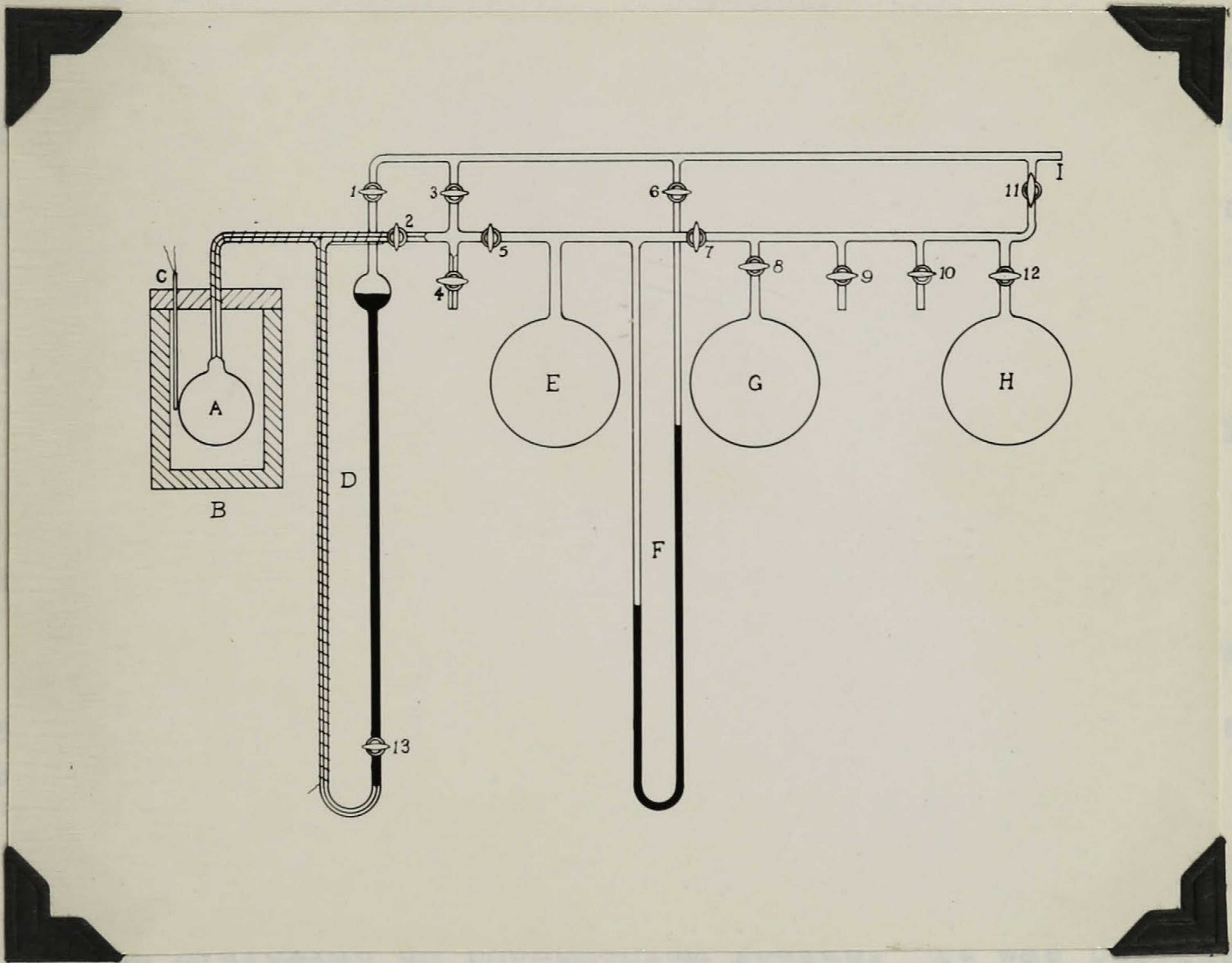


FIGURE 1.

were of importance, subsequent readings were not corrected for the temperature of the mercury. Samples for analysis could be withdrawn through tap 4. The apparatus was evacuated through I, a Langmuir condensation pump being used in series with a Hyvac oil pump. Pressures in the system could be read on a McLeod gauge.

B was an electrical resistance furnace and was controlled by hand adjustment of rheostats within 1° during the course of a run. Temperatures were measured with the chromel-alumel thermocouple C, in conjunction with a Cambridge potentiometer.

The nitrous oxide was obtained from a cylinder furnished by the Ohio Chemical and Manufacturing Company and was used directly without any further purification.

The methyl alcohol was prepared by a single careful fractionation of commercial methanol. It distilled between 64°.8 and 65°.0 C. (uncorr.).

The phosphine was prepared by the action of dilute potassium hydroxide on phosphonium iodide. It was purified by passing it through 50% KOH solution and through a trap cooled in an ice-salt mixture, in accordance with the directions given by Moser[19].

The carbon disulphide was the ordinary Merck product and was not subjected to any special treatment.

The Methyl Alcohol - Nitrous Oxide Reaction.

Course of the Reaction.

Gas analyses were made on the mixtures obtained as products from runs made at 570°C. in a reaction bulb packed with short lengths of pyrex tubing. As will appear later, the total pressure change and the nature of the pressure-time curve were both unaffected by packing the reaction bulb, so that it is safe to assume that the results obtained for this case will also hold for the unpacked bulb. The partial pressures of the methyl alcohol in these runs varied between 70 and 130 mm. but there was no evidence of any corresponding variation in the mechanism, either from the rate curves or from the composition of the products.

The analyses were made using separate Hempel pipettes and the results are therefore not as accurate as might be desired.

Since the decomposition of methyl alcohol proceeds at this temperature and must therefore affect to some extent the products of the more rapid reaction with the mixtures, it appeared desirable to carry out some analyses of the gas obtained from it.

Two such analyses gave

%CO - 35.5, 33.8

%CH_4 - 2.0, 2.0

% H_2 - 61.5, 62.9 .

These are in satisfactory agreement with values given elsewhere[20] for the decomposition products and indicate that the main reaction may be summed up as

$$CH_3OH \longrightarrow CO + 2H_2 \quad .$$

However, this would give an expansion of 200% while that actually found was always about 120%. It would seem, therefore, that considerable condensation must have taken place. Since there is undoubtedly some water formed, which is not shown in the analyses, it is impossible to draw any accurate conclusions as to the empirical composition of the condensate but it probably does not differ greatly from that of the alcohol itself. As this decomposition was only a side reaction in the oxidation which was being studied, it did not appear worthwhile to investigate it further. However, since the completion of this work Fletcher[21] has reported a more detailed study of the decomposition of methyl alcohol which is of some interest here. His measurements were made in a silica bulb, most of them at 669°C. Under these conditions the products consisted entirely of carbon monoxide and hydrogen and the total pressure change varied from 150 to 191%, depending chiefly on the pressure but being slightly reduced by increases in the relative surface area of the bulb. The rate was very slightly affected by packing the reaction vessel. This is in marked contrast to the present case where such treatment of the pyrex bulb increased the rate many-fold. He believed the low pressure increase to be due to a condensation reaction at the surface, if that is correct it would be expected to be more important when the decomposition reaction was a surface one than when it took place in the gas phase, as is actually the case. It is also possible that condensation would be greater at 570° than at 669°, although Fletcher's results between 626° and 730° gave no indication of such a change.

In the case of the products obtained with the mixture N_2O - CH_3OH the analysis is complicated if any excess nitrous oxide be present, because of its solubility in many of the customary absorbents[22]. For that reason the analyses were limited to the products obtained using mixtures with the ratio N_2O to CH_3OH equal to 3 to 2. Since, as will appear later, the pressure increase - time curves for all the mixtures were affine and the total pressure increases were the same, there cannot be any very great difference in the products obtained. However, it was found that, even with this mixture, the gas still contained nitrous oxide after the reaction was completed and that this dissolved sufficiently rapidly in fuming sulphuric and in acid cuprous chloride to make the results with these reagents quite useless. With the potassium hydroxide and alkaline pyrogallol the process of solution is very slow. For these reasons the CO_2 and O_2 were removed in the usual way, and the gas which was left was then transferred directly to the combustion pipette and burned with oxygen. On the assumption that the gas at this stage contained only CO, H_2, N_2O and N_2 - the amount of methane is almost certainly very small, so that this is reasonably correct - it was possible to determine the amounts of the individual constituents. In order to obtain a check and especially to determine whether any nitrous oxide was removed by the two absorbents used, some samples were burned without any previous treatment and the CO_2 and N_2 determined in the product. These then represent $CO + CO_2$ and $N_2 + N_2O$ in the original sample. The results of three such determinations were

	1.	2.	3.	Av.
$CO + CO_2$	23.6	26.5	24.3	24.8
$N_2 + N_2O$	45.9	44.9	45.2	45.3

Analyses by the more complete method gave

	CO_2	O_2	CO	H_2	N_2O	N_2	$CO + CO_2$	$N_2 + N_2O$
4.	3.7	1.5	19.3	28.1	8.9	38.5	23.0	47.4
5.	4.0	1.3	19.3	26.7	11.3	37.3	23.3	48.6

It is apparent that the ratio C:N is quite different from that which would correspond to the composition of the original mixture ($N_2O:CH_3OH = 3:2$, therefore $N_2 + N_2O:CO + CO_2 = 3:2$). This may be due to the condensation of some compound which contains carbon. It was necessary to assume that this had happened in the thermal decomposition of the methyl alcohol and it seemed probable that the condensate had an empirical formula approximating CH_4O. If we make these assumptions here it should be possible to use the carbon in the gas as the basis for a hydrogen-oxygen balance and obtain indications of the formation of water. The two analyses given in detail above lead to the following results:

	1.			2.	
	H	O		H	O
Calc.	92.0	57.5	Calc.	93.2	58.2
Found	56.2	38.6	Found	53.4	41.2
Diff.	35.8	18.9	Diff.	39.8	17.0

The calculated values are obtained as follows:- In the case of analysis 4., $CO + CO_2 = 23.0\%$. Then, if we say the gas contains 23.0 parts of C it should also contain 4X23 parts of H and $2\frac{1}{2} \times 23$ parts of O in order to correspond to 1 part CH_3OH + $1\frac{1}{2}$ parts of N_2O.

The values tabulated as found are - $H = 2 \times \%H_2$; $O = \%CO + \%N_2O + 2(\%CO_2 + \%O_2)$. The difference agrees satisfactorily with the composition H_2O.

If we assume the main reaction to be

$$CH_3OH + N_2O \longrightarrow HCHO + H_2O + N_2,$$

followed by

$$HCHO \longrightarrow H_2 + CO \;;$$

and the side reactions to be

$$CH_3OH + N_2O \longrightarrow CO_2 + 2H_2 + N_2$$

and

$$2N_2O \longrightarrow 2N_2 + O_2 \quad ,$$

the analytical results can be reproduced reasonably well for all the components of the gas except the nitrogen.

Thus, if we use the experimental values for CO, CO_2 and O_2 to determine the relative extents of the three reactions, the values given below are found for the other constituents:-

		H_2	H_2O	N_2O	N_2
4.	Found	28.1	18.4	8.9	38.5
	Calc.	26.7	19.3	8.5	26.0
5.	Found	26.7	18.4	11.3	37.3
	Calc.	27.3	19.3	9.1	25.9

The values given as found for H_2O are the averages of the values obtained from the data for H and O in the hydrogen - oxygen balances, thus for 4. the value is $\frac{1}{2}(35.8/2 + 18.9)$. The agreement is sufficiently close to indicate that these reactions are probably the correct ones. Of course, it must be to some extent fortuitous since the scheme ignores the methyl alcohol decomposition which would certainly have some effect. The high nitrogen is to be explained, as indicated previously, by the formation of some condensable carbon compound. This might require an oxidation process or the compound might take up oxygen after it had been formed, either alternative would account for the result obtained.

The three reactions above would give a total pressure increase slightly greater than twice the partial pressure of the alcohol in the original mixture. The experimental value varied between 160% and 180% with the average about 175% - a difference which is in the direction which would be expected if some substance were deposited. Actually, after the reaction bulbs had been used for a few runs they were found to have a very thin coating, which appeared to be carbon, over their surface. However, this was far too small to be responsible for so large a difference.

Rate of Reaction.

As the first step in the investigation of the rate of reaction it was necessary to show that the rates of pressure change with mixtures were greater under all conditions and at all stages than could be accounted for by the decomposition of the individual components. For this purpose runs were made with nitrous oxide alone and with methyl alcohol alone. In the first of these there was no appreciable pressure change over a time interval which would have corresponded to complete reaction with the mixture. This was not the case however with the methyl alcohol for its rate of decomposition was measurable over the entire range of temperatures used with the mixtures. It varied quite erratically and was particularly sensitive to the immediate past history of the reaction bulb. Thus when the blank runs were made directly after the mixture had been used the rate was generally very slow but increased progressively with successive evacuations and runs with methyl alcohol alone. Under all conditions, however, the mixture gave much the faster rate, the ratio of the two varying from 4 : 1 to 20 : 1, depending on the temperature and on the gas composition and pressure. As mentioned in the preceding section, the total pressure changes were different; referred to the methyl alcohol they were 175% for the mixture and 120% for the blank. It would evidently have been desirable to correct for this decomposition had that been possible but, in view of the wide variations, this could not be done. Later results did not justify a more extensive investigation of this point.

Figure 2 shows typical pressure change - time curves for both the mixture and the alcohol alone. Table 1 gives the data for some runs made with varying total gas pressure; Table 2 with varying gas composition. All were made at 570°C.

TABLE 1.

PRESSURE CHANGE IN $N_2O:CH_3OH = 5:1$ MIXTURES.

No.	1	2	3	4	5
P_{CH_3OH} (mm.)	73.0	48.0	35.5	24.5	7.8
Time (min.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)
0	0	0	0	0	0
1	10.0	4.8	4.0	3.0	0.8
2	20.4	11.8	8.4	6.0	2.0
3	30.8	18.0	12.8	9.2	3.0
4	40.8	23.6	16.4	12.2	4.4
5	50.0	30.0	21.8	15.4	5.6
6	58.8	35.8	25.8	18.4	6.2
7	68.0	41.2	29.8	21.4	7.8
8	76.6	46.6	33.8	24.2	8.8
10	89.8	56.6	41.0	29.2	10.4
12	102.4	64.6	47.2	34.0	11.8
14	112.8	74.2	53.2	38.0	12.8
16	120.8	80.6	58.0	41.0	-
20	126.8	83.4	62.6	45.0	14.0
25	126.8	83.6	62.6	45.0	14.0

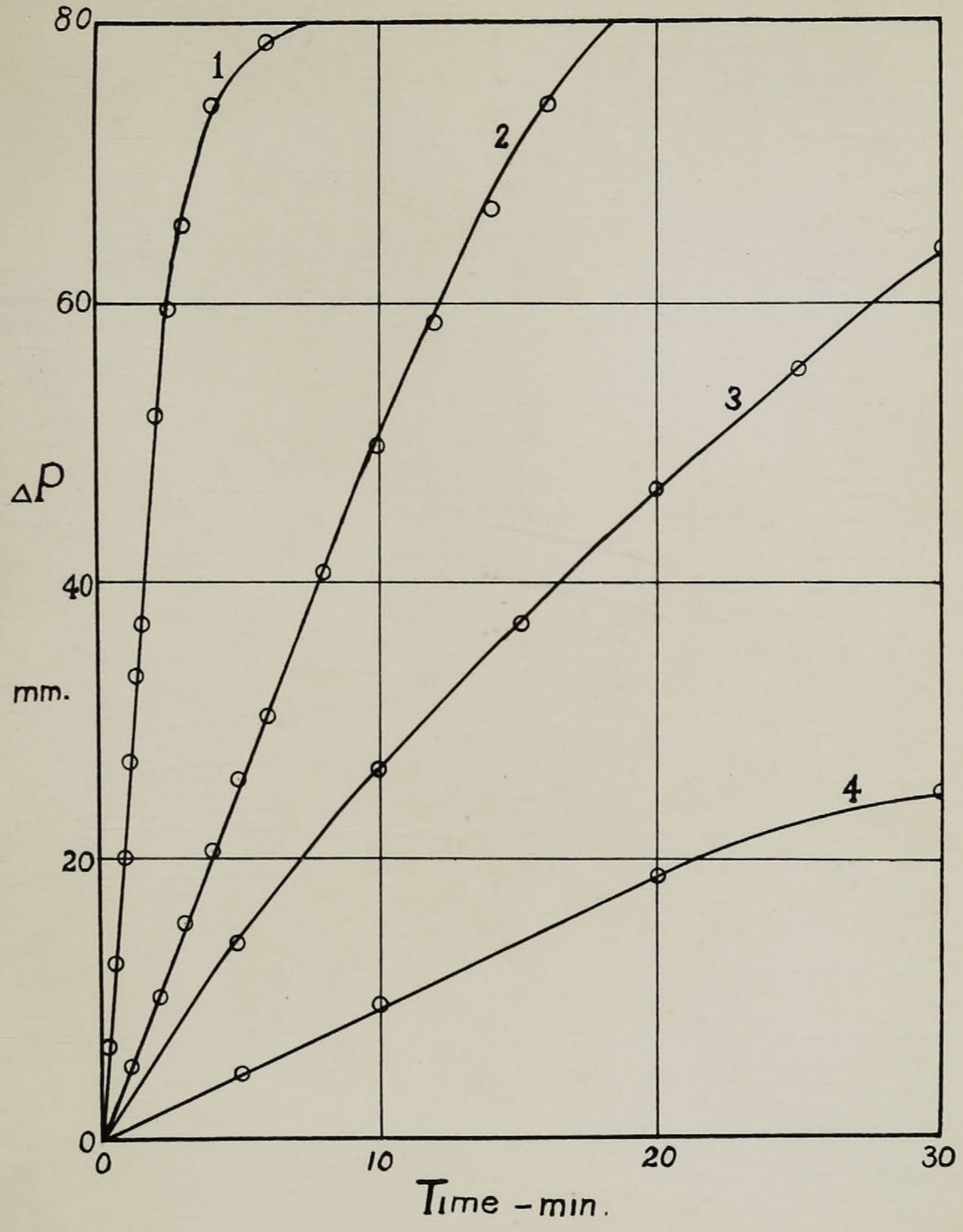


FIGURE 2.

TYPICAL PRESSURE - TIME CURVES - 570° C.

(1) 200 mm. N_2O, 50 mm. CH_3OH; packed bulb. (2) Ditto; unpacked.

(3) 75 mm. CH_3OH; packed bulb. (4) Ditto; unpacked.

TABLE 2.

PRESSURE CHANGE IN N_2O - CH_3OH MIXTURES.

No.	1	2	3	4	5
P_{CH_3OH} (mm.)	48	51	56	48	52
P_{N_2O} (mm.)	240	204	168	96	78
Time (min.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)
0	0	0	0	0	0
1	4.8	5.6	4.8	2.9	3.0
2	11.8	11.8	9.4	6.5	5.6
3	18.0	17.6	14.2	8.7	9.0
4	23.6	23.6	19.2	12.5	12.8
5	30.0	28.8	22.4	16.3	16.0
6	35.8	33.6	28.2	19.7	19.2
7	41.2	38.6	-	-	-
8	46.6	43.2	37.2	26.1	26.0
10	56.6	51.6	45.4	32.7	32.0
12	64.6	59.6	54.4	38.7	38.2
14	74.2	65.8	62.2	44.9	44.0
16	80.6	71.8	69.6	49.9	49.4
20	83.4	81.6	81.4	59.1	59.0
25	83.6	88.6	-	69.7	67.8
30	-	-	-	75.1	75.2
40	-	-	-	84.3	89.2
50	-	-	-	-	92.0

Since the individual curves do not conform to any simple order they cannot be used directly for a detailed study. It is preferable to determine the effect of variations in the initial pressure and gas composition on the time required to reach a certain conversion. For this purpose we have adopted the time for a pressure change equal to the initial alcohol content; this is referred to as t_{100}. If these times are to be strictly comparable it is essential that the course of the reaction be identical in all the cases, that is, that the time - percentage pressure increase curves be affine. To test this relation the curves were plotted with varying time scales so that some one point, in addition to the origin, was common to all of them; if they were affine they would then coincide throughout their entire length. Figure 3 shows a series of runs with mixtures of different composition and approximately the same alcohol pressure treated in this way. The agreement is quite satisfactory. Similar tests were carried out with runs made with different alcohol pressures and at different temperatures. The curves were again identical and are therefore not repeated here. It would also follow, of course, that, if the reaction were the same under all conditions, the total percentage pressure increase would also be the same. This is actually the case within reasonable limits as shown in Tables 3 and 4.

In Table 3 the runs are classified according to the composition of the mixture without regard to total pressure; in Table 4 according to alcohol pressure without regard to composition. Many runs were not carried to completion and so are

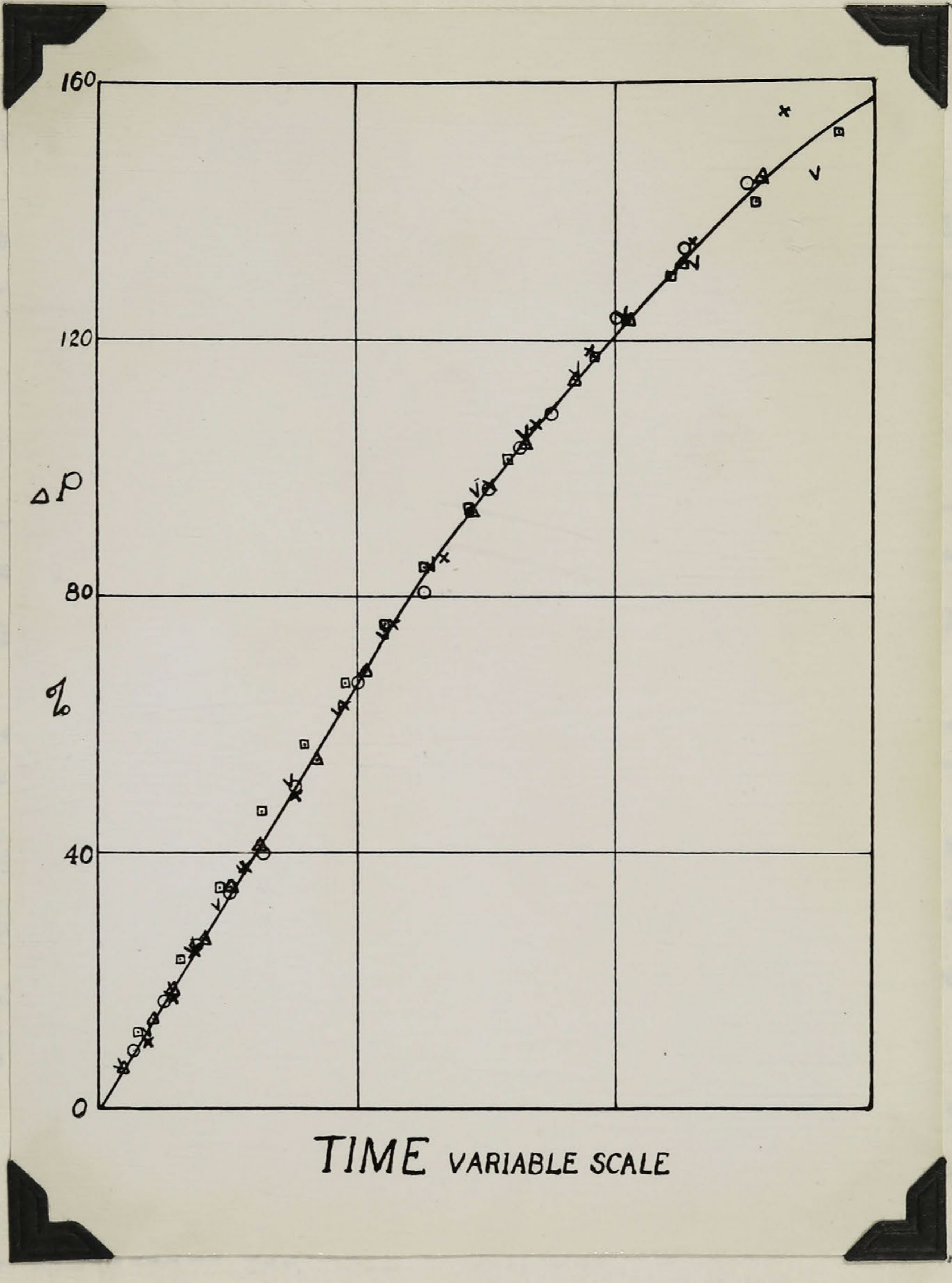


FIGURE 3.

AFFINE CURVES FOR VARIOUS N_2O - CH_3OH MIXTURES AT 570° C.

TABLE 3.

PRESSURE INCREASE

Ratio $N_2O:CH_3OH$	5:1	4:1	3:1	2:1	3:2
No. of Runs	18	19	11	14	6
Average Pressure Increase - %	178.3	173.4	173.4	173.6	170.3

TABLE 4.

PRESSURE INCREASE

Pressure of CH_3OH (mm.)	0 - 20	20 - 40	40 - 60	60 - 80
No. of Runs	12	20	22	16
Average Pressure Increase - %	176.9	176.2	173.5	173.1

not included. This applies especially to the 3:2 mixture where the rate was quite slow. In this group two of the final values were particularly low - 159% - and if they are disregarded the average becomes 176.0%.

At this point it should be mentioned that it was not always possible to obtain checks in t_{100} even when the experimental conditions appeared identical. The deviations were erratic and often quite considerable. In order to eliminate as many as possible of the variables a standard procedure was adopted. The reaction bulbs, which were always of pyrex, were evacuated for several hours at 570° C. before they were used. They were pumped out for one hour between successive experiments. This gave a pressure slightly below 10^{-5} mm. Since it was not possible to heat the glass above 650° without having it collapse the outgassing was not carried out above 570°, the temperature at which the runs were made. However, it often happened that, after the bulb had stood during the night under vacuum, results were obtained in all experiments which were entirely inconsistent with previous ones; while after a second night the values again checked the original ones. Irregular results were also obtained occasionally with individual runs. In general, however, they fell quite obviously into groups and there was no difficulty in choosing the ones which corresponded. In the first few runs with a new bulb there was always a slight drift which was not in evidence at any later stage. Since an examination of the bulb showed that a thin deposit of carbon had been formed on it some variations were to be expected. In the diagrams and tables which follow a number of the more erratic runs have been omitted.

The values of t_{100} as obtained with mixtures of different composition at different pressures are given in Table 5 and are plotted in Figure 4. The runs were made at 570° C. It is apparent that the general form of the curves is the same for the different mixtures. From this set of graphs the effect on t_{100} of variations in the nitrous oxide content while the alcohol pressure was constant can be deduced. Obviously this is given by the intersections of the curves with any vertical line. From an analogous plot of the same data with P_{N_2O} rather than P_{CH_3OH} as the abscissae the effect of nitrous oxide is obtained. The results are shown in Figure 5.

TABLE 5.

VARIATION IN t_{100}. TEMP. 570° C.

N_2O:CH_3OH	P_{CH_3OH} mm.	t_{100} min.	N_2O:CH_3OH	P_{CH_3OH} mm.	t_{100} min.
5:1	58.3	7.8	3:1	17.8	10.9
5:1	48.0	8.3	3:1	10.9	10.0
5:1	41.4	8.9	3:1	9.8	9.7
5:1	38.4	8.6	2:1	80.0	14.8
5:1	35.4	8.6	2:1	67.2	15.5
5:1	29.7	8.3	2:1	56.7	15.6
5:1	24.5	8.2	2:1	48.0	15.3
5:1	21.0	8.3	2:1	28.3	13.4
5:1	14.7	7.6	2:1	20.2	12.9
5:1	7.8	6.9	2:1	18.0	13.0
4:1	50.8	9.9	2:1	14.0	12.3
4:1	32.5	9.8	2:1	10.4	12.3
4:1	23.4	9.8	3:2	74.3	16.8
4:1	20.0	9.5	3:2	62.5	17.2
4:1	12.5	8.6	3:2	51.8	17.0
4:1	11.3	8.7	3:2	45.8	16.4
3:1	56.4	12.5	3:2	44.0	15.7
3:1	36.7	12.0	3:2	27.8	14.9
3:1	36.5	11.8	3:2	21.1	14.9
3:1	27.6	12.2	3:2	12.7	13.6
3:1	20.7	11.0	3:2	10.2	14.0

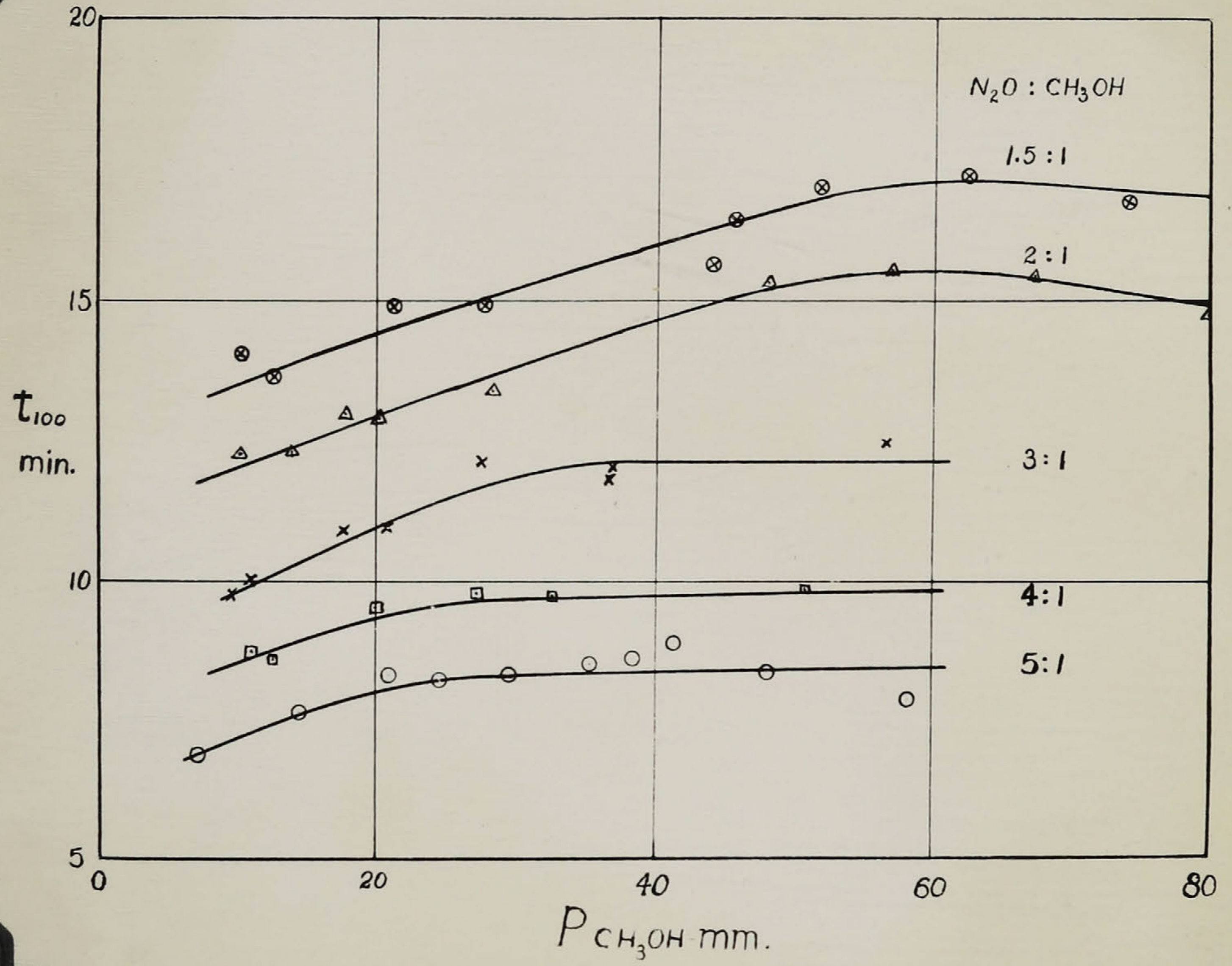


FIGURE 4.

EFFECT OF CONCENTRATION - 570° C.

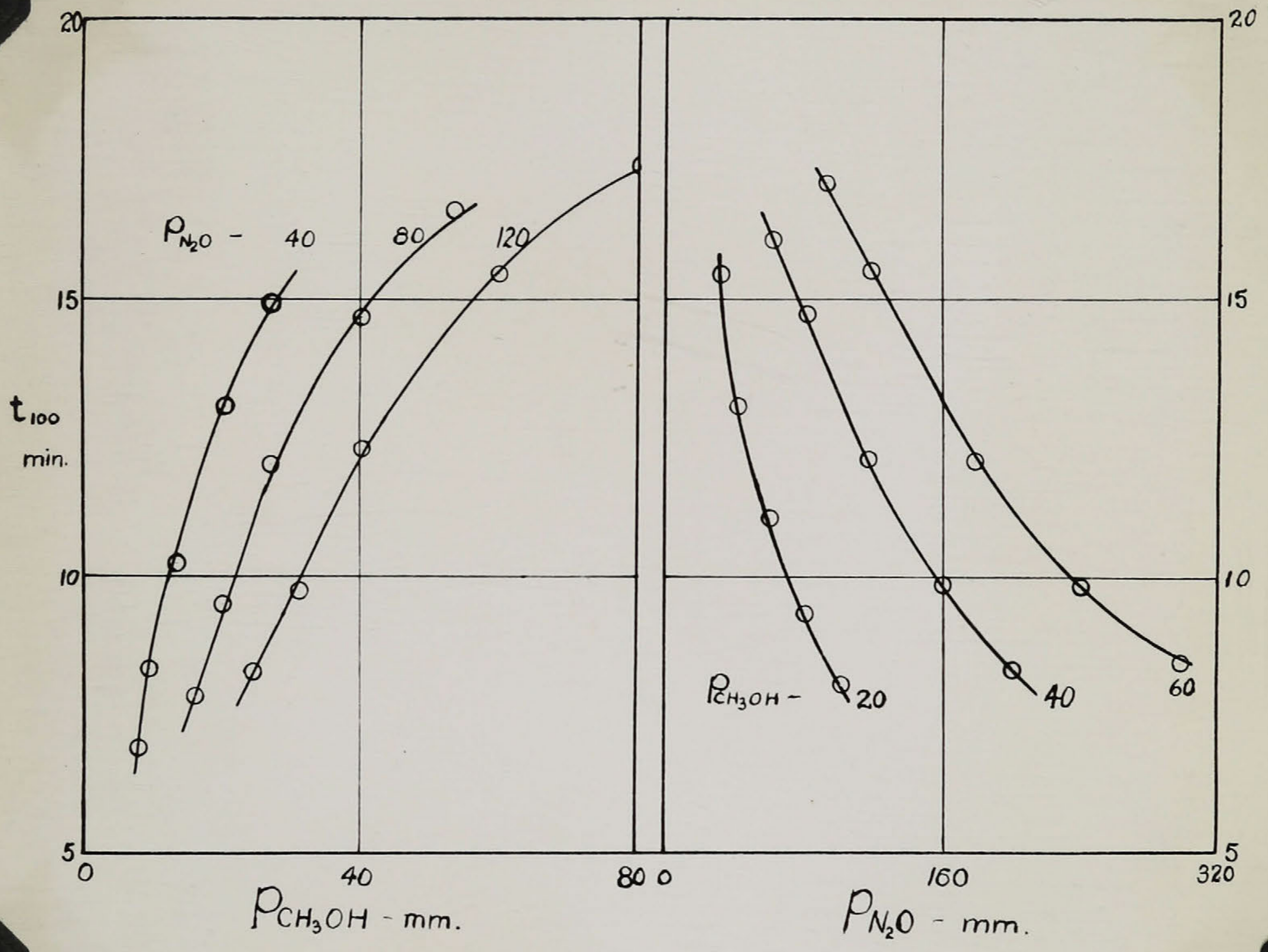


FIGURE 5.

EFFECT OF SINGLE REACTANTS - 570° C.

To determine the temperature coefficient of the reaction runs were made at different temperatures with a mixture containing 50 mm. of CH_3OH and 200 mm. of N_2O. Since the t_{100} - P_{CH_3OH} curve in this region is almost horizontal (Fig. 4) the use of constant pressures rather than constant concentrations introduces no appreciable error. In order to show the effect of packing the bulb on the rate of reaction, each of these runs was repeated in a similar bulb filled with one inch lengths of pyrex tubing. The surface was thus increased about six times, but the two surfaces were not strictly comparable since the original bulb had a thin coating, probably of carbon, from the earlier runs while the second contained clean tubing. It is also possible that the rough ends of the tubing might have been more effective than the smooth walls. Table 6 gives the results for t_{100}.

TABLE 6.

TEMPERATURE COEFFICIENT.

4:1 Mixture. Total Pressure 250 mm.

A - Unpacked Bulb. B - Packed Bulb.

Temp.° C.		500	520	535	550	570
t_{100} (min.)	A	162 195	90.8	48.5 49.0	22.4	9.3 10.2
	B	26.1	9.1	6.8	4.3 4.7	1.83
A/B		6.2 7.5	10.1	7.2	5.2 4.8	5.1 5.6

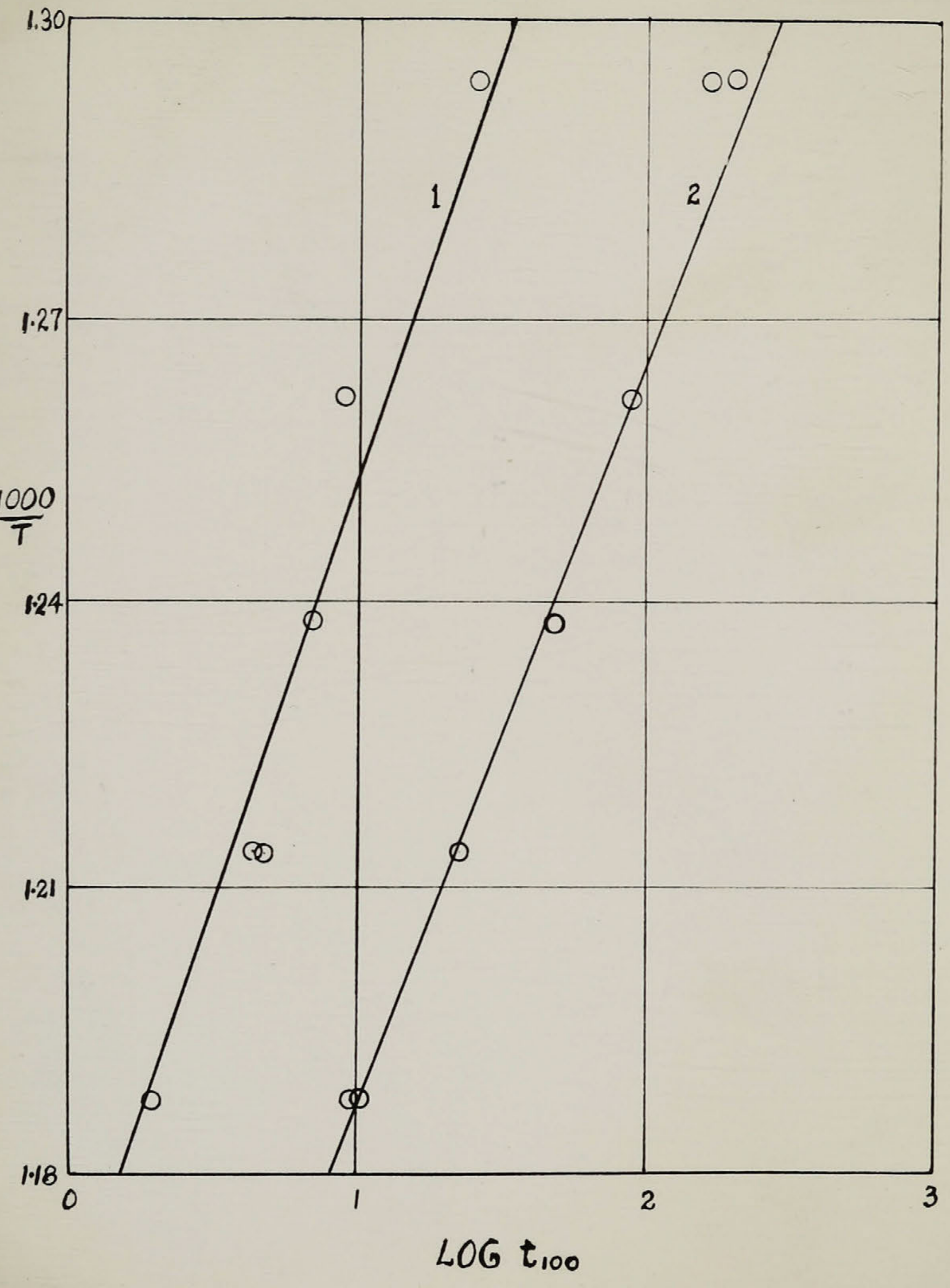


FIGURE 6.

TEMPERATURE COEFFICIENT.

1. Packed Bulb. 2. Unpacked Bulb.

$4N_2O$ $1CH_3OH$. Total Pressure - 250 mm.

To obtain the apparent heat of activation the two sets of values were used for plotting log t_{100} against 1000/T. The graphs are shown in Figure 6. In the case of the runs with the unpacked bulb the points for the four higher temperatures fell very nearly on a straight line which gave the value of E as 59,500 cals. Those with the packed bulb were erratic, which was perhaps to be expected since it had not been in use for more than a very few runs. It follows, therefore, that no particular significance is to be attached to the variation of the ratio A/B in the above table. The best line through these gave E = 52,000 cals. In both cases the same result, within the experimental error, was obtained if $t_{50} - t_{25}$ were used rather than t_{100}.

Since it is often of value in determining the mechanism of a reaction if the conditions under which explosions occur are known, a few runs were made with the packed bulb at temperatures higher than 570°. These proceeded at much greater rates than were obtained in the previous series but there were no explosions. Since the reaction bulb was of pyrex it was impossible to go above 625°. These runs, with two at 570° added are given in Table 7. With the faster runs the extrapolation to zero time may be somewhat in error.

TABLE 7.

EFFECT OF TEMPERATURE ON RATE. PACKED BULB.

Temp. °C.		570	600	625	625	570
P_{N_2O} (mm.)		188	375	330	141	128
P_{CH_3OH} (mm.)		47	75	66	94	85
Time Min.	Sec.	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)
0	0	0	0	0	0	0
0	15	6.4	27	40	31	8.0
0	30	12.6	54	77	62	14.4
0	45	20.0	77	98	87	24.2
1	0	26.8	94	105	111	33.0
1	15	33.0	108	105	125	41.0
1	30	39.0	113	-	135	48.0
1	45	-	117	-	142	55.2
2	0	52.0	117		145	62.0
3	0	65.6	117		145	81.6
5	0	78.6	-		-	109.4
10	0	80.6	-		-	135.0

Discussion.

It is evident from the forms of the curves in figures 4 and 5 that no simple rate equation will fit the facts over the whole range of conditions investigated. However, by making certain approximations, it is possible to arrive at a relation which agrees fairly well with the actual results for most of the runs.

Although the t_{100} - P_{CH_3OH} curves in figure 5 bend over at high pressures, tending towards a constant value for t_{100}, the lower portions might be considered as straight lines radiating from the origin (not shown in the figure) without greatly exceeding the experimental error and, therefore, could be represented by the equation

$$t_{100} = K \cdot P_{CH_3OH} \quad .$$

The t_{100} - P_{N_2O} curves are approximately of the form required by the relation

$$t_{100} = K/P_{N_2O}{}^{n} \quad .$$

For each curve the pressure of nitrous oxide increases 3.3 times in going from the lowest to the highest determined point, while the time is only halved over the same range. It follows from this that n has a value near 0.6 and the equation is

$$t_{100} = K/P_{N_2O}{}^{0.6} \quad .$$

Comparing these relations with equations 2, 5 and 6 of the general introduction and remembering that t_{100} is here defined in terms of the methyl alcohol concentration, it is evident that the rate equation for low pressures, that is, for much of the range investigated, is of the form

$$-d\,[CH_3OH]/dt = K\cdot[N_2O]^{0.6} \quad ,$$

while at higher pressures the concentration of methyl alcohol begins to be of importance and the equation tends towards

$$-d\,[CH_3OH]/dt = K\cdot[CH_3OH]\cdot[N_2O]^{0.6} \; .$$

Since these relations have been deduced to explain the effect on the rate of variations in the pressures of the single reactants (figure 5), it is of interest to see whether they will also explain that of variations in the total pressure with mixtures of constant composition (figure 4). For a reaction the order of which changes from less than one to greater than one with increasing pressure, as in the present case, the value for t_{100} should pass through a maximum, corresponding to the pressure where the order is exactly one, and should decrease on either side, the slope of the t_{100} - pressure curve increasing with the distance from the maximum. The actual results are evidently in general agreement with these requirements.

The individual pressure change - time curves should also be of a form corresponding to this order. However, they are not very sensitive to small changes in order, as is apparent since all mixtures investigated gave curves which appeared affine although there must actually have been a small change in order with change in initial pressure. The fact that the rate of pressure change remained very nearly constant until the reaction was half completed (figure 3) would require that the order be very small. To that extent, then, these curves support the previous conclusions.

The further kinetic interpretation of the results is not without difficulty.

It is evident from a consideration of the relations existing between the reaction rates for mixtures of nitrous oxide and methyl alcohol and those for the decompositions of each of the individual components, that the mechanism in the former case, whatever it may be, does not depend solely on a primary decomposition followed by a simple homogeneous or heterogeneous reaction between a product molecule and the other reactant molecule. These experiments, however, do not exclude the possibility of a chain mechanism with the chains started by such a decomposition.

Since the rate of reaction is proportional to the surface area, it would appear at first sight that the reaction is of the ordinary heterogeneous type. If this is the case, the expression for the rate at low pressures (see above) can be simply explained on the basis of fairly large adsorption of methyl alcohol and fairly small adsorption of nitrous oxide. The heat of activation, however, is between 50,000 and 60,000 calories. This is somewhat larger than the value which would be expected for a homogeneous bimolecular reaction in the temperature region employed. It is consequently very high for a heterogeneous reaction. Moreover, if the reaction is a heterogeneous one, this is only the apparent heat of activation and the true heat of activation must be higher than this. If the reaction were strongly retarded by the products or by one of the reactants, the apparent heat of activation might be higher than the true one. The results, however, give no indication of such an effect. It is, however, possible that variations in the relative adsorptions of the reactants may account for the high apparent heat of activation. Such variations might explain the dependence of the rate on alcohol concentration at high pressure. The heat of activation found is approximately equal to that of the dissociation of nitrous oxide. This can have no significance, however, since the reaction is not homogeneous.

In the hydrogen- nitrous oxide reaction Melville[11] found that the rate was approximately given by

$$-d[H_2]/dt = K\cdot[N_2O] \quad .$$

In this reaction the chains are initiated by the decomposition of nitrous oxide. It is therefore tempting to assume that the nitrous oxide-methyl alcohol reaction is also a chain reaction, in view of the rough formal similarity of the expressions for the rates and the exothermic character of the reaction. If this were the case, however, it would be necessary to assume that, unlike the hydrogen-nitrous oxide reaction, the chains are initiated at the wall and broken in the gas. The high heat of activation could be explained on the basis of a variable chain length, which makes the temperature coefficient a composite one. There is, however, no real evidence for a chain mechanism and the fact that the reaction shows no explosive characteristics makes a chain process doubtful.

In view of the differences in the mechanisms of the oxygen-methyl alcohol and nitrous oxide-methyl alcohol reactions and the uncertainty with regard to the latter, there is no point in attempting a comparison of the two. However, if the former reaction is dependent on the addition of a single oxygen atom to the alcohol, it is surprising that the analogous addition of the oxygen atom in nitrous oxide to the alcohol cannot take place homogeneously even at the much higher temperatures used in the present investigation.

THE PHOSPHINE-NITROUS OXIDE REACTION.

There was no evidence of any reaction in this system below 500°C. Between that temperature and 600°C. there appeared to be a small, irregular pressure increase. Since this was usually over in less than five minutes and rarely amounted to more than 15% of the phosphine pressure, it may not have been an oxidation which was the cause. At 600° with a mixture containing four parts of nitrous oxide to one of phosphine and at a total pressure of 250 mm. a pressure decrease occurred. At the same temperature, the same mixture at a pressure not greater than 320 mm. (this limit being based on the initial pressure in the mixing bulb) gave a violent explosion. When the reaction mixture was run into the reaction bulb at 210 mm. and the pressure then increased to 508 mm. by the addition of nitrogen, there was no explosion but the slow change proceeded as before. These results are shown in Table 8.

If the pressure changes corresponded to complete reaction, it should have been possible to condense out some of the product gas by cooling to room temperature. This was shown to be the case in run no. 2 of the table. At 600° the pressure was 231 mm., at 25° it was 71 mm., which would correspond to 208 mm. at 600°. Since the original pressure was 250 mm., the difference corresponded to 84% of the phosphine, probably, therefore, to complete reaction.

If the explosions were due to having crossed a lower limit, they should be favoured by the addition of foreign gases in accordance with the relation,

TABLE 8.

PRESSURE DECREASE IN PH_3 - N_2O MIXTURES.

No.	1	2	3
Temp. °C.	600	600	600
P_{PH_3} (mm.)	50	50	42
P_{N_2O} (mm.)	200	200	168
P_{N_2} (mm.)	-	-	298
Time (min.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)
0	0	0	0
1	0.6	0.8	1.0
5	9.0	10.0	9.2
10	12.4	13.2	11.4
20	14.0	15.0	12.2
30	14.8	17.4	12.4
40	15.0	-	-
60	-	19.0	-

$$p_1p_2(1 + up_i/(p_1 + p_2)) = \text{constant}$$

which was discussed in the general introduction. Unfortunately, the constant u cannot be calculated unless the mechanism of the reaction is at least partly known. Moreover, unless very special precautions are taken, the results are sometimes such as to indicate a marked decrease in the value of u as the pressure of the inert gases increases[23]. The fact that there was no explosion in run no. 3 is, therefore, not proof that there is no lower limit in this system. However, if the actual total pressure when the explosion occurred was 320 mm., there should have been an explosion in 3 unless u had a value less than 0.93. Actually, it seems probable that the explosion was a thermal one, since in a preliminary run with these gases a mixture of the same composition was heated from 125°, where its pressure was 245 mm. to 620°, where it was 543 mm., without any violent reaction. The heating from 500° to 600° took about 30 minutes and since at least enough phosphine must have been destroyed in this period to reduce the concentrations below those of a fresh mixture at 320 mm., the reaction must have proceeded at a moderate rate below 600° and might, therefore, increase to an explosive rate at 600°, due only to the temperature difference.

In the case of the runs made at lower temperatures the evacuation of the reaction bulb was carried out slowly, so that explosions would be observed if any were to occur - as would happen if there were limits at relatively low pressures. Nothing abnormal was observed.

The total pressure change during the reaction was so small that an accurate investigation would not have been possible without some special modifications in the apparatus. These preliminary runs were not sufficiently promising to justify such changes.

THE CARBON DISULPHIDE-NITROUS OXIDE REACTION.

This mixture was even less reactive than the preceding one and a readily measurable pressure change was not obtained until the decomposition of the nitrous oxide was fast enough to account for a large proportion of it. This is evident from Table 9. Obviously there was no point in continuing the study of the reaction.

TABLE 9.

PRESSURE INCREASE IN CS_2 - N_2O MIXTURES.

No.	1	2	3	4	5
Temp.° C.	600	620	620	620	620
P_{CS_2} (mm.)	27.0	22.5	-	101.5	69.0
P_{N_2O} (mm.)	162.0	135.0	194.0	-	376.0
Time(min.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)	ΔP (mm.)
0	0	0	0	0	0
5	1.4	2.6	1.0	1.2	16.0
10	3.0	4.8	1.8	1.6	23.0
20	6.0	8.6	-	-	33.0
30	8.0	11.6	6.4	2.6	41.0
40	10.0	13.8	-	-	-
50	-	-	12.6	-	-
60	13.0	18.6	-	-	-

Summary.

1. The reaction between N_2O and CH_3OH takes place at about 570°C. It is much more rapid than could be directly accounted for by a primary dissociation of the nitrous oxide. The methyl alcohol decomposition occurs at that temperature but its rate is much less than that of the oxidation.

2. The cold gaseous products are mainly carbon monoxide, hydrogen and nitrogen. A considerable amount of the carbon is missing in the gas. There is a slight deposit, probably of carbon, in the reaction bulb.

3. The rate of reaction is increased by an increase in surface to an extent approximately directly proportional to the increase in surface.

4. The apparent heat of activation is 56,000 ± 8,000 cals.

5. The rate equation varies from

$$-d[CH_3OH]/dt = K\cdot[N_2O]^{0.6} \quad \text{to} \quad -d[CH_3OH]/dt = K[CH_3OH]\cdot[N_2O]^{0.6}$$

as the alcohol pressure increases.

6. The reaction may be a chain one but, more probably, is simple heterogeneous.

7. The systems $PH_3 - N_2O$ and $CS_2 - N_2O$ do not react until 600° and are so complicated by the decomposition of the nitrous oxide that they would not repay thorough investigation.

PART 2.

THE OXIDATION OF ACETYLENE.

Introduction.

Since the oxidations of the different hydrocarbons have many characteristics in common, it is generally believed that their mechanisms are all modifications of one general type. In writing the introduction to a study of the oxidation of acetylene it is necessary, therefore, to consider all hydrocarbon oxidations. However, the literature on one phase or another of this field is so extensive that it is impossible to review it all in this limited space and many investigations which have not a very direct bearing on the work which is to follow cannot be mentioned. These will include all measurements of the velocity of explosion waves in hydrocarbon-oxygen or hydrocarbon-air mixtures, for the results in such work are largely dependent on physical rather than chemical properties. and much of the work on catalytic oxidations, for with the additional variable introduced by the presence of the catalyst the interpretation of the results in terms of kinetics becomes more difficult.

Before discussing the data from the individual investigations and the various theories which have been advanced it is desirable to present briefly the common characteristics referred to above.

While the products of the complete reactions consist chiefly of carbon monoxide, carbon dioxide, hydrogen and water, in relative amounts depending on the hydrocarbon, the temperature. the mixture composition and so forth, it is always possible, by interrupting the reaction at an early stage, to show that their formation is preceded by that of condensable oxygenated compounds. In many cases all stages intermediate between the hydrocarbon and the oxides of carbon can be detected if the conditions are suitably controlled. At ordinary pressures, however, aldehydes constitute the main constituents of the liquid products.

The rates of the reactions vary with the pressures of the components in such a way as to indicate a high order - between two and four. With approximately equimolecular mixtures the effects of the single reactants show that this variation is largely due to the change in the hydrocarbon concentrations, the oxygen having very little effect and, in some cases, even retarding the reaction. The forms of the rate equations are, however, influenced by mixture composition. so that an increase in the oxygen concentration may reduce the rate with gases high in oxygen and increase it in gases low in oxygen. The addition of inert foreign gases has little effect on the rates but others may have a specific action, either increasing or decreasing the rate.

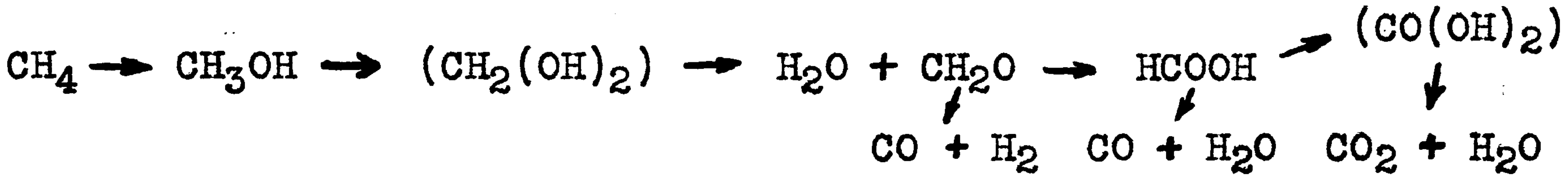
The temperatures at which reaction begins depend on the hydrocarbon but the higher members of a series oxidize more readily than the lower ones and the same is, in general, true of the unsaturates compared with the corresponding saturates. Branched chain hydrocarbons are usually more resistant to oxidation than the normal ones. The temperature coefficients of the reaction velocities vary over a wide range without showing any pronounced regularities.

The rates are very sensitive to the condition of the surface of the reaction vessel and so are not readily reproducible. Packing the bulb normally reduces the rate, at the same time altering the course of the reaction so as to favour the formation of carbon dioxide.

Above certain temperatures the combustions become explosive but the transitions are not particularly sharp, for chemical change can be detected for a considerable range below these. At any one temperature the slow reactions are often characterized by induction periods of variable lengths and the analogous phenomena may be obtained with the explosive reactions, where there may be very definite lags between the heating of the gases and their detonation.

It will be evident that some of these characteristics are identical with those which were described in the general introduction as belonging to chain reactions. Indeed, these oxidations are believed to be of that type, except, of course, by those who refuse to concede the operation of such a mechanism under any conditions. In addition to this indirect evidence there is, however, at least one direct indication of the chains here, for Spence and Taylor (24) have shown that the addition of ozone to ethylene-oxygen mixtures in the temperature region where reaction in its absence is very slow results in the reaction of an abnormal amount of oxygen, that is, chains are initiated by the ozone.

With regard to the exact nature of the first step in the oxidations there is considerable controversy, several alternatives having been proposed. Of these the so-called "hydroxylation theory" and "peroxide theory" have been most widely accepted. According to the former each step in the process involves the replacement of a hydrogen in the molecule by a hydroxyl, or else the elimination of water from a dihydroxy compound. The possibility of decomposition at the intermediate stages is also considered. For the case of methane the scheme takes the form:



$$CH_4 \rightarrow CH_3OH \rightarrow (CH_2(OH)_2) \rightarrow H_2O + CH_2O \rightarrow HCOOH \rightarrow (CO(OH)_2)$$
$$CH_2O \rightarrow CO + H_2 \qquad HCOOH \rightarrow CO + H_2O \qquad (CO(OH)_2) \rightarrow CO_2 + H_2O$$

According to the second theory the first step is the association of an oxygen and a fuel molecule to give a "moloxide" or "peroxide". This may decompose spontaneously, may react on collision with a further oxygen molecule giving normal products, or may react on collision with a further fuel molecule giving products of high energy content which can act as chain carriers. The actual chemical nature of the initial peroxide has not been determined and some minor differences may occur in the formulation of the scheme. In its original form this theory might represent the oxidation of methane as follows:

$$CH_4 + O_2 \rightarrow CH_3OOH$$
$$CH_3OOH \rightarrow CH_2O + H_2O$$
$$CH_3OOH + O_2 \rightarrow \text{normal products.}$$
$$CH_3OOH + CH_4 \rightarrow \text{active products.}$$

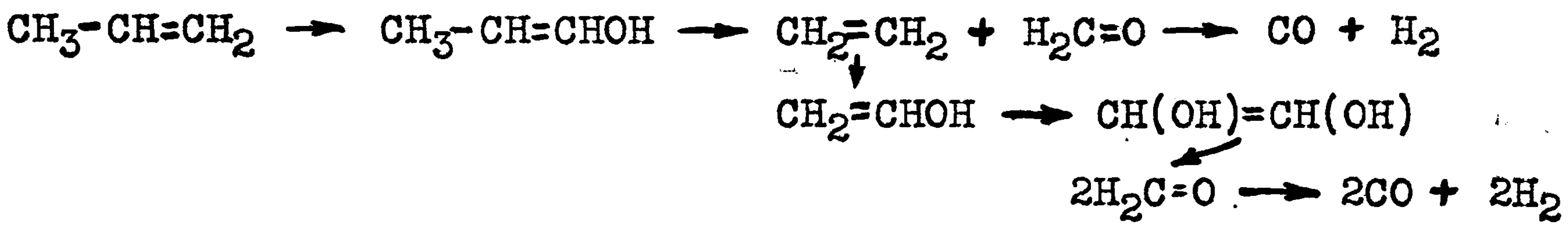
The hydroxylation theory was originally suggested by Armstrong (25), who postulated the intervention of water molecules at each step of the process. However, measurements of the rates of reaction in well-dried mixtures of hydrocarbons and oxygen (26) showed that they were greater, if anything, in these than in mixtures saturated with water vapour and the idea that water was essential to the process was very soon abandoned. In its modified form the theory was adopted by Bone, as a satisfactory explanation of the results of his numerous investigations of hydrocarbon oxidations (27). At the time when it was first developed the only alternative theories were those which held that hydrocarbon oxidations involved a preferential combustion of the carbon (28) or the hydrogen and in replacing these misconceptions the new theory undoubtedly performed a valuable service. It is not so certain, however, that it can be maintained unchanged in the face of present knowledge. Nevertheless, since it is by no means left without proponents, it is essential that the evidence in favour of it be considered. Fortunately this has been summarized by Bone in a number of lectures (29), in the more recent of which he has been able to quote a great deal of later work from his laboratories (30, 31, 32).

The explosion of equimolecular mixtures of ethylene and oxygen and of acetylene and oxygen results in the almost complete conversion of the hydrocarbon into carbon monoxide and hydrogen without the formation of free carbon or of steam. It is obvious that these experiments eliminate the possibility of a preferential combustion of the hydrogen. On the other hand, the similar treatment of an equimolecular mixture of ethane and oxygen, or of an ethylene-oxygen mixture containing low oxygen, results in the formation of clouds of carbon and of steam. In this case the carbon cannot be preferentially burned. It follows that the oxygen must first be incorporated into the hydrocarbon molecule giving an oxygenated product. In this regard there are two possibilities, either the compound formed will contain a single oxygen atom or the whole oxygen molecule will be taken up. Bone considers the balance of evidence to be in favour of the former.

From the rough measurements of rates in his early experiments he concluded that, at constant total pressure, the oxidation was almost equally rapid in mixtures with the hydrocarbon/oxygen ratio 2/1 or 1/1, but that a further increase in oxygen greatly reduced the rate. Since the formation of a monohydroxy derivative - that is, an alcohol - would require the interaction of two hydrocarbon molecules with each oxygen molecule, it would be expected that it would proceed most rapidly in the mixture containing the gases in that proportion. The results of his experiments were, therefore, slightly in favour of that hypothesis. Actually, in the later work mentioned above it has been shown that the 2/1 mixture gives much the greater rate, a point which Bone considers of very great importance.

Further support was derived from the behaviour of the olefinic hydrocarbons on explosion with varying amounts of oxygen, the results cited above for ethylene also holding for the other members of the series. Thus mixtures of the composition

$C_nH_{2n} + n/2O_2$ could be exploded without any separation of carbon or material steam formation. However, if the oxygen were reduced below that amount or if the olefine were replaced by a saturated hydrocarbon, the amount of carbon liberated and of steam formed each increased progressively. Using propylene as an example Bone explains the former of these results by the following reactions:



$$\begin{tikzcd}
CH_3\text{-}CH{=}CH_2 \arrow[r] & CH_3\text{-}CH{=}CHOH \arrow[r] & CH_2{=}CH_2 + H_2C{=}O \arrow[r] \arrow[d] & CO + H_2 & \\
 & & CH_2{=}CHOH \arrow[r] & CH(OH){=}CH(OH) \arrow[d] & \\
 & & & 2H_2C{=}O \arrow[r] & 2CO + 2H_2
\end{tikzcd}$$

In the latter case, where the oxygen present was not sufficient to complete the process, some of the CH=CHOH complexes would break down giving both carbon and steam. He does not believe that any other theory can offer an equally satisfactory explanation.

In the oxidation of ethylene under conditions which would favour the preservation of the intermediate products it was found that acetaldehyde was produced in moderate quantities. This could only arise through the transfer of one of the hydrogens originally present in the ethylene and is not easily explained. The hydroxylation theory, however, accounts for the result by postulating the isomerization of the unstable vinyl alcohol, supposedly formed in the first step of the process.

At the time when this theory was first introduced and, indeed, for the next twenty five years, there was no direct evidence for the formation of alcohols in the oxidation of hydrocarbons by molecular oxygen, although aldehydes could usually be detected without difficulty. For some time, therefore, Bone was forced to rely for support for this particular step in his series of reactions on the work of Drugman (33), who found that ethyl alcohol was formed when ozone acted on ethane. Its actual amount was much less than that of the acetaldehyde formed and no methyl alcohol was detected in the products of the methane-ozone reaction. Recently, however, alcohols have been isolated by Landa (34) in the oxidation products of white paraffin, by Layng and Soukup (35) and Bibb and Lucas (36) in the products of the methane oxidation catalyzed by nitrogen oxides, and by Yoshikawa (37), Newitt and his co-workers (32), Pichler and Reder (38), and Wiezevich and Frolich (39) in the products of hydrocarbon oxidations at high pressures. The hydroxylation theory has, therefore, a somewhat firmer basis.

It is to be noted, however, that no attempt has ever been made to explain by it the chain nature of the reaction, due, apparently, to the reluctance of Bone and his associates to admit the possibility of such a mechanism. The two facts which seem to point most directly to the presence of reaction chains - retardation by surface and the form of the rate equations, which indicate slight retardation by oxygen and an abnormal effect of hydrocarbon concentration - are never discussed in his papers, although he has confirmed the existence of the former (30d) and to a certain extent of the latter (30). However, by scrupulously restricting his investigations to mixtures of constant total pressure, he has been able to explain the variations in rate which he observed by assuming that a mixture containing hydrocarbon and oxygen in the ratio 2:1 gives the maximum rate and that any change from this composition must result in a slower reaction. Nevertheless, since any theory which is to be acceptable to the great majority of those interested in this field must contain the idea of reaction chains, it is important to consider whether they could be introduced into the hydroxylation theory. The properties of chain carriers require that they be very active substances which cannot take part in many collisions without passing on their energy to reactant molecules. It should be apparent, therefore, that none of the substances which Bone has postulated as intermediate products can fulfil these requirements, since most of them are relatively stable, while the unstable ones (such as the dihyroxy compounds) would probably react without liberating any great amount of energy. There remains, however, the possibility of chains in which the energy of reaction of one of the oxidation steps is retained by a product until it can be transferred to a hydrocarbon or oxygen molecule. Such a mechanism would be difficult to prove or disprove.

Moreover, there are several direct objections to the hydroxylation theory. Much of the evidence which Bone has brought forward to support it is drawn from the results of explosions and, while he has claimed that the processes involved in slow combustion, flame and detonation are all essentially the same, there is definite spectrographic evidence for the existence of radicals and atoms in each of the latter two phenomena and Haber (40) has suggested a mechanism which makes these the intermediate substances in the oxidations. Bone. however, claims that they are only the products of side reactions induced by the high temperature, which may or may not be correct. Moreover, in the explanation of many of these results he has found it necessary to assume "non-stop runs" through the monohydroxy to the dihydroxy stage - indeed, this assumption occurs with great frequency in both his one papers and those of the workers who associate with him in the support of his theory - and it is difficult to see why results which require this supposition cannot be explained at least equally well by one involving the association of the oxygen molecule as a whole with the hydrocarbon.

The variation of rate with mixture composition, resulting in a maximum with the hydrocarbon:oxygen ratio of 2:1, might also be accounted for on other grounds, since a chain reaction allows considerable liberty in the form of the rate equation. It is also worthy of mention that Bone has only shown that the rate with 2:1 mixtures is greater than that with 3:1 or 1:1 mixtures. It is quite possible that the true maximum occurs at some intermediate composition.

The formation of acetaldehyde from ethylene, which has been considered one of the strong points for the theory, can also be explained in another way, for Mardles (41) has shown that ethylene oxide yields some acetaldehyde when passed with air through a heated glass tube, and ethylene oxide is formed in the oxidation of ethylene (42). Moreover, ethylene oxide, in turn, may have come from an ethylene peroxide, for in the Prileschajew reaction (43) alkylene oxides are prepared from peroxides and olefines.

The actual formation of alcohols under a variety of circumstances is a point which cannot be refuted but the interpretation placed on these results may be questioned.

When ozone is used as the oxidizing agent it would naturally be expected that some reaction involving a single oxygen atom would occur, since the ozone decomposition is supposed to give an atom and a molecule of oxygen. The formation of an alcohol in such cases is, therefore, no support for the hydroxylation theory. The same would apply to the results obtained with the oxides of nitrogen, for they are assumed to act as oxygen carriers by virtue of their ability to change their state of oxidation. Moreover, Smith and Milner (44) report that little of the oxides of nitrogen can be recovered as such, since they are reduced to nitrogen, and that the yields of formaldehyde - the only intermediate product which they determined - were never greater than the oxides of nitrogen used.

In the work of Landa, cited above, methyl and ethyl alcohols were formed by the oxidation of white paraffin under conditions where reaction in the liquid phase was at least a possibility. In any case, it is doubtful whether the isolation of these simple alcohols from so complex a hydrocarbon can be considered as indicating that they are formed as the first step in the oxidation of methane or ethane.

In the high pressure work the experiments of Wiezevich and Frolich were carried out with natural gas and they found that most of the methyl alcohol came from the ethane, which cannot, therefore, be interpreted in support of the hydroxylation theory. Newitt and Haffner (32a), however, used pure methane and obtained methyl alcohol in high yields, but they state explicitly that the reaction was accelerated by an increase in the surface:volume ratio and so was heterogeneous. Since the reaction is retarded by such a change at atmospheric pressure (45, 46, 47), the mechanisms are obviously not the same and it is hardly justifiable to assume that results from the one case apply to the other. The investigation carried out by Yoshikawa (37) covered almost the same conditions as that just discussed, yet he reports that packing reduced the rate. If that be the case, the experiments at high and low pressures are closely related and might support the hydroxylation theory, but this point must be definitely cleared up. In the similar experiments with ethane (32b, d) and benzene hydrocarbons (32c) the effect of surface was not studied.

In justice to the peroxide theory which is to be discussed later, it should be stated that it does not exclude the formation of alcohols but merely argues that they are not formed in the initial step of the process and are not an essential link in the chain. The conditions of these experiments - high pressure and high hydrocarbon:oxygen ratio - would be expected to favour their formation by that mechanism also.

In order to account for the failure to detect any alcohols at atmospheric pressure, it has been customary for the proponents of the hydroxylation theory to assume that they are oxidized or decomposed so rapidly that they cannot survive in sufficient quantities to give their characteristic tests, and to support these assumptions by pointing out that the alcohols are oxidized much more readily than the hydrocarbons. While this is unquestionably correct for methane and methyl alcohol in equal concentrations (45), the relative stabilities are reversed as the series is ascended. Thus Layng and Youker (48) have shown that n-heptane oxidizes much more rapidly than n-heptyl alcohol and Stephens (49) has obtained similar results with ethylbenzene and phenylmethyl carbinol. Mardles (41) concluded from his results that ethyl and amyl alcohols were less readily oxidized than ethane and pentane but, while his conclusions seem justified in the latter case, in the former they are based only on a higher temperature coefficient for the oxidation, which hardly seems sufficient, especially since his curves show the ethyl alcohol oxidation proceeding at lower temperatures than that of ethane.

However. it would seem that relations between the alcohols and the corresponding aldehydes would be of more importance than those between the alcohols and the hydrocarbons, for if the aldehydes are relatively unstable and yet can accumulate in considerable quantities the same should be true for the alcohols. In this regard we may consider formaldehyde and methyl alcohol as typical examples, since the oxidation of methane has been thoroughly investigated. The most recent study of the decompositions are those of Fletcher (21, 50). He found that they proceeded at approximately the same rates if the formaldehde were kept at 570° and the methyl alcohol at 670°. The temperature coefficients were 44,500 and 68,000 cals., respectively, so that the rate of the formaldehyde decomposition would fall off less rapidly than that of the alcohol decomposition and at the temperatures where the methane oxidation is usually studied the former would unquestionably be much the more rapid. The results of Bone and Smith for formaldehyde (51) and of Bone and Davis (52) for methyl alcohol are in general agreement with those of Fletcher.

The oxidation of formaldehyde (45, 53) also proceeds about 100° below that of methyl alcohol (45), but in this case the results must be extrapolated to higher temperatures if they are to be related to the methane oxidation and this tends to bring the rates together. However, it will be largely neutralized by the effect of changing pressures, for the methyl alcohol oxidation is roughly third order with respect to methyl alcohol concentration, while that of formaldehyde is less than second order with respect to formaldehyde concentration. Since these substances never reach high concentrations during hydrocarbon combustions, it is actually the relations for low pressures which are desired and from the above it follows that the rate in the CH_3OH-O_2 system will fall off much more steeply with decreasing pressure than that in the $HCHO-O_2$ one. It must be concluded, therefore, that although methyl alcohol is much more stable than formaldehyde under the conditions of the experiments, it is never found in the products of methane oxidation at ordinary pressures while formaldehyde does occur.

That this cannot be due to the fact that formaldehyde is formed at a later step than methyl alcohol may be readily shown. In many of the experiments a flow method has been used under conditions such that very little methane reacted. If methyl alcohol is formed, its rate of formation will, therefore, be nearly constant throughout and may be put equal to x moles per second. Then, no matter how small the equilibrium concentration may be, the alcohol will accumulate until its rate of removal is the same, and since formaldehyde can only be formed from the alcohol - according to the hydroxylation theory - its maximum rate of formation will also be x. It follows that its equilibrium concentration cannot be greater than that of the alcohol unless it is less readily destroyed, which is the opposite to what is actually the case. On this basis, then, one would expect the methyl alcohol in the products to be in much greater concentration than the formaldehyde. It is interesting to note that this is the case in all of the high pressure experiments previously quoted, the ratios varying from 5:1 to 80:1. Of course, the failure to detect alcohol at low pressure might be explained if it were produced in a high energy state and were, therefore, abnormally reactive, but the energies liberated in the oxidations of methane to methyl alcohol and of methyl alcohol to formaldehyde are within a few thousand calories of one another, so that this particular assumption seems unlikely. In any case, it would probably have to be abandoned in accounting for the results at high pressures.

Another possible explanation would be that there was a great difference in the sensitivity of the qualitative tests but, while this might be great enough to account for the results in the static runs where the amounts concerned are small, it can hardly hold for runs by the flow method where large volumes of gas are used. With this latter method Blair and Wheeler made very careful studies of hydrocarbon-oxygen (54) and hydrocarbon-ozone (55) reactions without obtaining alcohols, although aldehydes were produced in quantity. Similar results are reported by Berl and Fischer (56), Tropsch and Roelen (57) and Frolich, Harrington and Waitt (58) who used similar arrangements, in the last case the oxidizing agent being air containing nitric acid vapour. In one experiment Berl and Fischer recovered 100% of the oxidized methane as formaldehyde when sulphur trioxide was the oxidant. It is very unlikely, therefore, that methyl alcohol was formed at all in that run.

The formation of alcohols as the primary product of the interaction of oxygen and hydrocarbons seems improbable on theoretical grounds. If it is to occur at a bimolecular collision it must involve scission of the oxygen molecule with the liberation of an oxygen atom. As Marek (59) points out this is rather unlikely. Moreover, Bennett and Mardles (60) believe that such a split would result in the profuse liberation of electrons, which they find does not occur. The other alternative, which Bone seems to favour, is that reaction takes place at a termolecular collision. As pointed out in the general introduction there are very few well established examples of such reactions and it is doubtful, therefore, whether the whole series of hydrocarbon oxidations would proceed by such a mechanism. Moreover, the hydroxylation scheme, on this basis, would require that each step be a termolecular reaction and, since the concentrations of some of the intermediate products are so small that they cannot be detected, the probability of three or more successive stages taking place only at termolecular collisions must be vanishingly small. In referring to these objections Bone states, in the footnote to one of his latest papers (29c) - "This, however, does not seem formidable to me; for in slow combustion it may well need the combined pull of two hydrocarbon molecules to dissociate an oxygen molecule, and in flames oxygen atoms may act. Moreover, in view of the overwhelming affinity between them, it is conceivable that when a hydrocarbon molecule meets one of oxygen, the two might hold each other in transient physical association until hit by a second hydrocarbon molecule, with the consequent immediate formation of two molecules of the monohydroxy compound as the first recognizable chemical result." Except for the fact that he chooses to call the product of the initial step a "transient physical association" rather than a peroxide, this scheme is identical with one proposed by Hinshelwood (61), which Bone is attacking at the point where the footnote is appended. So far as the variations in rate are concerned, their explanation certainly will not be affected by the nomenclature of the intermediate products but, for the reasons advanced in the preceding discussion, the validity of the hydroxylation theory as a whole seems doubtful and the peroxide theory appears more satisfactory.

The first evidence for the formation of peroxides during oxidations was found by Bach (62) and Engler and Wild (63) who obtained quantitative proof of their presence during the autoxidation of certain organic liquids. Several years later Wartenberg and Sieg (64) advanced the theory that all combustions had as their initial step the formation of addition compounds. This was only developed into the peroxide theory of hydrocarbon oxidation after the work of Callendar (65) and Moureu, Dufraisse and Chaux (66), the former being interested in the action of antiknocks, the latter in the mechanism of autoxidation. Callendar found that the oxidation of heptane might give 70% yields of aldehydes, but that these were not the primary products, since carbon dioxide and water appeared at the same time. The addition of antiknocks could reduce these amounts to 10%. After a careful investigation of the problem he concluded that the initial product was a peroxide and that the aldehyde was formed by its decomposition. The phenomenon of knocking was explained as due to the accumulation of these peroxides until they reached a concentration where violent decomposition took place, and some confirmation for this view was derived from the fact that the addition of acetoyl or benzoyl peroxides to a motor fuel greatly increased knocking. Callendar was also able to detect peroxides in the products from the normal operation of a motor by making use of their property of liberating iodine from potassium iodide solutions. Somewhat earlier Egerton and Gates (67) concluded from studies of the action of antiknocks that this must consist in the removal of a purely "chemical" catalyst and that the latter must be formed in the combustion of an aldehyde and must assist both the aldehyde and the initial stage of the combustion. In view of Callendar's work they modified their ideas somewhat and suggested (68) that "reaction will commence when a sufficiently energetic molecule of fuel combines momentarily with an energetic oxygen molecule. A temporary peroxide in a high energy state is thereby formed." This may break down or oxidize giving products of high energy content which carry the chain. Collision with a molecule of antiknock may destroy the peroxide thus breaking the chain.

In an investigation of the oxidation of hexane, Brunner and Rideal (69) made quantitative determinations of the peroxide concentration at different times during the reaction and concluded that it reached a maximum at the end of the induction period, the rapid pressure increase which followed being traceable to the decomposition of the peroxides. Since the latter were mostly hydrolyzed in solution, giving hydrogen peroxide, their constitution could not be determined but, in order to explain the formation of water-soluble fatty acids, Brunner postulated the constitution

$CH_3-\underset{O-}{CH}-\underset{-O}{CH}-C_3H_7$.

Pope, Dykstra and Edgar (70), working with the isomeric octanes were unable to get very satisfactory tests for peroxides and pointed out that the aldehydes may absorb oxygen when shaken in air, forming compounds which liberate iodine from potassium iodide. Earlier determinations of peroxides may, therefore, be considerably in error.

The most unequivocal evidence for peroxide formation is contained in the work of Mondain-Monval and his associates. After some preliminary investigations of the minimum temperatures for the oxidation of different hydrocarbons (71), they discovered that by operating at moderate temperatures they obtained a product separating into two layers and could isolate a substance having properties similar to those of CH_3OOH (72). While so simple a compound could not be the primary peroxide postulated by Callendar - this work was carried out with pentane and the higher hydrocarbons, methane and ethane gave no peroxides - it might be derived from them. More recently they have obtained a similar substance from the oxidation of acetylene (73).

Peroxides have also been detected in appreciable quantities in the oxidation products of propane (74). Lenher (75) has identified dioxymethyl peroxide among those of ethylene. In this case, however, the compound is believed to be formed by the interaction of hydrogen peroxide and formaldehyde, and so only represents a side reaction. In their experiments at high pressures Newitt and his co-workers (32) have found no traces of peroxides, while Bone in the corresponding reactions at ordinary pressures found none in the case of methane (30d) and only traces in those of ethane (30b) and ethylene (30e). Since these small amounts never appeared until aldehydes were present he believed that they were due to a secondary peroxidation of the aldehydes and were of no significance in so far as the actual mechanism was concerned, indeed, that has been his attitude towards all such results. Since the peroxidation of aldehydes certainly occurs very readily (76), there is likely to be some difficulty in convincing him that any other alternatives are possible. At present he insists that the only real proof of the peroxide theory would be the isolation and identification of the initial peroxides, but that stand seems hardly logical in one who supported the hydroxylation theory during its first twenty-five years, although no alcohols - relatively stable compounds - could be shown to be formed. A statement which Prof. Bone made during that period (29a) might be used equally well to express the stand of those whom he now opposes: " the fact that a substance cannot permanently exist at a given temperature does not justify the assertion that it cannot be formed at that temperature by the operation of factors which are not concerned in its decomposition."

Prettre (77) has recently suggested that both theories may be correct. Thus for the long chain hydrocarbons which oxidize below 300° he believes that the peroxide theory applies, while above that temperature the compounds required by the hydroxylation theory appear. Knock is attributed to peroxides. While the peroxides isolated have not been those required by Callendar's theory, Prettre believes that other work has shown that the primary ones could logically be transformed into aldehydes and peroxides containing few carbon atoms.

An entirely different theory has been advanced by Lewis (78). He found that when mixtures of a saturated hydrocarbon and air were slowly heated in a sealed bulb, the first indication of chemical change was an increase in pressure. Since either of the previous theories would require a decrease in the number of molecules, they could not explain this result and he suggested that the first step was the combination of oxygen with the least closely bound of the hydrogens giving an unsaturated hydrocarbon and water. This concept was adopted by Berl, Heise and Winnacker (79) who combined it with the peroxide theory by assuming that the second step was the formation of a peroxide from the unsaturated hydrocarbon. It has also been used by Steacie and Plewes (80) to explain their results with ethane. Mardles (41), on the other hand, has objected to it on the ground that the oxidation characteristics of olefines and saturated hydrocarbons are quite different. He accounts for the formation of ethylene in the oxidation of ethane as a side reaction of the type

$$F(O_2) + C_2H_6 \longrightarrow FO + C_2H_4 + H_2O \ .$$

However, since Steacie and Plewes report one case where the ethylene represented 63% of the original ethane, that assumption seems no longer justified. Perhaps the strongest objection to this theory and also to some extent to any theory involving peroxides is that they have been shown to induce knocking (65), yet unsaturated hydrocarbons have antiknock properties (81).

However, peroxides have been shown to accumulate when a cracked gasoline deteriorates (82, 83), while at the same time its antiknock value decreases.

Individual mechanisms more or less closely related to one or other of the types just discussed are frequently proposed. Thus, Pope, Dykstra and Edgar (70) state that their results are best represented by the scheme:

$$R\text{-}CH_2CH_3 + O_2 \rightarrow R\text{-}CH_2CHO + H_2O$$

$$R\text{-}CH_2CHO + O_2 \rightarrow R\text{-}CHO + H_2O + CO \quad \text{(main reaction)}$$

$$R\text{-}CH_2CHO + 1.5O_2 \rightarrow R\text{-}CHO + H_2O + CO_2 \quad \text{(side reaction).}$$

Pease represents the propane oxidation as follows (84)

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

$$C_3H_8 + \tfrac{1}{2}O_2 \rightarrow C_3H_6 + H_2O$$

$$C_3H_8 + 2O_2 \rightarrow CO + 2H_2O + CH_3CHO$$

In this case, however, a more extensive investigation (74) has convinced its author that the scheme cannot be entirely correct.

It has been suggested (2a) that aldehydes and their oxidation products are the important factors in so far as the chain processes are concerned, but this is doubtful since Steacie and Plewes (85) have shown that acetaldehyde has very little effect on the oxidation of ethylene or of ethane.

The first attempt to account for the form of the rate equation by applying these theories was that of Thompson and Hinshelwood (61), who, as a result of their work on ethylene, proposed the scheme:

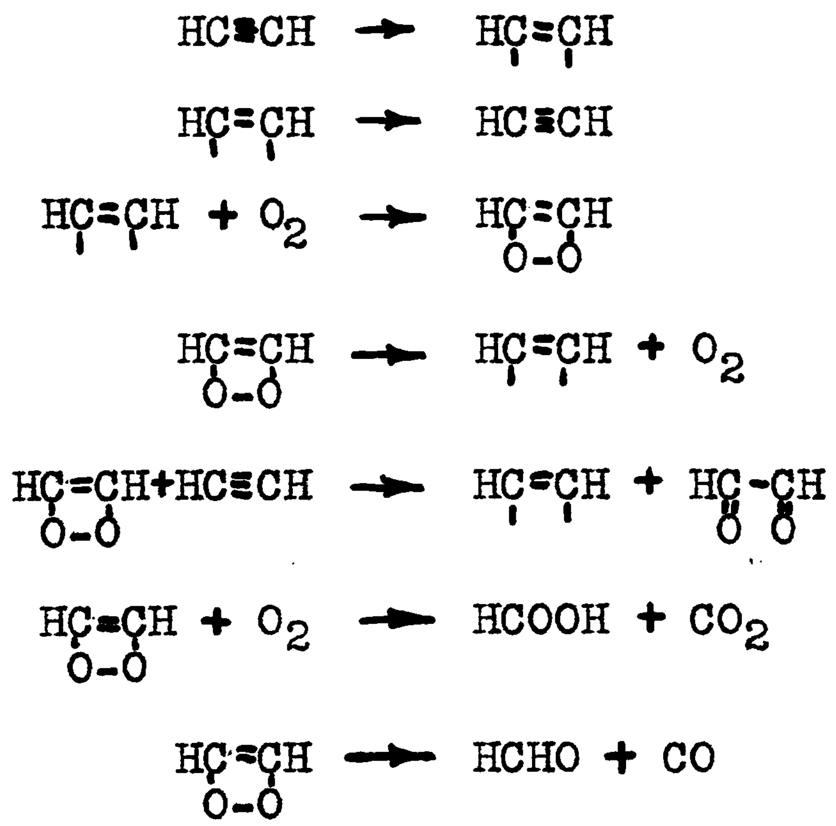
$$C_2H_4 + O_2 \rightarrow C_2H_4 \cdot O_2 \quad \text{(a peroxide)}$$

$$C_2H_4 + C_2H_4 \cdot O_2 \rightarrow 2CH_2{=}CHOH^{*} \quad \text{(continue the chain)}$$

$$O_2 + C_2H_4 \cdot O_2 \rightarrow \text{Products} \ . \quad \text{(breaks the chain)}$$

This has been referred to previously (p. 81) in connection with Bone's suggestion that a loose molecular association might result from a hydrocarbon-oxygen collision. It has the advantage of accounting for a high order with respect to the hydrocarbon and a low one with respect to oxygen.

A more detailed mechanism has been developed by Bodenstein (86). Although it was originally designed to fit the results of a study of the acetaldehyde oxidation (87), he believes that it can be applied to hydrocarbon oxidations as well. For acetylene he formulates it as follows:



$$\begin{array}{ll}
1. & HC\equiv CH \rightarrow \begin{matrix}HC{=}CH\\ |\quad\ |\end{matrix} \\
1'. & \begin{matrix}HC{=}CH\\ |\quad\ |\end{matrix} \rightarrow HC\equiv CH \\
2. & \begin{matrix}HC{=}CH\\ |\quad\ |\end{matrix} + O_2 \rightarrow \begin{matrix}HC{=}CH\\ |\quad\ |\\ O{-}O\end{matrix} \\
3. & \begin{matrix}HC{=}CH\\ |\quad\ |\\ O{-}O\end{matrix} \rightarrow \begin{matrix}HC{=}CH\\ |\quad\ |\end{matrix} + O_2 \\
4. & \begin{matrix}HC{=}CH\\ |\quad\ |\\ O{-}O\end{matrix} + HC\equiv CH \rightarrow \begin{matrix}HC{=}CH\\ |\quad\ |\end{matrix} + \begin{matrix}HC{-}CH\\ \|\quad\ \|\\ O\quad\ O\end{matrix} \\
5. & \begin{matrix}HC{=}CH\\ |\quad\ |\\ O{-}O\end{matrix} + O_2 \rightarrow HCOOH + CO_2 \\
6. & \begin{matrix}HC{=}CH\\ |\quad\ |\\ O{-}O\end{matrix} \rightarrow HCHO + CO
\end{array}$$

By making assumptions as to the relative values of the rate constants of the individual reactions he obtains from this the rate equation

$$-d[C_2H_2]/dt = \frac{K[C_2H_2](2[C_2H_2] + [O_2] + 250)}{[O_2] + 2250} ,$$

which is in fairly good agreement with the actual results (88, 89). The actual formulae assigned to the intermediate products are not of primary importance and could probably be varied somewhat without affecting the form of the result. The representation of the active form of the hydrocarbon by a partial splitting of the unsaturated linkage receives some support from the work of Lenher on ethylene (42) and propylene (90). The polymerization of these substances takes place much more rapidly in the presence of oxygen than in its absence, ethylene yielding mostly propylene, and propylene mostly hexylene. In the former case the reactions are explained by assuming the presence of an active modification of ethylene, $\underset{|}{C}H_2-\underset{|}{C}H_2$, and of methylene radicals, $\underset{|}{C}H_2-$. Lenher, however, believes that these arise from the decomposition of the complex $\genfrac{}{}{0pt}{}{H_2C}{H_2C}{>}O-O$, which is formed from the original molecules without the necessity of any preliminary loosening of the bonds.

In the preceding all of the more important theories which have been advanced to account for the various phenomena accompanying hydrocarbon oxidation have been briefly reviewed; some minor alterations which different workers have made in order to fit their particular results may justifiably be omitted here, should they have direct application later they will be discussed there. The investigations which have been carried out on the oxidation of acetylene must now be considered in somewhat greater detail.

Most of the studies of the slow oxidation of this hydrocarbon have been made by the flow method, the only one by the static method being that of Bone and Andrew (27e). Since it was made before the importance of reaction kinetics was realized, it has little bearing on that phase of the subject. However, it served to locate the zone of slow reaction at 250° to 350°, and showed that the products were mostly CO, CO_2 and H_2O, the ratio CO/CO_2 varying from 2 to 20, with the average about 4. Since there was no evidence for the formation of a monohydroxy compound they postulated a "non-stop run" to the unstable dihydroxy compound, $HOC{\equiv}COH$, which decomposed directly into carbon monoxide and formaldehyde. Since there has been no indication of the presence of $HOC{\equiv}CH$ at any time, Bone has not insisted that it is formed, and discussions of the acetylene oxidation have, therefore, been to some extent free from the controversy which has characterized those of the broader field of hydrocarbon oxidations.

From the results of investigations by the flow method, mainly at 320°, Kistiakowsky and Lenher (88) and Spence and Kistiakowsky (89) concluded that the rate of reaction was proportional to the acetylene and oxygen concentrations when the latter was very small and proportional to the square of the acetylene concentration when it was somewhat higher. Nitrogen and excess oxygen had slight retarding effects. The reaction had an induction period of several seconds and was greatly retarded by packing the reaction bulb. In an ordinary bulb the CO/CO_2 ratio was between four and five, in a packed bulb it was less than a half. The intermediate products isolated were glyoxal, formic acid and formaldehyde. The former of these had been found by Briner and Wunenburger (91) among the products of the interaction of ozone and acetylene at low temperatures and Bone seems to have conceded (29c, 92) that glyoxal rather than HOC≡COH is the first stage in the normal oxidation. No attempt is made in these papers (88, 89) to develop a mechanism, although the tendency seems to be to consider that an important step is

$$C_2H_2O_2 \rightarrow CO + HCHO \quad .$$

In view of recent work of Steacie and Horwood (93) this is improbable, for glyoxal does not decompose appreciably at 320° and at higher temperatures a great deal of carbon or tar is deposited.

When the acetylene-oxygen reaction is catalyzed by the presence of nitric acid vapour (94) the reacting temperature is lowered as much as 80° and the products are chiefly trimeric glyoxal.

After a more extended investigation of the normal reaction Spence (95) suggested the following mechanism:

(1) $C_2H_2 \rightarrow C_2H_2'$

(2) $C_2H_2' \rightarrow C_2H_2$

(3) $C_2H_2' + O_2 \rightarrow C_2H_2O_2''$

(4) $C_2H_2O_2'' \rightarrow C_2H_2' + O_2$

(5) $C_2H_2O_2'' + C_2H_2 \rightarrow C_2H_2' + C_2H_2O_2'$

(6) $C_2H_2O_2' + C_2H_2 \rightarrow C_2H_2' + C_2H_2O_2$

(7) $C_2H_2O_2'' + O_2 \rightarrow 2CO + H_2O_2$

$$(8) \qquad C_2H_2O_2' + O_2 \rightarrow CO + CO_2 + H_2O$$

$$(9) \qquad C_2H_2O_2' \rightarrow CO + HCHO$$

$$(10) \qquad 2C_2H_2O_2' \rightarrow CO + CHO\text{-}CO\text{-}CH_2OH \ .$$

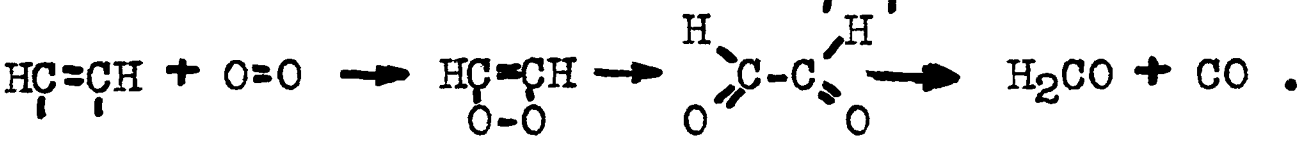
In the original paper $C_2H_2O_2''$ and $C_2H_2O_2'$ are referred to as "different energy levels" in the system $C_2H_2O_2$, but recently Spence (96) has indicated that he believes "different forms" would be better. Reaction (5) introduces the possibility of chain branching which his results have shown to occur. Reaction (10) was included because the liquid products showed the property of delayed titration which is characteristic of the glycerosone obtained by Norrish and Griffiths (97) from the photochemical decomposition of glyoxal. From certain deductions as to the rate constants Spence develops the equation

$$-d[C_2H_2]/dt = K \frac{[C_2H_2][O_2](2.6[C_2H_2] + [O_2])}{[O_2]^2 + 4000} \ .$$

It has been mentioned previously that Mondain-Monval and Willard (73) obtained a yellow oil with peroxidic properties when they interrupted the acetylene oxidation at the temperature where a faint green luminescene appeared.

On theoretical grounds Mecke (98) concluded that, in the photochemical oxidation of acetylene, the ultra violet light would split the valence bond of the acetylene and the excited molecule might associate directly with oxygen forming glyoxal, thus,

$$HC{\equiv}CH + h\nu \rightarrow H\dot{C}{=}\dot{C}H$$



From his preliminary work on this photochemical oxidation Livingston (99) concluded that, if glyoxal were more readily oxidized than decomposed, the chief product would be oxalic acid, which was in agreement with his results. However, subsequent work (100) has shown that the quantum yield is between 3 and 5 at 40° C., which he believes is too great for the simple glyoxal mechanism.

A. RUNS IN PRESENCE OF P_2O_5.

Experimental.

A few preliminary runs were made with the apparatus shown in Part 1, figure 1. It was found that the pressure increase accompanying the reaction was very small - of the order of 10% of the acetylene pressure - and, therefore, could not be used directly as an accurate measure of reaction. However, water vapour is formed during the oxidation and if this could be removed as quickly as it was produced, or at least kept to a low pressure, there would be a much greater change. Melville (11a) was able to achieve such a result with the nitrous oxide-hydrogen reaction and there seemed no reason why the method could not be used here.

In the modified apparatus, therefore, the simple reaction bulb was replaced by that shown in figure 1 of the present section. The actual reaction vessel, B, was a 200 cc. bulb. The neck, C, was 2 cm. in diameter and 12 cm. long. It extended approximately 6 cm. outside of the furnace, A. About 4½ cm. from the end, D, an indentation was made in the glass and the space between this and the end was filled with phosphorus pentoxide. It was cooled by water circulating through the coil, E. The furnace was placed on its side rather than vertically as in the previous experiments.

In actual practice it was found that the phosphoric acid formed during a run frothed badly during the subsequent evacuation and small amounts were carried over the indentation. However, the bulb was tilted slightly so that this did not run

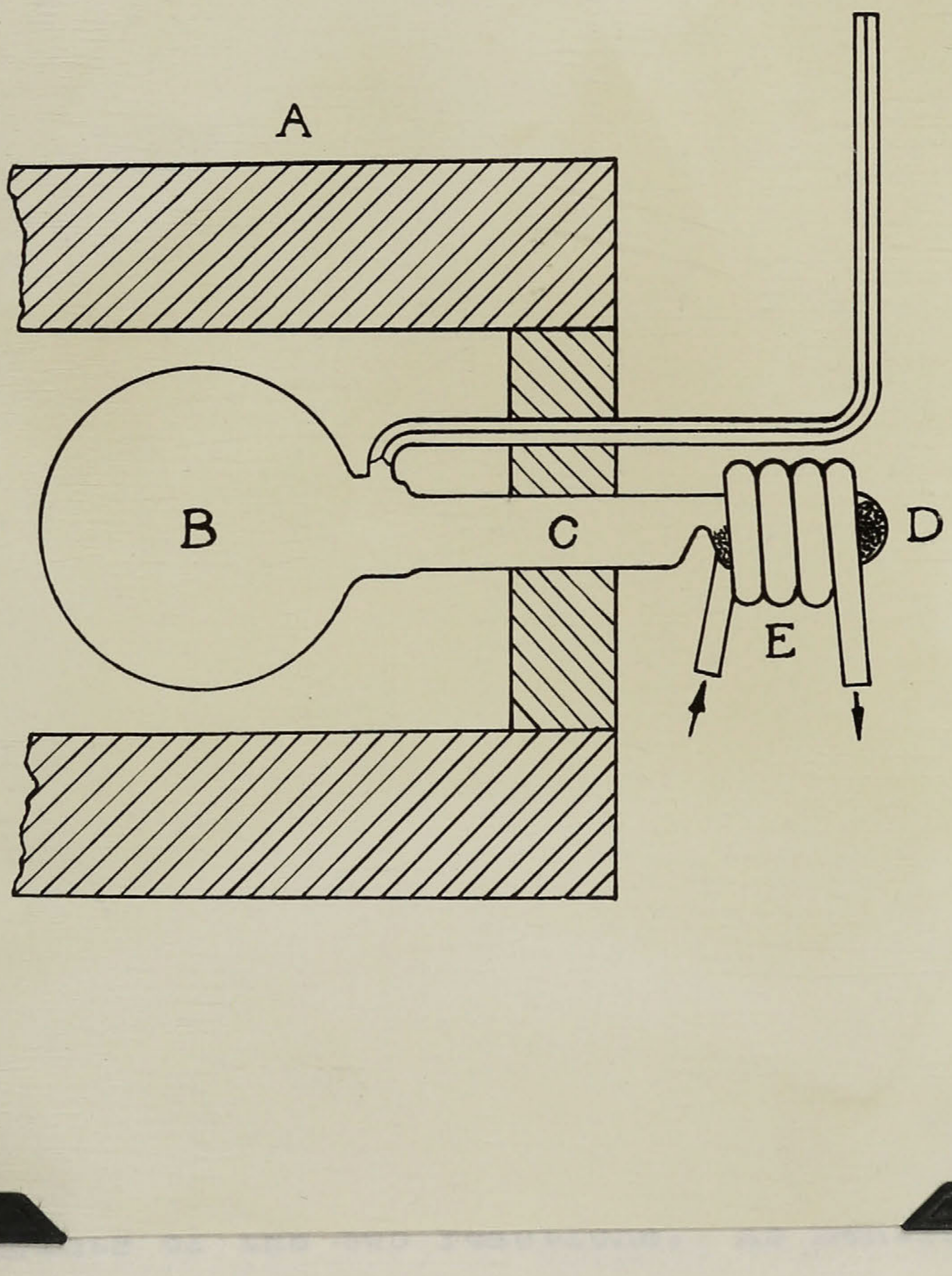


FIGURE 1.
REACTION BULB.

into the heated part and it did not affect the results.

Blanks with the reaction mixture at 200° and with acetylene at 370° gave no pressure change. It follows, therefore, that the cool P_2O_5 had no effect on the mixture and that thermal decomposition or polymerization of the acetylene did not affect the results.

The gas analyses, like those in Part 1, were made using separate Hempel pipettes.

The Course of the Reaction.

The results obtained by previous investigators, using the flow method, would indicate that in these experiments, where the intermediate oxidation products are not swept out of the hot zone but, presumably, either decompose or are further oxidized, the products of the reaction could be largely accounted for by the two equations:

$$C_2H_2 + 1\tfrac{1}{2}O_2 \rightarrow 2CO + H_2O$$

$$C_2H_2 + 2\tfrac{1}{2}O_2 \rightarrow 2CO_2 + H_2O \quad .$$

In an ordinary bulb the pressure change at completion would then vary between an increase equal to one half the acetylene pressure and a decrease of the same amount, according to the relative amounts of the two reactions. As mentioned above, the change actually obtained was an increase of about 10%. It is evident, however, from the above equations that the removal of the water would cause a decrease of between 50% and 150%, if the process of removal did not introduce any other disturbing factors. Of course, the method used permitted the diffusion of the intermediate products from the hot to the cold region where they could condense out or undergo further reactions in the presence of the P_2O_5. The pressure change cannot be predicted, therefore, from the preliminary results with the simpler arrangement. Actually, it was found to amount to a decrease equal to about 65% of the acetylene pressure, although, as the analyses given in table 1 show, this never corresponded to complete reaction.

The samples in all cases were withdrawn after the system had given no pressure change over a ten minute interval. At 320° this required 210 minutes, at 350° - 120 minutes and at 370° - 90 minutes. Since the corresponding times to a pressure decrease of 30% were 24, 14 and 10 minutes, respectively, it is evident that it would have required a very long time for the oxidation of all the acetylene.

In the table the values for C_2H_2 reacted, and O_2 reacted are arrived at on the basis of an original gas of the composition C_2H_2 - 24.5%, O_2 - 71.1% and N_2 - 4.4%. This is the average of two analyses made on two mixtures made up to the composition O_2:C_2H_2 = 3:1. They gave %C_2H_2 - 24.5, 24.4; %O_2 - 71.4, 70.8; %N_2 - 4.1, 4.8. These would indicate that the acetylene contained 2% nitrogen and the oxygen 5.2% nitrogen. These values have been used later in calculating the composition of other gas mixtures.

The residue reported in the table almost certainly contained some hydrogen, but at that stage in the analyses the

TABLE 1.

GAS ANALYSES.

$P_{C_2H_2}$ = 70 mm., P_{O_2} = 210 mm. - (Approx.).

No.	1	2	3	4	5
Temp. °C.	370	370	350	320	320
Total ΔP (% of $P_{C_2H_2}$)	64.6	62.6	64.5	65.3	65.7
% CO_2	11.5	10.3	9.4	9.4	8.8
% C_2H_2	2.3	3.4	2.8	5.7	6.0
% O_2	46.0	45.5	53.3	49.0	50.0
% CO	32.8	32.4	27.2	28.6	28.6
% Residue	7.4	8.4	7.3	7.3	6.6
% of C_2H_2 Reacted	92.2	88.2	90.2	80.4	79.6
$\frac{O_2\text{ Reacted}}{C_2H_2\text{ Reacted}}$	1.44	1.51	1.19	1.53	1.51
$\frac{CO + CO_2\text{ Formed}}{C_2H_2\text{ Reacted}}$	1.64	1.66	1.39	1.61	1.60

volume of the samples was only about 1.5 cc. and since this must have been largely nitrogen no combustions were carried out. Since the carbon monoxide and dioxide in the gas were insufficient to account for all of the acetylene which had reacted some carbon compound must have condensed out, probably on the P_2O_5 for this became blackened. No carbon was deposited in the hot bulb under any of the experimental conditions.

It is evident that the total pressure changes at 100% reaction would not have been identical for the three temperatures. Extrapolation to this point gives the values: 320° - 81.2, 82.5;

350° - 71.5; 370° - 70.9, 71.0.

The Rate of Reaction.

It was found that an increase in the total pressure of acetylene-oxygen mixtures increased the rate of reaction. Such a change would also make it more difficult for the water formed in the reaction to diffuse to the P_2O_5 and, therefore, the equilibrium pressure of the water formed would not be constant for different runs. If, then, similar percentage pressure decreases were to represent the same stage in the oxidation it was essential that, under all conditions, the water content of the gas be low enough that variations in it did not affect the pressure readings. However, since the accuracy attained in this type of experiment is rarely greater than 2% the above condition did not need to hold so rigidly in practice. The only method of determining whether the results were satisfactory was to check them by gas analyses. Table 2 gives the composition of samples taken when the pressure decreases were 25% and 40% of the acetylene pressure. The runs were made with differing total pressures at 320° and 370° as indicated. In all cases the original mixture contained three parts of oxygen to one of acetylene.

The acetylene contents of the samples agree satisfactorily in both periods of the runs at 320° but there was a decided difference between these and the ones at 370°. However, the smaller total pressure change at this higher temperature would account for part of the discrepancy.

TABLE 2.

GAS ANALYSES - PARTIAL COMPLETION.

No.	1	2	3	4	5	6	7
Temp.°C.	320	320	320	320	320	370	370
$P_{C_2H_2}$ (mm.)	61	102	118	80	93	71	58
% Pressure Decrease	25	25	25	40	40	25	40
% CO_2	3.9	5.3	4.4	6.8	6.5	5.5	7.3
% C_2H_2	13.6	13.2	13.1	9.5	9.7	11.8	8.1
% O_2	63.0	60.5	65.0	55.9	59.7	53.5	51.5
% CO	14.3	15.8	12.0	22.3	19.4	20.8	25.0
% Residue	5.2	5.2	5.5	5.5	4.7	8.4	8.1

It appeared, therefore, that the times for any pressure change greater than 25%, and perhaps even for lower ones, could be used as the basis for comparisons. However, at 40% the rate of further change was so small that in some cases at 320° a slight error, either in the initial pressures or in the readings at that point, could cause a variation of two or three minutes in the value for the corresponding time. On the other hand, it was desirable to make the time as long as possible in order to reduce the effect of any disturbances in the first minute, although there was no indication here of the induction period which others have reported (88, 89, 95). For these reasons the time to a pressure change equal to 30% of the initial pressure of the acetylene was chosen. This will be referred to as t_{30}. The relation between it and percentage reacted was proven by gas analyses on runs at 350°, but the discussion of the results may be more profitably postponed until the variations in t_{30} have been described. It should be sufficient to state here that t_{30} may be used in the customary manner for determining the order of the reaction.

TABLE 3.

PRESSURE CHANGES IN C_2H_2 - O_2 MIXTURES - 350° C.

No. 1 - Pressure Increase. Others - Pressure Decreases.

No.	1	2	3	4	5	6	7
$P_{C_2H_2}$ (mm.)	61	80	63	75	66	83	65
P_{O_2} (mm.)	183	240	189	300	264	166	130
Time (min.)				Pressure Changes in mm.			
0	0	0	0	0	0	0	0
1	0.4	1.0	1.0	1.4	1.2	1.2	1.0
2	1.0	2.6	2.2	2.6	2.2	3.0	2.2
5	1.6	7.2	6.0	7.2	6.2	8.8	5.8
10	3.0	17.0	13.0	15.6	14.0	17.2	13.8
13	-	21.8	16.8	-	-	-	-
14	-	-	-	20.8	19.4	23.8	18.2
15	4.6	25.0	19.2	22.4	20.6	25.6	19.4
20	5.6	30.8	23.0	27.2	25.0	30.8	22.8
25	-	35.2	-	31.0	29.4	38.2	26.4
30	6.0	39.0	28.8	-	-	-	-
40	6.2	-	32.0	-	-	-	-

The test usually applied to determine whether changes in the experimental conditions affect the course of reaction, that is, finding whether the time-percentage pressure change curves for different runs are affine, has also been used here. The agreement was surprisingly good in view of the fact that diffusion entered into the results. Figure 2 shows the plot of six of the runs given in table 3. In the table, run no. 1, which was made with an ordinary bulb without the P_2O_5, has been added to illustrate the difference in the magnitude of the pressure changes.

In figure 3 the values of t_{30} for a number of runs at 320° are plotted against the partial pressure of the acetylene at the beginning of the runs. It was found to be impractical to carry the investigation below a point where the 30% pressure decrease amounted to less than 10 mm., since the results in that region were extremely erratic and apparently much higher than would be expected from the form of the curves. However, in these cases a change of one millimeter at that stage of the reaction required about 15 minutes, so that the difference may perhaps have been experimental error.

At first there appeared to be no regular relation between the various points on the diagram but when the order in which the runs were made was considered some uniformity appeared. Thus, the runs with the 3:1 mixture may be divided into two series, one which contains the first ones made in the reaction bulb, the other those which were carried out some time later after the runs with the other mixtures had been completed.

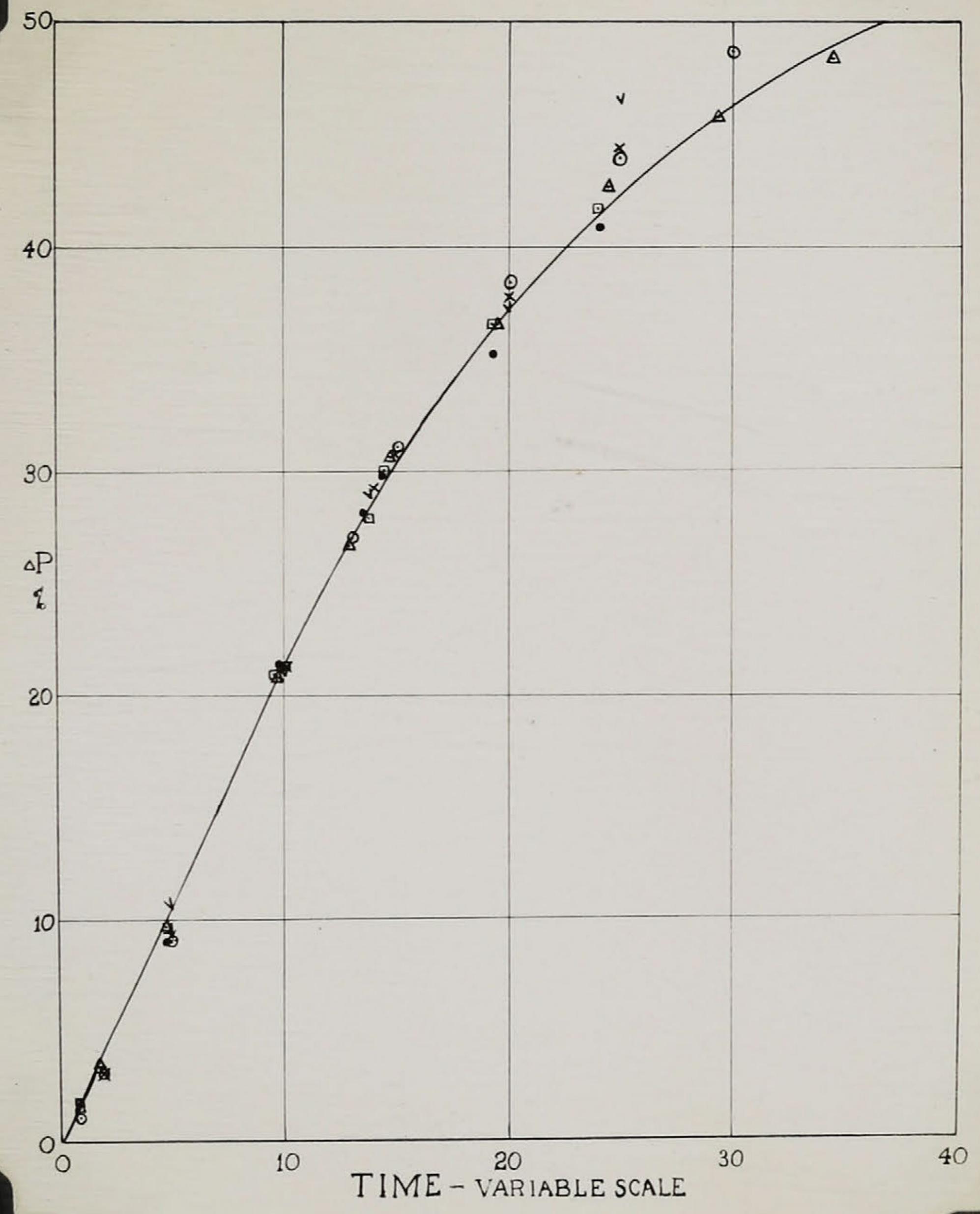


FIGURE 2.

AFFINE CURVES - (see TABLE 3).

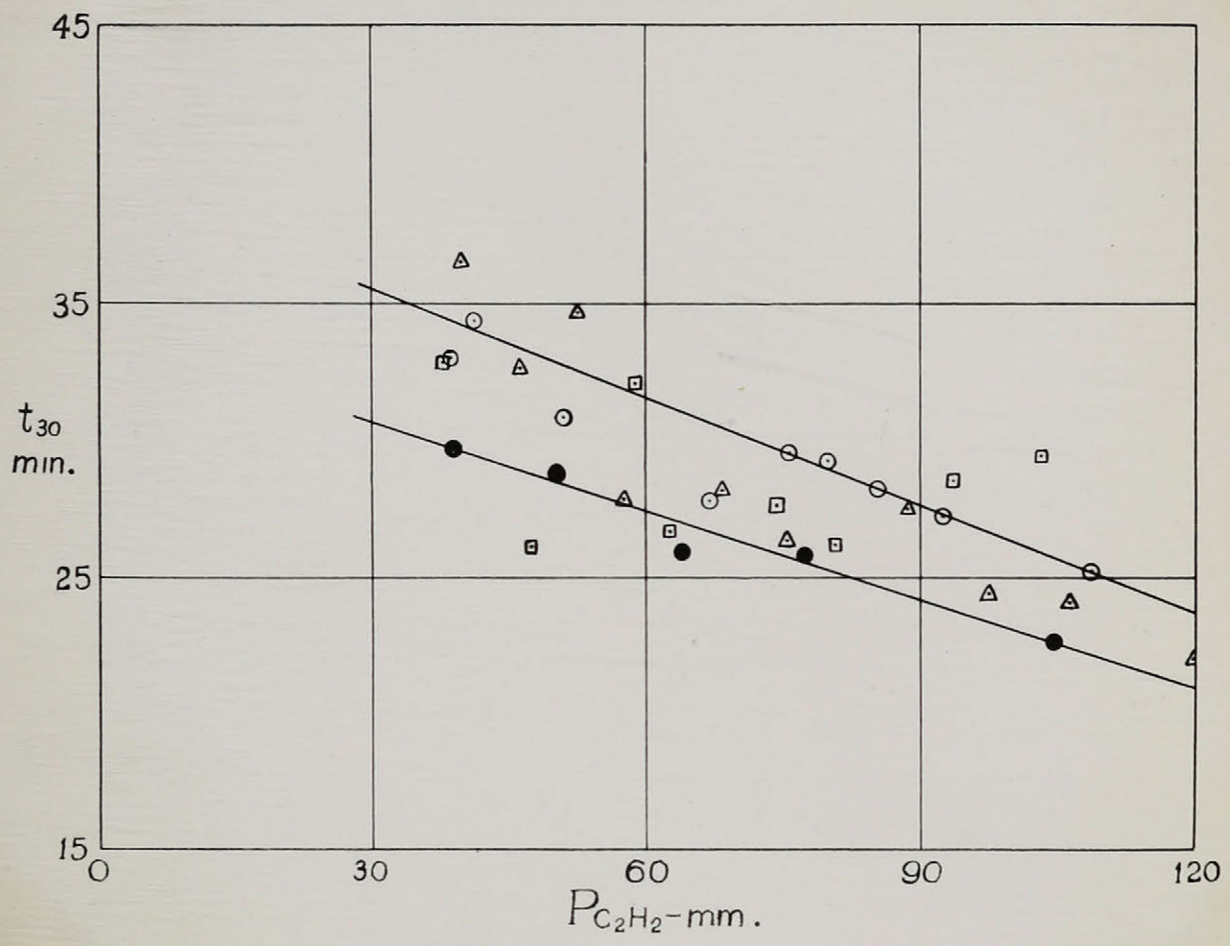


FIGURE 3.

VARIATIONS IN t_{30}. TEMP. 320° C.

⊙ - 3:1 Mixture, First Series. △ - 2:1 Mixture.

● - 3:1 Mixture, Second Series. ⊡ - 4:1 Mixture.

Ratios given in parts oxygen to parts acetylene.

The corresponding points fall fairly well into two groups giving the two straight lines shown in figure 3. Most of the other points are near or between the lines. It is apparent, therefore, that, in addition to the variations from run to run which are usual in hydrocarbon oxidations, there has been a slow drift in the rate. Since this was in the direction of increasing rate, it could not have been due to a decrease in the efficiency of the P_2O_5, unless the reaction were catalyzed by water vapour. It appeared more probable that the change was caused by a change in the surface of the bulb. Making allowances for these factors, the rate was independent of the oxygen concentration and proportional to a power of the acetylene concentration greater than one.

It seemed possible that more reproducible results might be obtained at a higher temperature. For that reason runs were made at 350°. In all cases the evacuation between the runs was continued for two hours or as much longer as was required to reduce the pressure below 10^{-3} mm. The values which were obtained for t_{30} are plotted in figure 4. They were evidently still very erratic but 70% of them are within one minute of the line shown. Since there was no marked drift with time in this series, the order in which the runs were made has not been indicated. With a considerable number of them the mixtures were withdrawn for analysis at t_{30}. The results are given in table 4.

In the table the analyses have been arranged according to the composition and pressure of the initial mixtures. A rearrangement to the order in which they were carried out does

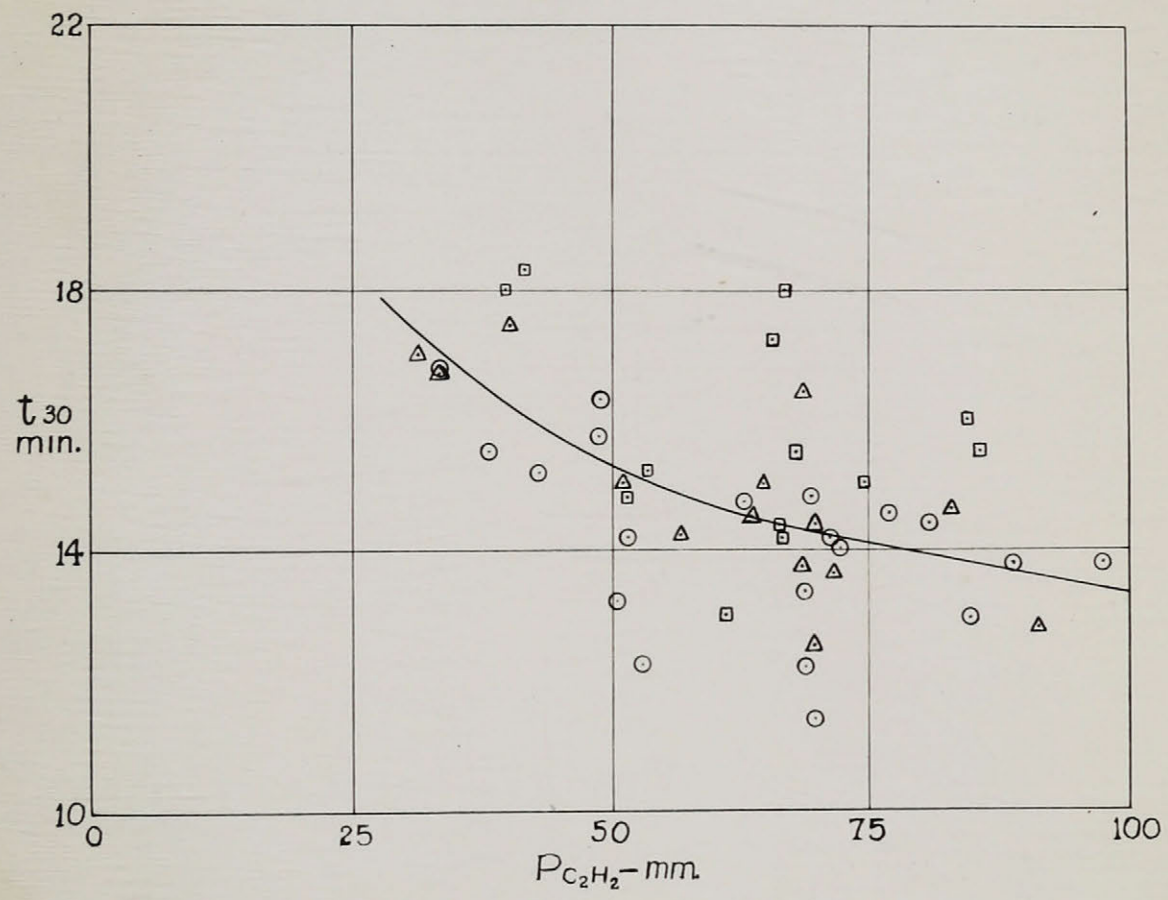


FIGURE 4.

VARIATION IN t_{30}. TEMP. 350°C.

△ - 2:1 Mixture. ⊙ - 3:1 Mixture.

⊡ - 4:1 Mixture.

Ratios given in parts oxygen to parts acetylene.

TABLE 4.

GAS ANALYSES AT t_{30}. TEMP. - 350°C.

A = O_2 Reacted/C_2H_2 Reacted.

B = CO + CO_2 Formed/C_2H_2 Reacted. C = %C_2H_2 Reacted.

No.	$P_{C_2H_2}$ (mm.)	t_{30} (min.)	Composition of Sample - %					A	B	C
			CO_2	C_2H_2	O_2	CO	Res.			
			Original Mixture - O_2/C_2H_2 = 3.							
1	50.2	13.4	4.2	12.6	58.0	18.2	7.0	1.37	1.62	52.2
2	51.6	14.2	4.8	9.5	54.4	22.4	8.9	1.32	1.61	64.1
3	52.8	12.2	5.3	12.0	58.7	16.7	7.3	1.25	1.52	54.7
4	68.4	12.2	5.6	11.2	57.7	17.9	7.6	1.26	1.54	57.6
5	68.6	13.5	4.6	12.3	58.0	19.5	5.6	1.34	1.70	53.5
6	68.8	11.4	5.2	11.3	58.8	18.6	6.1	1.19	1.57	57.1
7	70.8	14.2	4.9	11.8	54.9	19.6	8.8	1.49	1.67	55.5
8	71.8	14.0	4.4	12.7	58.0	19.0	5.9	1.37	1.69	52.2
9	84.4	13.1	5.5	11.1	57.0	20.0	6.4	1.30	1.66	58.0
10	88.6	13.8	5.2	10.7	57.1	20.2	6.8	1.25	1.61	59.6
Av.			5.0	11.5	57.3	19.2	7.0	1.31	1.62	55.4
			Original Mixture - O_2/C_2H_2 = 2.							
11	63.0	14.5	5.6	16.9	41.9	27.6	8.0	1.46	1.71	53.5
12	68.6	16.4	7.1	12.9	45.0	27.8	7.1	1.09	1.49	64.5
13	69.0	12.5	6.4	14.9	44.0	25.5	9.2	1.22	1.50	59.0
14	69.8	14.4	7.1	14.9	41.8	27.0	9.2	1.33	1.59	59.0
Av.			6.5	14.9	43.2	27.0	8.4	1.27	1.57	59.0
			Original Mixture - O_2/C_2H_2 = 4.							
15	60.4	13.0	4.2	8.8	66.7	13.9	6.4	1.25	1.50	57.7
16	66.2	14.2	3.8	8.7	66.9	14.0	6.6	1.22	1.48	58.2
17	66.8	18.0	3.3	8.2	68.9	14.8	4.8	0.92	1.43	60.7
Av.			3.8	8.6	67.5	14.2	5.9	1.13	1.47	58.9

not show any greater regularity. Apparently, therefore, the variations here are as erratic as those in t_{30} and are, indeed, of about the same order. Thus, the average for the percentage of the acetylene reacted is 57.5, while all but three of the results are between 53.5 and 61.5, that is, within 7% of the average. It is impossible, however, to establish any definite relation between the two variations; an increase in t_{30} does not necessarily mean an increase in the percentage reacted. Nevertheless, we may conclude from the results that, on the average, a pressure decrease of 30% of $P_{C_2H_2}$ at 350° represents the same stage of the reaction, regardless of the pressure and composition of the original mixture. The values for t_{30} may, therefore, be used to determine the order of the reaction. They confirm the conclusions drawn from the results at 320°, namely, the rate is independent of the oxygen concentration and dependent on a power of the acetylene concentration slightly greater than one. In addition, there appears to be definite evidence of a change in the curve towards the direction of lower rates as the pressure is decreased beyond the limit where accurate results can be obtained. The long time required for 90% reaction as compared with the time for 57% reaction - 120 minutes compared with about 14 minutes - furnishes further evidence of this effect.

Temperature Coefficient.

Runs were made over the range 300°- 370° in order to determine the effect of temperature on the rate of reaction. In cases like that at 350°, where widely different values had been obtained for t_{30} with the same mixture and the same pressure, those which were obtained in this particular series were used, that is, two runs were made at each of 370°, 320°, 350° and 300° in that order and the results from these were the only ones taken. They are given in table 5 and their logarithms are plotted against the reciprocals of the temperatures in figure 5.

TABLE 5.

TEMPERATURE COEFFICIENT.

$P_{C_2H_2}$ - 70 mm. P_{O_2} - 210 mm.

Temp. °C.	300	320	350	370
t_{30}	30.7	23.8	14.0	10.5
	31.5	23.9	14.3	10.6

The points fall fairly well on a straight line which would correspond to an apparent heat of activation of 11,600 cals. This should be increased somewhat since the runs were made at constant pressure rather than constant composition. However, a much greater correction is required since, as the gas analyses in table 6 show, t_{30} represents different stages of reaction at different temperatures. The above is, therefore, only a minimum value.

It would have been desirable to carry out the gas analyses on the same runs as were used for the temperature coefficient. Unfortunately, this was only done in two cases; it is believed, however, that those actually tabulated are reasonably close to what the others would have given.

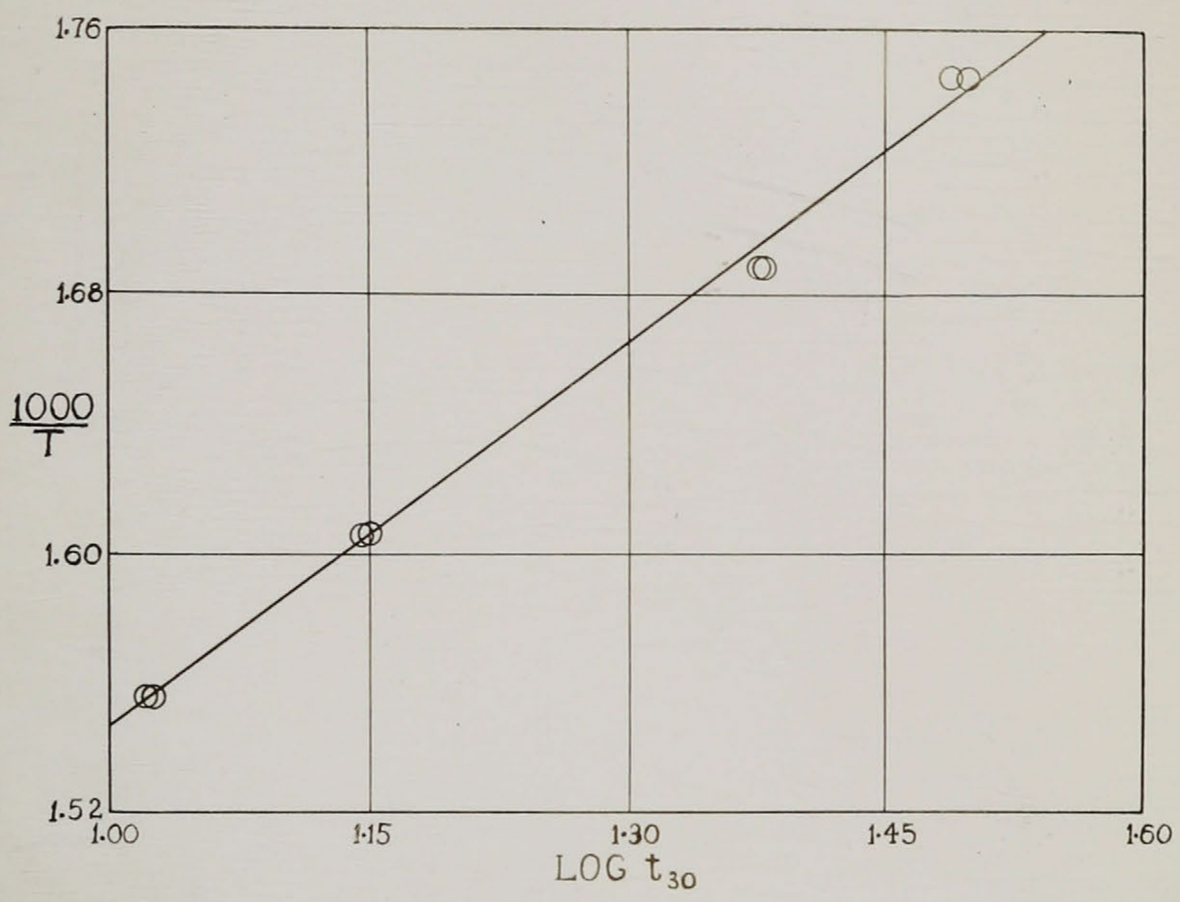


FIGURE 5.

TEMPERATURE COEFFICIENT - see TABLE 5.

TABLE 6.

GAS ANALYSES AT t_{30}.

Temp.°C.	300	300	350	370	370
% CO_2	3.0	4.0	4.9	5.4	5.4
% C_2H_2	14.8	13.9	11.9	10.2	9.6
% O_2	64.6	64.4	57.5	53.8	54.5
% CO	12.3	11.9	18.9	21.5	23.0
% Residue	5.3	7.0	6.8	9.1	7.5
%C_2H_2 Reacted	44.1	47.8	55.2	61.6	63.7

The analyses for 300° were obtained from the same runs as are reported in table 5, that for 350° is the average of numbers 4 - 8 in table 4, while those for 370° were from additional runs which gave t_{30} as 10.3 and 10.1.

The approximate magnitude of the correction to be applied to the above value of E may be deduced from some data in connection with those runs at 320° which are reported in table 2. The corresponding values for time and %C_2H_2 reacted in those cases were, roughly:

No.	% Reacted	Time	No.	% Reacted	Time
1	48	24	4	65	47
2	49	21	5	64	42
3	50	22			

Therefore,

$$\frac{\text{Time for 64\% reaction}}{\text{Time for 49\% reaction}} = 2.$$

If the course of the reaction is the same at all temperatures this ratio will be constant. Moreover, it is approximately that required to make the runs at 300° and 370° in table 5 comparable. It would appear, therefore, that the temperature coefficient would correspond more nearly to a change in t_{30} from 62 minutes at 300° to 10.5 minutes at 370°, t_{30} referring to about 62% reaction. These values give $E = 18,500$ cals. This is very different from the 34,700 cals. reported by Spence and Kistiakowsky (89) but it seems highly improbable that any correction will bring the present result up to one comparable with theirs, especially since it would require more than a four-fold change in t_{30} over the range 300° to 370°.

Effect of Packing.

While it is desirable from theoretical considerations to carry out experiments in reaction bulbs with as great a difference in surface:volume ratio as possible, in the present case it was necessary to avoid as far as was practical any arrangement which would offer undue resistance to the diffusion of the water vapour to the P_2O_5. Thorough packing was therefore impossible. The packed bulb which was used contained 56 inches of 3/8 inch diameter pyrex tubing, cut in varying lengths and oriented as nearly as possible parallel to the neck of the reaction bulb. The surface was thus increased by about 3.5 times.

At 350°, two runs gave t_{30} equal to 25.5 and 24.3; at 370°, four runs gave 15.0, 14.0, 13.6 and 15.1. These were all made with a mixture containing three parts of oxygen to one of acetylene at a total pressure of 280 mm. and, therefore, the times are to be compared with values of about 14.2 and 10.5, respectively, for the unpacked bulb. Gas analyses were again carried out. The results are shown in table 7.

TABLE 7.

GAS ANALYSES.

1, 2, 3 and 4 at t_{30}; 5 and 6 after 120 minutes.

No.	1	2	3	4	5	6
Temp. °C.	350	350	370	370	370	370
% CO_2	5.1	4.6	5.9	5.8	9.8	9.2
% C_2H_2	10.2	10.5	8.8	9.2	3.1	2.6
% O_2	57.4	56.2	55.9	56.6	47.9	50.0
% CO	20.5	20.9	21.2	21.4	31.9	30.3
% Residue	6.8	7.8	8.2	7.0	7.3	7.9
%C_2H_2 Reacted	61.6	60.4	67.0	65.3	89.4	91.0

It is evident that t_{30} has not the same relation to the amount reacted here as it had with the unpacked bulb, since there it was the time required for the reaction of 55.2% of the acetylene at 350° or of 62.6% at 370° (see table 6), while here the average values are 61.0% and 66.1%, respectively. It is also obvious that the apparent decrease in rate obtained on packing was partly due to this difference in the meaning of the values which were being compared, but it does not seem probable that, in the case of the runs at 350°, the change from 55.2%

to 61.0% would have involved an increase in the time of about 10 minutes, that is, of 70%. We may conclude, therefore, that an increase in the surface resulted in a decrease in the reaction rate, but that the decrease was considerably less than 37% (the apparent change at 370°) when the increase in surface was 350%.

Analyses 5 and 6 in the above table agree fairly well with numbers 1 and 2 in table 1. It seems, therefore, that there had been no change in the course of the reaction on packing the bulb. This conclusion is contrary to that drawn by Kistiakowsky and Lenher (88) but, in view of the differences in method, in temperature and in the magnitude of the rate change, comparison is hardly justified. Their investigation involved experiments with the flow method between 250° and 315° and their packed reaction bulb was filled with pyrex glass of 6 - 14 mesh. This reduced the rate to about 10% of that in the open tube and changed the composition of the products so that the CO which had previously been 3 to 4 times the CO_2 dropped to 1/2 to 1/3 of it. Since the relative effect of packing on the rate in the present experiments was several times smaller, it is conceivable that the change in gas composition might not have been greater than the experimental error.

Discussion.

Since the experiments carried out with this special reaction bulb are really only preliminary to those which are to be described next, there is no point in discussing the results in detail here and the findings will only be summarized.

Since there is no real relation between what has been referred to as t_{30} and the percentage reaction, the method used is not satisfactory for a study of the kinetics of the reaction. It would appear probable that the variations with temperature and with packing were due to corresponding variations in the efficiency of the water removal, but that is not necessarily the case since there will be ample evidence in the succeeding experiments to show that there is no close relation between pressure change and percentage reaction even in an ordinary bulb.

Despite these flaws in the method it seems definitely established that under the conditions studied the rate is independent of the oxygen concentration and dependent on a power of the acetylene concentration only slightly greater than one. It is somewhat retarded by packing. The temperature coefficient corresponds to an apparent energy of activation of about 20,000 cals.

It was the intention to use these results to assist in an investigation of the rate in an ordinary bulb using gas analyses as the measure of reaction.

B. RUNS IN SIMPLE REACTION BULB.

Experimental.

Since the pressure change accompanying the acetylene-oxygen reaction is not great enough in an ordinary bulb to permit accurate measurements and is not consistent enough in a bulb fitted with a side-neck containing P_2O_5 to give reliable results, it is necessary to adopt an entirely different method for measuring the rate. Gas analyses have been used for that purpose in the experiments which are reported in this section.

The apparatus proper was that shown in figure 1, Part 1. The oxygen and acetylene were obtained as in the preceding work, the former being taken directly from cylinders of the commercial gas, the latter being generated from calcium carbide, washed with solutions of potassium hydroxide, chromic acid, mercuric chloride in hydrochloric acid and alkaline hydrosulphite, dried over calcium chloride and phosphorus pentoxide, condensed out with liquid air and carefully fractionated, all as directed by Moser (19). With the greater accuracy here possible in the analyses it was found that the oxygen was 98.6 to 99.0% absorbed in pyrogallol and the acetylene 98.7 to 99.4% soluble in fuming sulphuric acid.

Since gas analyses are a direct determination of the conditions in the reacting systems, they are preferable for theoretical purposes to pressure measurements, for, in the latter case, the results are of value only if the relation between pressure change and percentage reaction is entirely unaffected by any variations in the conditions of the experiments. While this has generally been assumed to be the case, the evidence on which that assumption is based is somewhat limited and in at least a few cases there is reason to doubt the justification for its unrestricted use. In the present case, the measurement of rate by means of gas analyses is especially valuable for Bone (29b, c) has objected to theories other than his hydoxylation one on the grounds that such theories are supported entirely by measurements of pressure changes, while he considers gas analyses of paramount importance.

If any degree of accuracy is to be attained in this work it is essential that the gas analyses themselves be as free from error as possible. For that reason this part of the investigation was not undertaken until a more satisfactory gas analysis apparatus than the Hempel pipettes became available. The type used was the Burrell Master Model-A. The burette was of 100 cc. volume, graduated in 0.2 cc. The manifold was so constructed that it could be entirely filled with the confining liquid (3% H_2SO_4, 20% Na_2SO_4) before and during the analysis. By a proper manipulation of the sampler it was thus possible to withdraw the gas from the reaction bulb, transfer it to the gas burette and carry out the analysis without introducing any air. The accuracy of the results should, therefore, be conditioned only by the accuracy to which the burette could be read. No attempt was made to carry this beyond the nearest 0.1 cc. Since the volume of the sample varied between 10 and 45 cc. the percentage error depends on the conditions of the experiment. At 320° with 200 cc. reaction bulbs considerably more than half the gas could be removed for analysis. In the tables which follow the volume of the sample and. therefore. the maximum accuracy in each experiment can be estimated from the total pressure since at 60 cm. the sample was about 42 cc., that is, 0.7 times the pressure and at 17 cm. about 10 cc., that is, 0.6 times the pressure. No analyses were made on samples smaller than 10 cc.

The reagents used were potassium hydroxide, fuming sulphuric acid, potassium pyrogallate and acid cuprous chloride. When the hydrogen content was desired, oxygen was added and the hydrogen burned in the slow combustion pipette - since it was never more than 0.4 cc. it was unnecessary to introduce the gases separately. In most cases the hydrogen and nitrogen are reported together. It is apparent from the many analyses which will be tabulated later that the results are far more satisfactory than those in the preceding work. The most obvious difference is in the residue which will usually be about 2% here, although it went as high as 9% in the earlier results, the high value being due to the unavoidable entrance of air.

As in the previous work all conclusions as to the kinetics of the reaction are based on the variation in the time, t, for a definite percentage reaction as the conditions of the experiment are varied.

Since the limitations in reading the burette introduce the possibility of an error of constant magnitude throughout each run, it is desirable to compare times when the effect of this on t is as small as possible. The choice of the stage of the reaction with which t is to correspond is, therefore, of some importance. By making the appropriate mathematical calculations it can be shown that, for a reaction which is of the nth order throughout, the relative error in t for a constant error in x will be least when

$$a^{n-1} = n(a - x)^{n-1} .$$

(The assumption of a constant error in x is, of course, dependent on a constant volume of the sample. While this is very nearly true for the present case, it would not necessarily hold for other reactions.) Since preliminary work indicated an order of about 2.5 under the conditions studied here, the optimum value for x becomes 0.45a.

The introduction of the gas into the reaction bulb and the removal of the sample each required about five seconds and each would tend to cause small errors in t. Obviously their relative effects would be less the greater t. It is probable, therefore, that the best results will be obtained by comparing the times for about 50% reaction and this is approximately the stage used in much of the work which follows.

It had been hoped that the runs in the presence of P_2O_5 could be used as an indication of the variation of t with pressure, so that this work would only be of a confirmatory nature. However, it was soon evident that relations under the new conditions were entirely different and it was necessary to treat the system as an essentially new one. For the more or less exploratory work which that involves the method using gas analyses is rather unsatisfactory since each run is equivalent to a single point in a percentage reaction-time curve. In order to facilitate the work it is essential to be able to extrapolate the results, at least over small intervals of time. This is only practical if the order of the reaction remains a constant during the change; if the rate varies with time according to the equation

$$w = Ne^{\varphi t}$$

(w - rate, t - time, N, φ - characteristic constants) suggested by Semenoff (101) such treatment would be rather difficult. Fortunately, as will be shown later, this reaction seems to agree fairly well with the former of these conditions. It is, therefore, possible to obtain the rate (dx/dt) at time t in terms of the average rate (x/t) to time t. For the general case

$$\text{Rate at } t/\text{av. rate} = \frac{1}{x(n - 1)}\left\{(a - x) - \frac{(a - x)^n}{a^{n-1}}\right\}$$

In the earlier runs where this extrapolation was most valuable x was approximately 0.43a and, for an order of 2.6, which appears the most likely value, this gave the above ratio equal to 0.5. This has been used throughout, although in some of the later work a lower value would have been more accurate. In applying this result the percentage reactions should be used to be strictly correct. However, since the volume of the non-condensable gases does not vary rapidly during the oxidation, the carbon monoxide content of the samples can be considered a measure of reaction. In the work to follow, the extrapolations have, therefore, been based on this unless, of course, the differences in the analyses were such as to indicate that this was not justified. In that event the results were not used. Needless to state, no extrapolations were made unless the difference from the desired value was clearly greater than the experimental error. In view of the approximations involved in this treatment the final values can hardly be exact. However, the part of any value of t estimated in this way was rarely greater than 20%, so that a large error in making the extrapolation would have a relatively small effect on the final result. Moreover, any conclusions which may be drawn from this work will be based on direct determinations of t. In the graphs which will appear later the extrapolated points are generally in much poorer agreement than those determined directly. This is not the fault of the method described above but is to be expected since, after a few preliminary runs, most of the analyses were made at times corresponding to a straight line on the log p - log t diagrams. Obviously, then, direct results will be on this line while the only ones requiring extrapolation will be irregular ones, and the corrected values of t derived from them must also be irregular.

Pressure changes were not of very great use as guides in the exploratory work, for they varied with almost every variation in the experimental conditions. This is illustrated by the curves in figure 6, which are typical of all those obtained in this investigation. The figures given in brackets in the data pertaining to the curves are, respectively, the pressure change, relative to the acetylene pressure, at the time

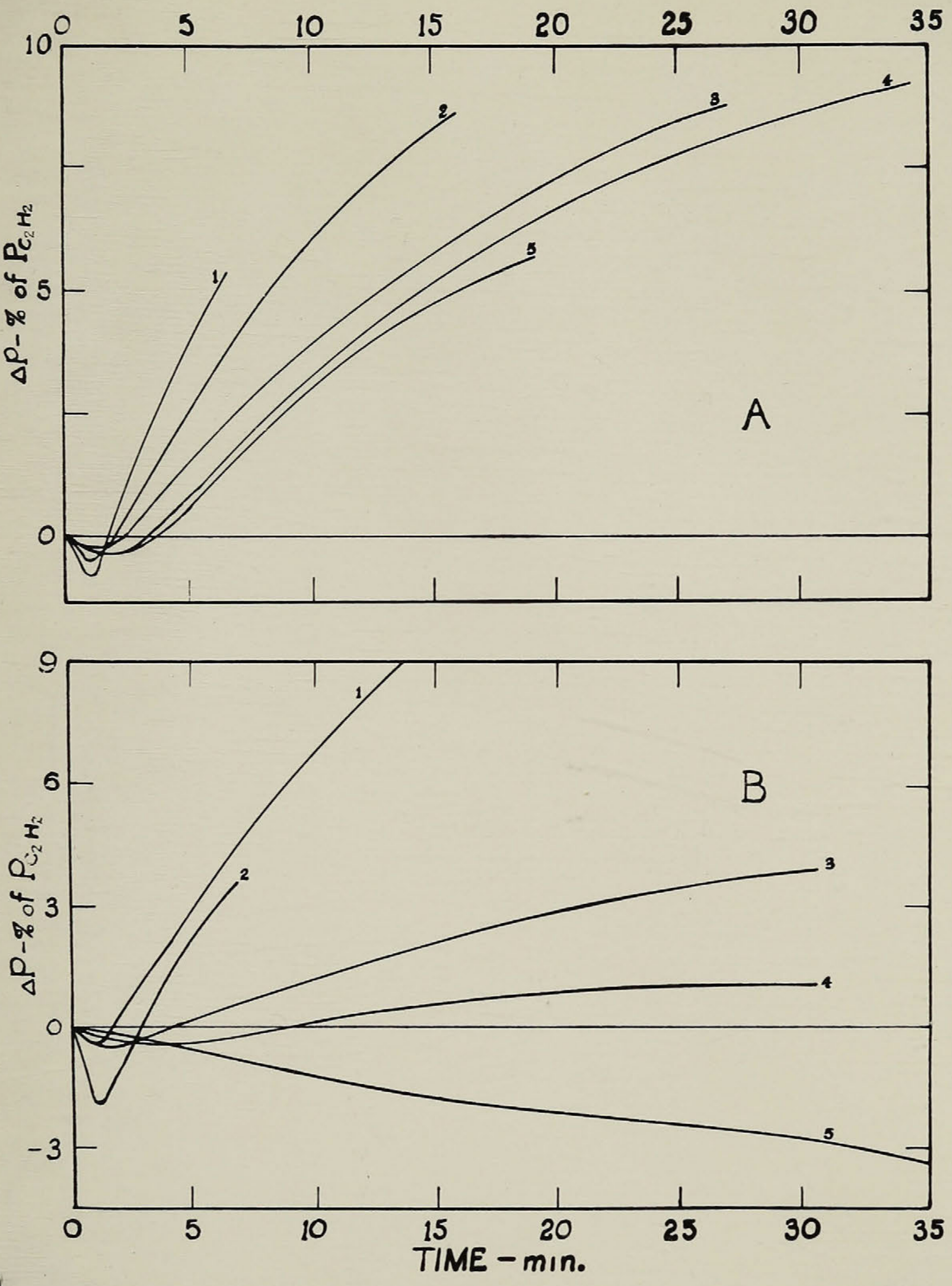


FIGURE 6.

Pressure Change-Time Curves.

A - Coated Pyrex Bulb. B - Silica Bulbs (1, 2 - Spherical, 3 - Cylindrical, 4, 5 - Cylindrical, Packed.)

	$P_{C_2H_2}$ (cm.)	P_{O_2} (cm.)			$P_{C_2H_2}$ (cm.)	P_{O_2} (cm.)	
A1	26.9	26.9	(4.9, 46.5)	B1	14.0	14.0	(9.2, 53.5)
A2	16.5	32.9	(8.4, 46.0)	B2	21.9	21.9	(3.7, 51.0)
A3	12.5	12.5	(8.6, 45.0)	B3	17.0	34.0	(3.8, 32.0)
A4	10.6	21.3	(9.2, 43.0)	B4	20.0	40.0	(1.0, 29.0)
A5	15.2	45.7	(5.5, 45.5)	B5	12.7	25.5	(-3.4, 28.0)

when the sample was taken for analysis and the approximate percentage reaction. Almost without exception, it was found that, for corresponding stages of the reaction, the relative pressure changes were greater the lower the initial pressure. In a pyrex bulb the range with the same mixture was never greater than from 5 to 9.5% of the acetylene pressure and was usually somewhat lower, in a silica one, however, it was as much as from 3 to 11%. Presumably this is due to differences in the concentration of some substance formed by the union of oxygen and acetylene molecules. That such a compound is formed is obvious from the pressure decrease at the start of each run.

The relative pressure change is also affected by alterations in the O_2:C_2H_2 ratio but in this case there is a corresponding change in the CO:CO_2 ratio, so that such a result was to be expected. Pressure readings were, therefore, of little use as a measure of reaction in this work although, when duplicate runs were being made, they did indicate whether or not checks might be expected.

The form of the curves is of interest in connection with the nature of induction periods. Kontorovna and Neumann (102) have recently stated that in unimolecular reactions these cannot be explained, as has sometimes been done, by assuming two reactions with the pressure changes neutralizing one another in the first stages. They argued that in the case of concurrent reactions such as those the curves would have a form similar to that obtained here. While the question of an induction period is not involved in the present case, the results might be considered to support that argument. Similar curves have also been obtained by Brunner and Rideal (69) in the study of the hexane oxidation and by Pidgeon and Egerton (103) in that of the oxidations of both hexane and amylene.

It is apparent that the various curves shown in the figure are not affine and no attempt has been made to make this more evident. However, it is almost certain that this is not due to differences in the course of the main reaction but is caused only by differences in the relative stages reached in the secondary changes. That being the case, comparisons of runs made under differing conditions are quite justified.

The rates obtained in any reaction bulb varied somewhat as the bulb aged. The order in which the runs were made is, therefore, of importance and in reporting the results the number of each run in the series as a whole will generally be given. The measurements in the presence of P_2O_5 have been included in this numbering. Those with the present arrangement begin at 134.

Runs in Pyrex Bulb.

The first series of experiments were made at 320° in the 200 cc. spherical pyrex bulb with which the work in Part 1 on CS_2 - N_2O had been carried out. It was thoroughly outgassed at 550° before being used here. The results are given in table 8 with some data from the previous work added for comparison. The O_2:C_2H_2 ratio was 2:1 and the gases were allowed to mix thoroughly before being admitted to the bulb.

TABLE 8.

RUNS IN PYREX BULB WITH 2:1 MIXTURE AT 320°C.

$P = P_{C_2H_2}$; % R = % C_2H_2 Reacted; t_{25} = Time to 50% R, t_{40} to 65% R

Bulb with P_2O_5. Runs 46 - 54

P	t_{25}	t_{40}	P	t_{25}	t_{40}	P	t_{25}	t_{40}
4.6	25.6	56.6	6.8	22.3	51.3	9.8	19.2	40.3
5.3	26.1	65.6	7.6	19.9	44.8	10.6	18.8	42.7
5.8	22.1	49.3	8.9	21.0	50.6	12.3	18.2	33.9

Simple Bulb. Runs 134 - 185

P	t	% R	P	t	% R	P	t	% R
9.0	25	39.2	12.4	28	58.3	12.5	28	64.4
13.1	25	48.0	12.5	28	61.2	10.0	37	64.3
10.4	25	37.8	9.9	40	64.0	7.9	50	62.6
8.2	25	34.8	7.9	52	59.8	6.3	70	53.7
15.7	20	43.5	15.7	20	60.3	18.0	16	62.5
5.8	45	37.6	12.5	27.5	61.5	14.3	22	63.0
19.7	16	49.7	9.9	36	62.0	11.4	30	64.4
15.8	20	46.7	7.9	45	58.4	9.0	39	63.6
12.7	26	45.0	15.5	20	62.3	7.2	54	63.0
10.2	35	37.9	12.4	28	62.0	5.7	76	53.0
8.1	45	47.1	9.8	40	64.0	15.8	19.5	64.4
15.7	20	49.3	7.8	55	60.0	12.6	26	63.0
12.5	28	49.5	18.0	16.5	61.9	10.0	35	59.2
15.6	15	47.5	14.4	24	63.5	18.2	16	62.8
15.7	20	55.8	11.5	31	63.8	14.4	22	63.2
12.7	28	57.2	9.1	42	65.0	11.5	28	40.8
15.6	20	54.5	15.7	20	62.7	9.1	37	43.3
15.7	20	58.8						

Since no analyses were made at t_{25} or t_{40} with 2:1 mixtures at 320° in the previous work, the corresponding percentage reactions are not definitely known. The values given at the head of the table are arrived at on the basis of the analyses in table 2, which refer to a 3:1 mixture. They should be very nearly correct for the 2:1 mixture.

With the ordinary reaction bulb there is some condensation when the sample is removed and since this results in a volume change of unknown amount, the percentage reaction cannot be calculated directly. In this table it has been obtained on the assumption that 5% of the total carbon has gone to form condensable organic compounds and is not represented in the analyses. From the CO, CO_2 and C_2H_2 contents of the non-condensable gases the amount of acetylene reacted can then be calculated. The assumption is based on later work and is accurate enough for the present purpose. The runs in the simple bulb are in the order in which they were carried out if read down the table rather than across it. Pressures are in cms. of mercury and times in minutes. The very marked drift is at once apparent and has been emphasized by underlining one set of values with approximately the same pressure and time.

In view of this variation it is not possible to compare very closely the results with the two arrangements. However, the rates are of about the same magnitude. The outstanding difference is in the order which, while only slightly greater than one in the presence of P_2O_5, is evidently well above two in the later experiments.

A drift in the first few experiments is quite characteristic of hydrocarbon oxidations and so was not surprising in the present case. It was hoped that a steady state would finally be reached but at run 185 the rate reverted to its original value. Heating to 550° with and without air did not restore the more rapid rate. Since it was probable that the same cycle would again be repeated, runs in an ordinary pyrex bulb were abandoned.

Runs in Coated Pyrex Bulb.

More reproducible results are often obtained with hydrocarbon oxidations if the glass of the reaction bulb is coated with some salt. Therefore, a bulb similar to the previous one was rinsed once with a saturated solution of potassium chloride, outgassed at 550° and put into use. Since heating to 500° seemed to favour the initial slow rate in the previous experiments, this bulb was given that treatment every two or three days. After the first run the results were fairly reproducible, the rate being only slightly less than the maximum reached in the preceding series. This is in contrast to the results of Spence (95) who reports that "the well-known inhibitory effect of potassium chloride in hydocarbon oxidations can be observed in the slow oxidation of acetylene." Before the necessary number of runs could be obtained with this bulb it was inadvertently overheated and had to be discarded. For that reason none of the results from it will be given in detail here. They indicated an order greater than 2.3.

The next bulb was the ordinary pyrex one used above but was rinsed once with a normal solution of sodium chloride and then once with distilled water, a treatment which Lenher and Kistiakowsky (88) found to speed up the acetylene-oxygen reaction and to make the results more reproducible. In the present work the rate was increased but the drift was very pronounced and only three runs were made with this bulb.

After a further rinsing with distilled water followed by saturated potassium chloride solution the same bulb was found to give more satisfactory results.

Some selected analyses from the first series with it are given in table 9 and runs 212 - 276, except for a few where no analyses were made and a few at low pressure for which the points were erratic and fall outside the diagram, are shown in figure 7. The lines are drawn to fit the points directly determined, without considering the extrapolated ones. In both the table and the figure - and in all subsequent work - $P_{C_2H_2}$ is calculated from the total pressure on the assumption that the composition of the mixtures is exactly that indicated by the $O_2:C_2H_2$ ratios and that no nitrogen is present. This means that all values should be reduced by a constant percentage but since this would only mean a slight shift in the lines without changing their slope, it is of no importance. In the absence of any more direct evidence at this point, analyses with different mixtures are considered to represent the same percentage reaction when the $(CO + CO_2)/C_2H_2$ ratios are the same. On this basis the lines in the figure represent similar stages of reaction in 2:1, 3:1 and 5:1 mixtures. With the 1:1 mixture,

TABLE 9.

GAS ANALYSES SELECTED FROM RUNS 212 - 276.

A = CO/CO_2.　　　B = $(CO + CO_2)/C_2H_2$.

No.	$P_{C_2H_2}$ (cm.)	t (min.)	Composition of Sample - % CO_2	C_2H_2	O_2	CO	H_2	N_2	A	B
			Original Mixture - O_2/C_2H_2 = 2.							
221	6.4	69.0	5.0	20.7	49.6	22.3		2.4	4.46	1.32
216	7.2	58.0	5.5	20.9	49.0	22.4		2.2	4.07	1.33
220	8.0	50.0	5.2	20.3	49.0	22.9		2.6	4.40	1.38
225	9.2	41.0	5.1	20.8	48.9	23.0		2.2	4.50	1.35
228	10.0	36.5	5.0	21.0	49.0	22.5		2.5	4.50	1.31
214	11.3	31.5	5.5	20.9	48.6	22.7		2.3	4.13	1.35
218	12.8	26.0	5.5	20.8	49.0	22.4		2.3	4.07	1.34
239	14.6	21.5	5.6	20.9	49.5	22.3		1.7	3.98	1.34
217	15.9	19.0	5.5	20.9	49.0	22.4		2.2	4.07	1.34
238	18.4	15.5	5.9	20.9	49.2	22.3		1.8	3.78	1.35
Av.			5.4	20.7	49.1	22.5		2.2	4.17	1.34
			Original Mixture - $O_2/C_2H_2/N_2$ = 2/1/1.							
234	11.9	28.5	3.9	15.1	35.9	16.3	0.3	28.5	4.18	1.34
235	9.5	39.0	3.9	15.1	35.7	16.3	0.3	28.7	4.18	1.34
			Original Mixture - O_2/C_2H_2 = 3.							
254	7.6	63.0	4.4	15.7	61.8	16.2		1.9	3.68	1.31
248	10.0	40.0	3.9	15.8	62.0	16.5		1.8	4.23	1.29
252	10.1	40.0	4.4	15.3	62.0	16.4		1.9	3.73	1.36
243	15.3	20.5	4.3	15.7	61.7	16.4		1.9	3.82	1.32
251	15.4	21.5	4.3	15.5	62.0	16.4		1.8	3.82	1.34
Av.			4.3	15.6	61.9	16.4		1.8	3.82	1.33

TABLE 9 (Cont'd).

No.	$P_{C_2H_2}$	t	Composition of Sample - %						A	B
	(cm.)	(min.)	CO_2	C_2H_2	O_2	CO	H_2	N_2		
			Original Mixture - O_2/C_2H_2 = 5.							
256	10.3	44.0	2.9	10.4	74.1	10.9	1.7		3.76	1.33
257	8.3	61.0	2.8	10.2	74.3	10.7	2.0		3.82	1.32
258	6.6	87.0	3.0	10.4	74.4	10.4	1.8		3.47	1.29
Av.			2.9	10.3	74.3	10.7	1.8		3.70	1.31
			Original Mixture - O_2/C_2H_2 = 1.							
261	19.5	11.8	8.1	32.3	21.5	35.8	2.3		4.42	1.36

although individual groups of points agree very well - notably the four points at acetylene pressures of about 15.8 cm. (log p = 1.2) - over a pressure range they are so erratic that no line could be drawn. For the 2:1 and 3:1 runs the extrapolations are made to the average CO content of the tabulated ones; for those with the 5:1 mixture no extrapolation was necessary; while for those with the 1:1 mixture a CO content of 35.7% was made the standard.

The lines indicate an order varying from 2.4 with the 2:1 mixture to 2.6 with the 5:1 mixture, although if the extrapolated points had been considered in the former case the order there would also have been about 2.6. Oxygen appears to have a retarding effect corresponding to a negative order of from 0.2 to 0.3. However, when runs were made with the 2:1 mixture after this series was completed it was found that the rate was somewhat slower than that first obtained. For that reason it is not advisable to draw any definite conclusions from the relative

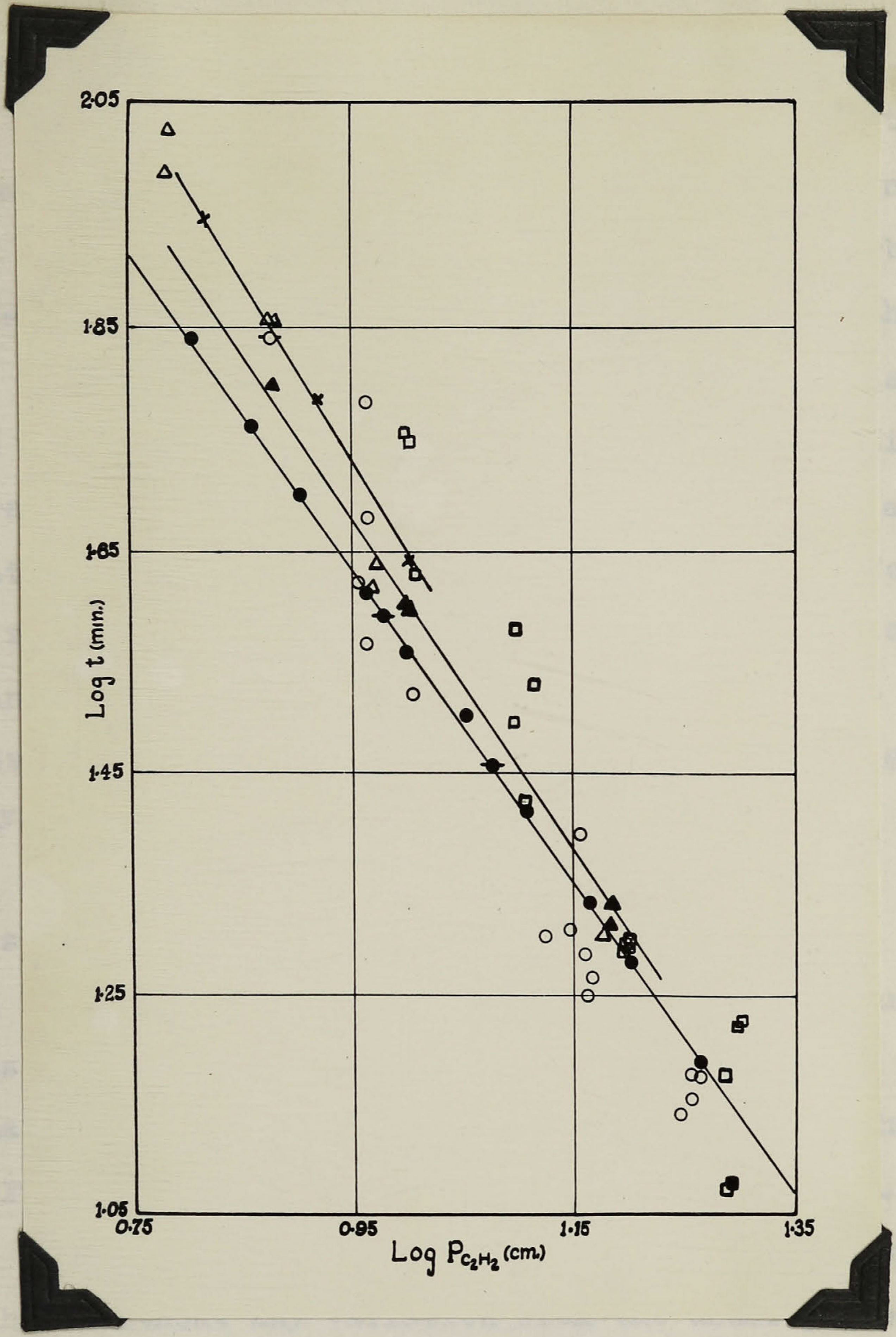


FIGURE 7.

EFFECT OF PRESSURE ON RATE.   RUNS 212 - 276.

■ - 1:1 Mixture, direct.   □ - Ditto, extrapolated.

● - 2:1 Mixture, direct.   ○ - Ditto, extrapolated.

-●- - 2:1 Mixture ✚ N_2, direct. -○- - Ditto, extrapolated.

▲ - 3:1 Mixture, direct.   △ - Ditto, extrapolated.

✗ - 5:1 Mixture, direct.

positions of the lines for the different mixtures.

In the runs with nitrogen added (table 9) the percentage reactions are 42.8 and 43.2 and the carbon missing from the gas is 4.6 and 5.2% of the total. Since several carbon balances will be given later these will not be discussed further.

In view of the change in rate, the bulb was removed, rinsed again with saturated potassium chloride solution and the runs repeated. The rate continued the same as that at end rather than at the first of the previous series. After a few preliminary runs results which agreed satisfactorily were obtained. Some analyses from runs 282 - 330 are given in table 10. The results from the series are shown in figure 8. Two groups where the oxygen content was abnormally high, possibly due to small errors in making up the mixtures, have been omitted. The treatment is the same as in the previous case. There are no runs with a 1:1 mixture. A third point with the 5:1 mixture would lie just outside the diagram and would indicate that the line for that mixture should be slightly above that for the other two. From this figure the order would be about 2.85.

Between runs 330 and 331 the bulb stood about a day and a half without any variation from the usual procedure in such cases, yet there was a very distinct change in the rate of reaction. Runs 331 to 364 are, therefore, considered as a separate series. Some of the analyses are given in table 11. The results are plotted in figure 9. It will be noted that the first twelve runs all agree very well. This constitutes the most satisfactory group of results as yet discussed and conclusions drawn from them should be reasonably accurate.

TABLE 10.

GAS ANALYSES SELECTED FROM RUNS 282 - 330.

A = CO/CO_2. B = $(CO + CO_2)/C_2H_2$.

No.	$P_{C_2H_2}$ (cm.)	t (min.)	Composition of Sample - %					A	B
			CO_2	C_2H_2	O_2	CO	$H_2 + N_2$		
Original Mixture - O_2/C_2H_2 = 2.									
328	13.4	23.0	5.3	21.2	48.8	22.6	2.1	4.26	1.32
323	13.4	23.2	5.1	21.6	48.7	22.7	1.9	4.45	1.29
296	11.5	30.0	5.7	21.4	48.5	22.3	2.1	3.91	1.31
324	10.8	34.0	5.0	21.5	49.3	22.4	1.8	4.48	1.27
329	10.7	35.0	5.1	21.2	48.8	23.0	1.9	4.50	1.32
297	9.0	42.0	5.3	21.6	49.1	22.2	1.8	4.20	1.27
325	8.6	53.0	5.4	21.0	49.7	22.2	1.7	4.11	1.31
Av.			5.3	21.4	49.0	22.5	1.9	4.27	1.30
Original Mixture - O_2/C_2H_2 = 3.									
318	13.8	22.0	4.1	15.2	62.2	16.5	2.0	4.03	1.35
306	13.5	23.0	4.1	15.2	62.8	16.0	1.9	3.90	1.32
302	12.4	26.0	4.0	15.4	62.6	16.0	2.0	4.00	1.30
315	12.2	27.0	4.0	15.6	62.2	16.4	1.8	4.10	1.31
319	11.1	32.0	3.9	15.3	62.2	16.6	2.0	4.25	1.34
316	9.8	41.0	3.7	15.4	62.3	16.5	2.1	4.46	1.31
320	8.8	49.5	3.8	15.6	62.4	16.0	2.2	4.21	1.27
317	7.9	61.0	3.8	15.2	62.9	16.2	1.9	4.26	1.32
Av.			3.9	15.4	62.4	16.3	2.0	4.15	1.31
Original Mixture - O_2/C_2H_2 = 5.									
298	10.0	46.0	2.7	10.3	74.1	11.1	1.8	4.11	1.34
299	7.9	65.0	3.0	10.7	74.0	10.7	1.6	3.57	1.28
300	6.4	90.0	2.7	10.6	74.1	10.6	2.0	3.93	1.25
Av.			2.8	10.5	74.1	10.8	1.8	3.87	1.29

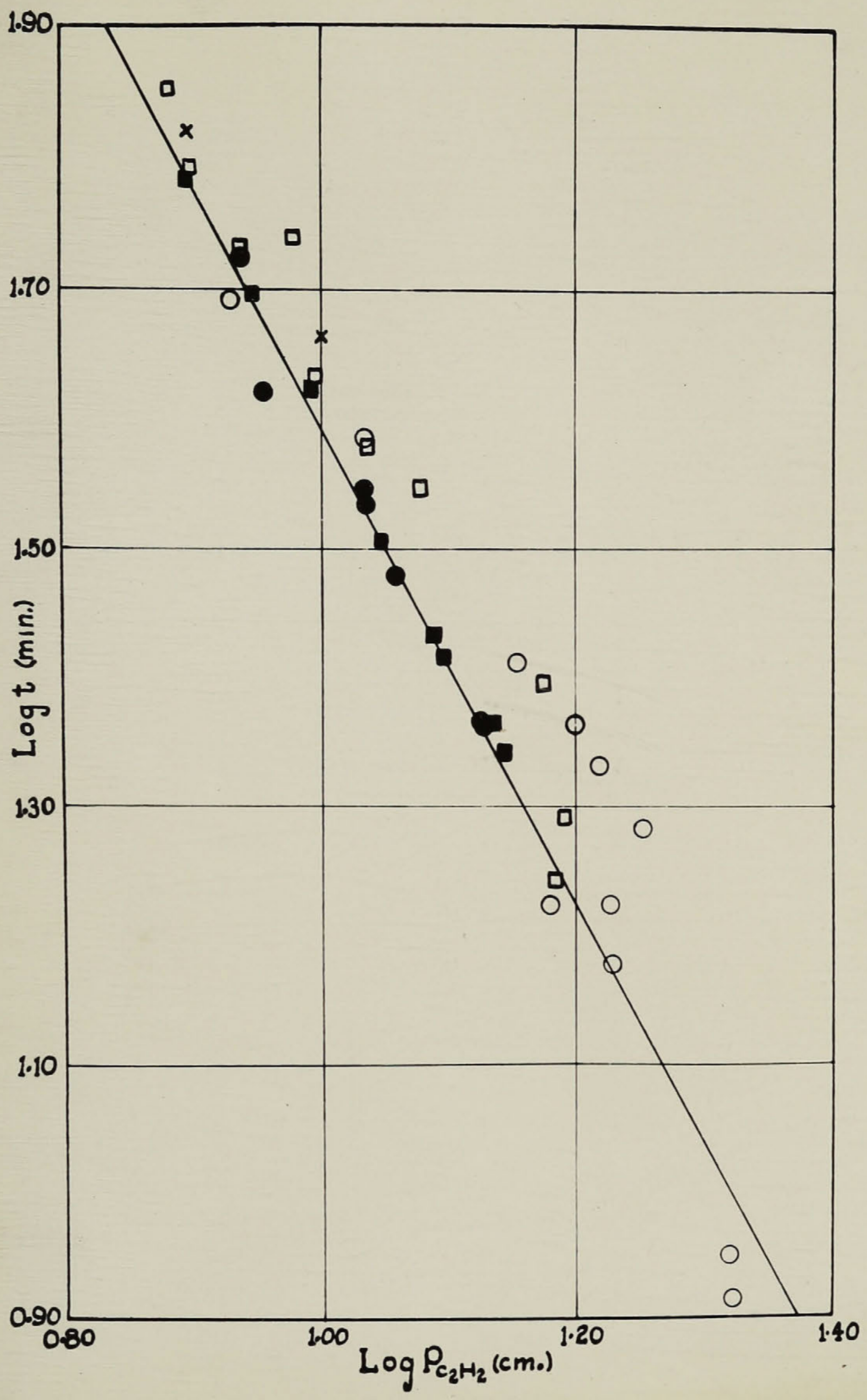


FIGURE 8.

EFFECT OF PRESSURE ON RATE. RUNS 282 - 330.

● - 2:1 Mixture, direct. ○ - Ditto, extrapolated.

■ - 3:1 Mixture, direct. ◻ - Ditto, extrapolated.

✗- 5:1 Mixture, direct.

TABLE 11.

GAS ANALYSES SELECTED FROM RUNS 331 - 364.

$A = CO/CO_2$. $B = (CO + CO_2)/C_2H_2$.

No.	$P_{C_2H_2}$ (cm.)	t (min.)	Composition of Sample - %						A	B
			CO_2	C_2H_2	O_2	CO	H_2	N_2		
Original Mixture - $O_2/C_2H_2 = 1$.										
357	21.5	9.8	8.8	31.6	20.2	37.4	2.0		4.25	1.46
362	19.6	11.6	8.3	32.1	20.0	37.4	2.2		4.50	1.42
363	15.7	17.8	8.2	31.4	21.3	37.2	1.9		4.54	1.44
364	12.5	27.6	8.0	31.5	21.6	37.0	1.9		4.63	1.43
360	10.8	36.4	8.1	31.6	20.6	37.5	2.2		4.63	1.44
Av.			8.3	31.6	20.7	37.5	2.0		4.51	1.44
Original Mixture - $O_2/C_2H_2 = 2$.										
331	20.5	10.6	6.1	20.3	48.0	23.9	1.7		3.92	1.48
332	16.5	16.0	6.0	20.2	47.6	24.2	2.0		4.03	1.49
349	14.6	19.6	5.6	20.1	48.0	24.3	2.0		4.34	1.49
333	13.2	23.6	5.8	20.3	47.8	24.3	1.8		4.20	1.48
334	10.5	34.6	5.6	20.5	48.4	23.7	1.8		4.24	1.43
335	8.4	51.8	5.4	20.5	48.2	24.1	1.8		4.47	1.44
Av.			5.8	20.3	48.0	24.1	1.8		4.20	1.47
Original Mixture - $O_2/C_2H_2/N_2 = 2/1/1$.										
336	15.2	18.2	4.1	14.6	34.6	17.5	0.7	28.5	4.26	1.48
337	12.2	26.6	4.0	14.7	34.3	17.6	0.6	28.8	4.40	1.47
Original Mixture - $O_2/C_2H_2 = 3$.										
354	15.8	17.5	4.3	14.5	62.0	17.4	1.8		4.05	1.50
355	12.7	25.6	4.1	14.8	62.6	16.8	1.7		4.10	1.41
352	10.0	38.8	4.2	14.8	61.5	17.7	1.8		4.22	1.48
353	7.9	57.2	4.2	14.6	62.0	17.4	1.8		4.14	1.48
Av.			4.2	14.7	62.0	17.3	1.8		4.13	1.47

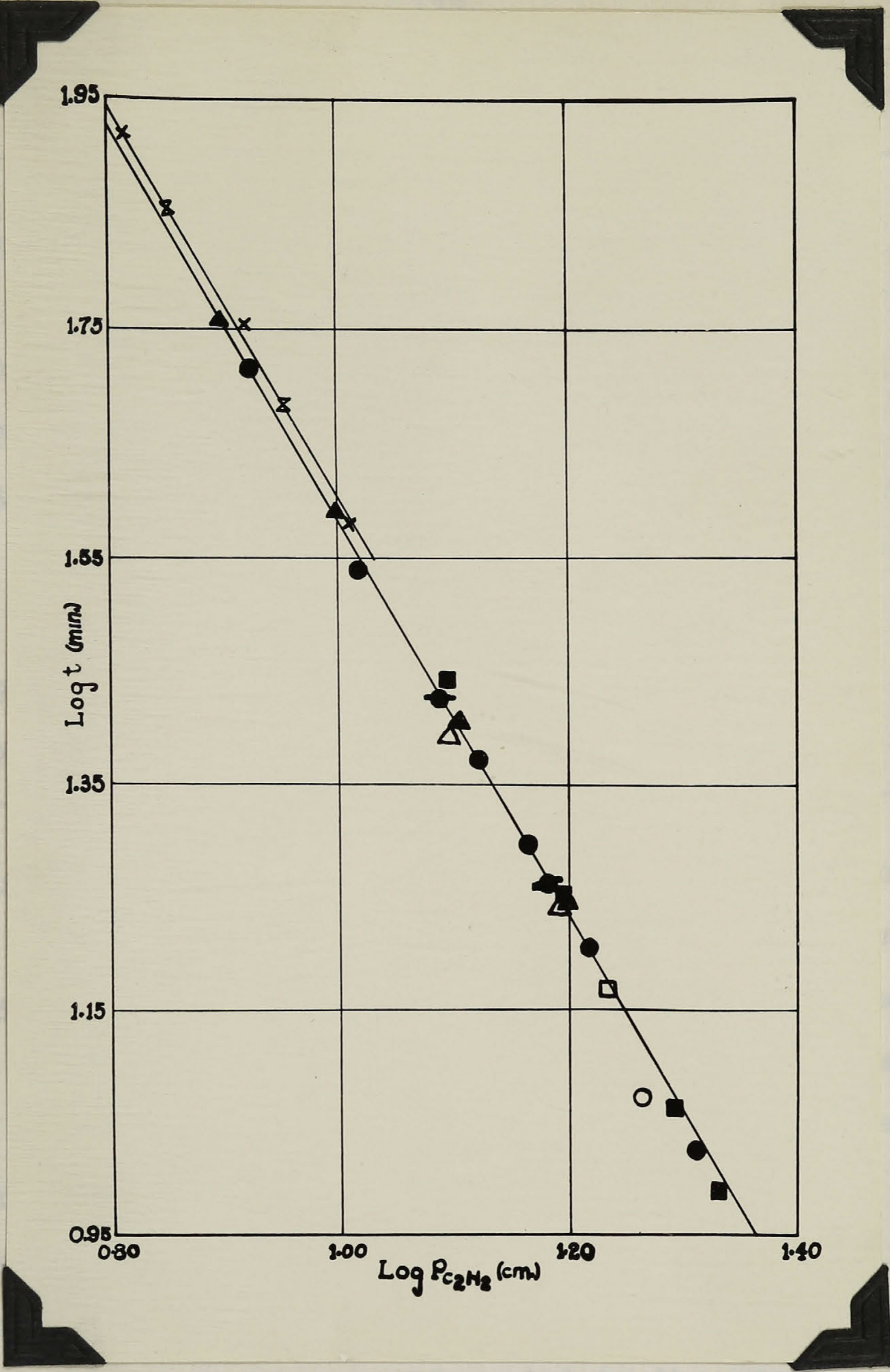


FIGURE 9.

EFFECT OF PRESSURE ON RATE. RUNS 331 - 364.

■ - 1:1 Mixture, direct. □ - Ditto, extrapolated.

● - 2:1 Mixture, direct. ○ - Ditto, extrapolated.

▲ - 3:1 Mixture, direct. △ - Ditto, extrapolated.

✕ - 5:1 Mixture, direct. ⧗ - 5:1 Mixture + N_2, direct.

-●- - 2:1 Mixture + N_2, direct.

TABLE 11 (Cont'd).

No.	$P_{C_2H_2}$ (cm.)	t (min.)	Composition of Sample - % CO_2	C_2H_2	O_2	CO	H_2	N_2	A	B
			Original Mixture - $O_2/C_2H_2 = 5$.							
338	10.3	38.0	3.1	9.6	74.0	11.6		1.7	3.74	1.53
339	8.2	56.5	2.9	9.7	74.0	11.7		1.7	4.03	1.51
340	6.5	83.0	2.9	9.5	74.4	11.4		1.8	3.93	1.51
Av.			3.0	9.6	74.1	11.6		1.7	3.90	1.52
			Original Mixture - $O_2/C_2H_2/N_2 = 5/1/1$.							
341	9.0	48.0	2.4	8.1	63.4	9.6	-	16.5	4.00	1.48
342	7.1	71.5	2.5	8.1	63.2	9.4	-	16.8	3.76	1.48

Unfortunately, after run 342 a breakage occurred which necessitated a delay of a day and a half and when the experiments were resumed, there were, at first, exceptionally large variations in the results. For that reason runs 343 to 347 have been dropped. At 348 the rate was approaching its original value, as shown by the corresponding point on the graph, this being the only extrapolated one with a 2:1 mixture. 349 was again on the line. Three runs with the 1:1 mixture have been omitted because the analyses could not have corresponded to the average at any stage of the reaction. However, aside from these variations, the series is in very good agreement. The lines give an order of 2.7 and indicate retardation by oxygen when it is in large excess but little, if any, effect when it is in moderate concentration.

Material balances may be set up for the runs in which a known amount of nitrogen was present. The calculation for run 336 will be given in detail here in order to illustrate the method, and in the presentation of any other data of this kind the intermediate steps will be omitted.

Two analyses of the mixture used in this and the following run agreed exactly on the composition C_2H_2 - 24.6%, O_2 - 49.0%, N_2 - 26.4%. In other words for each 26.4 parts of N the gas contained 24.6 parts C, 24.6 parts H and 49.0 parts O. The product gas contained 28.5% N_2. If this be called 57 parts N, it was originally associated with 53.1 parts C, 53.1 parts H and 105.8 parts O; any shortage from this in the actual analysis must correspond to condensable matter. Calculating the other constituents in the same way as the nitrogen, it is found that the gas contained 4.1 + 29.2 + 17.5 = 50.8 parts C (that is, %CO_2 + 2%C_2H_2 + %CO), 29.2 + 1.4 = 30.6 parts H and 8.2 + 69.2 + 17.5 = 94.9 parts O. The condensate, therefore, must have contained 2.3 parts C, 22.5 parts H and 10.9 parts O. The carbon will probably have been in the form of a mixture of formaldehyde, formic acid and glyoxal (88, 89). If it is arbitrarily assumed to have had the empirical formula CHO - certainly not correct, but probably a fair approximation - there is left over 20.2 parts H and 8.6 parts O. While this is not the composition of water it is near enough to it to justify the calculation. In these runs the percent of the acetylene which has reacted can also be determined. For 336 it is obviously 23.9/53.1 or 45.0%. For 337 it is 45.2%. Two analyses of the mixture used in runs 341 and 342 gave C_2H_2 - 14.1, 14.2; O_2 - 69.8, 69.6; N_2 - 16.1, 16.2. The percentage reactions are therefore 44.3 and 45.3.

The material balances for runs 337, 341 and 342 are:

	337			341			342		
	C	H	O	C	H	O	C	H	O
Calc.	53.6	53.6	107.0	29.1	29.1	143.0	29.6	29.6	145.4
Found	51.0	30.6	94.2	28.2	16.2	141.2	28.1	16.2	140.8
Diff.	2.6	23.0	12.8	0.9	12.9	1.8	1.5	13.4	4.6
If CHO	2.6	2.6	2.6	0.9	0.9	0.9	1.5	1.5	1.5
	-	20.4	10.2	-	12.0	0.9	-	11.9	3.1

The agreement with the formula H_2O is perfect for 337, but very poor for the other two. However, in these latter cases a small error in the nitrogen content has a large influence on the calculated oxygen, so that very exact results could not be expected. It is to be noted that in all but one of the four cases almost exactly 5% of the total carbon is in the condensable matter. This supports the assumption made in the calculation of the percentages reacted in table 8.

Runs with a Silica Bulb.

After run 364 there was another change in the rate obtained in the KCl-coated pyrex bulb. It was, therefore, replaced by a 200 cc. spherical silica bulb. At first the rates in this increased as much as 20% between successive runs and although the first determination showed the reaction to be slower in this than in the previous bulbs, the relations were soon reversed. After a few runs, however, the rate settled down and was then practically constant over a considerable time.

In this part of the investigation the series of lines shown in figure 10 was drawn up and all samples for analysis were taken at times read from the appropriate line. In the earlier runs with this bulb the dotted line was taken as the one for the 1:1 mixture but it was later found that better agreement was obtained if the full one, which is parallel to the other three, was used. All the slopes then correspond to orders of 2.7, which is that found in the last series of runs with the coated pyrex bulb. The relative positions assigned to the lines are largely arbitrary, their justification will depend on the results which are to follow. They correspond approximately to a negative order of 0.1 with respect to oxygen. This is believed to be the limit of accuracy in determining this value by the present method.

It is impractical to reproduce here the results of all of the experiments made with the silica bulb. Representative selections, only, will be given. Tables 12 and 13 contain all but two of the runs 395 - 424, the two omitted being duplicates of no particular interest. The series covers the four mixtures indicated in figure 10 and contains runs with added nitrogen for all but the high oxygen one. The times for the 1:1 mixture were taken from the dotted line in the figure. Table 14 contains the analyses of the initial mixtures which contained nitrogen, and the material balances calculated for the corresponding runs.

The percentage reactions for the different mixtures agree fairly well, although the variations are great enough to

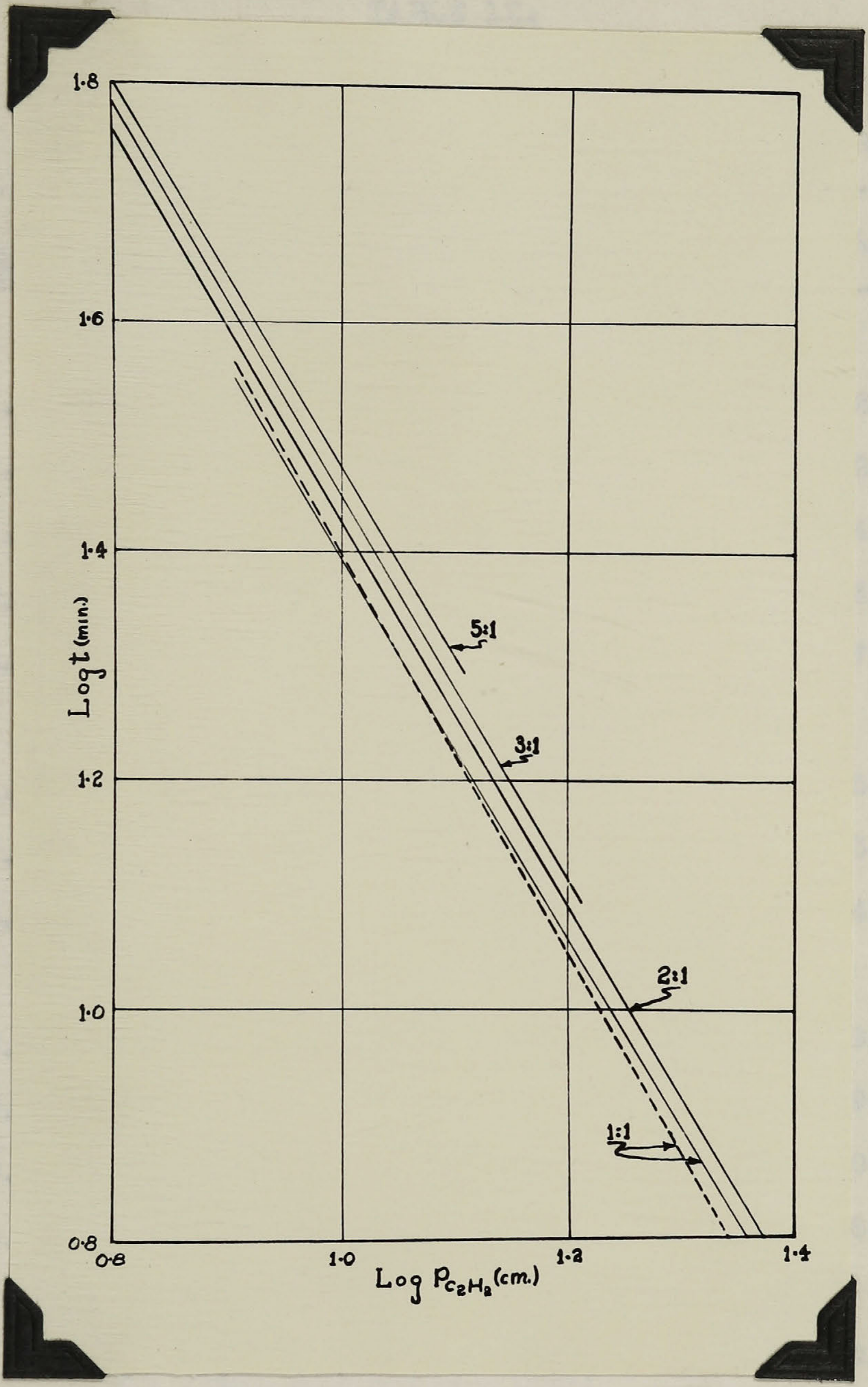


FIGURE 10.

EFFECT OF PRESSURE ON RATE.

Assumed for spherical silica bulb.

TABLE 12.

GAS ANALYSES FROM RUNS 395 - 424.

A = CO/CO_2. B = $(CO + CO_2)/C_2H_2$. C = $\%C_2H_2$ Reacted.

No.	$P_{C_2H_2}$ (cm.)	t (min.)	Composition of Sample - %						A	B	C
			CO_2	C_2H_2	O_2	CO	H_2	N_2			
			Original Mixture - $O_2/C_2H_2/N_2$ = 1/1/1.								
412	21.3	6.55	5.8	18.8	11.3	24.6	0.9	38.6	4.24	1.63	48.9
413	17.0	9.8	5.9	18.7	11.2	25.0	0.8	38.4	4.24	1.65	48.9
414	13.5	14.8	5.4	19.1	12.3	23.8	0.7	38.7	4.41	1.53	48.3
415	10.8	22.0	5.6	18.3	10.7	25.9	1.0	38.5	4.63	1.72	50.0
416	8.7	34.6	5.6	18.0	9.9	26.7	1.2	38.6	4.77	1.79	51.1
			Original Mixture - O_2/C_2H_2 = 1.								
409	21.7	6.45	9.6	29.5	14.9	43.4	2.6		4.52	1.79	-
410	17.3	9.5	9.4	30.3	16.5	41.1	2.7		4.38	1.67	-
411	13.7	14.3	9.7	29.1	15.4	42.9	2.9		4.42	1.81	-
			Original Mixture - $O_2/C_2H_2/N_2$ = 2/1/1.								
400	15.8	12.6	4.4	14.2	34.4	17.5	0.4	29.1	3.98	1.54	47.8
401	12.7	18.4	4.7	13.6	33.9	18.3	0.6	28.9	3.90	1.69	49.6
402	10.2	26.6	4.7	13.4	33.3	19.2	0.4	29.0	4.09	1.78	50.5
403	8.2	38.8	5.0	13.6	33.0	19.0	0.5	28.9	3.80	1.76	49.6
			Original Mixture - O_2/C_2H_2 = 2.								
395	21.2	7.7	6.3	19.6	47.2	25.1	1.8		3.98	1.60	-
396	17.0	11.1	6.3	19.9	46.7	25.4	1.7		4.03	1.59	-
397	13.5	16.0	6.5	19.6	46.2	25.8	1.9		3.97	1.65	-
398	10.9	23.8	6.5	19.0	45.4	27.3	1.8		4.20	1.78	-
399	8.6	35.0	6.0	18.6	44.9	28.7	1.8		4.78	1.87	-

TABLE 13.

SAME AS TABLE 12.

No.	$P_{C_2H_2}$ (cm.)	t (min.)	Composition of Sample - %						A	B	C
			CO_2	C_2H_2	O_2	CO	H_2	N_2			
			Original Mixture - $O_2/C_2H_2/N_2$ = 3/1/1.								
422	12.5	19.4	3.9	10.6	47.9	13.8	0.5	23.3	3.54	1.67	48.7
423	10.2	27.6	4.0	10.1	47.4	14.8	0.6	23.1	3.70	1.86	50.6
424	8.1	40.6	4.0	9.5	46.9	15.4	0.7	23.5	3.84	2.04	54.4
			Original Mixture - O_2/C_2H_2 = 3.								
404	15.8	13.8	5.0	13.7	61.0	18.5	1.8		3.70	1.71	-
405	12.7	19.2	5.1	13.6	60.3	19.3	1.7		3.78	1.79	-
406	10.2	27.4	4.7	13.9	59.9	19.7	1.8		4.20	1.76	-
407	8.1	40.6	5.1	13.4	59.4	20.3	1.8		3.98	1.89	-
408	6.5	58.6	4.9	13.0	59.3	21.0	1.8		4.28	1.99	-
			Original Mixture - O_2/C_2H_2 = 5.								
419	10.4	27.8	3.2	9.7	74.0	11.3	1.8		3.53	1.50	-
420	8.3	40.2	3.5	8.7	73.5	12.5	1.8		3.57	1.84	-
421	6.8	57.8	3.3	8.4	73.3	13.2	1.8		4.00	1.96	-

leave the correct relative positions of the log $P_{C_2H_2}$ - log t lines in doubt. A more evident discrepancy is to be found in the percentage reactions for different pressures with the same mixture. This tends to increase as the pressure decreases. The same effect is also apparent in the runs without added nitrogen, where the percentage reaction could not be accurately determined, for in these cases the ratio $(CO + CO_2)/C_2H_2$ which should be a measure of reaction increases in the same way.

TABLE 14.

ANALYSES OF MIXTURES AND MATERIAL BALANCES.

Analyses

	1:1:1 Mixture			2:1:1 Mixture			3:1:1 Mixture		
	a	b	Av.	a	b	Av.	a	b	Av.
$\%C_2H_2$	32.8	32.5	32.6	24.4	24.3	24.4	19.4	19.4	19.4
$\%O_2$	33.1	33.3	33.2	49.6	49.4	49.5	58.7	58.7	58.7
$\%N_2$	34.1	34.2	34.2	26.0	26.3	26.1	21.9	21.9	21.9

Material Balances.

	412			413			414		
	C	H	O	C	H	O	C	H	O
Calc.	73.6	73.6	74.9	73.2	73.2	74.5	73.8	73.8	75.1
Found	68.0	39.4	58.8	68.3	39.0	59.2	67.4	39.6	59.2
Diff.	5.6	34.2	16.1	4.9	34.2	15.3	6.4	34.2	15.9

	415			416			400		
Calc.	73.4	73.4	74.7	73.6	73.6	74.9	54.4	54.4	110.2
Found	68.1	38.6	58.5	68.3	38.4	57.7	50.3	29.2	95.1
Diff.	5.3	34.8	16.2	5.3	35.2	17.2	4.1	25.2	15.1

	401			402			403		
Calc.	54.0	54.0	109.4	54.2	54.2	110.0	54.0	54.0	109.4
Found	50.2	28.4	95.5	50.7	27.6	95.2	51.2	28.2	95.0
	3.8	25.6	13.9	3.5	26.6	14.8	2.8	25.8	14.4

% of Total Carbon in Condensable.

Run	412	413	414	415	416	400	401	402	403	422	423	424
%	7.6	6.7	8.7	7.2	7.2	7.5	7.0	6.5	5.2	5.8	4.7	5.5

TABLE 14 (Cont'd).

Material Balances.

	422			423			424		
	C	H	O	C	H	O	C	H	O
Calc.	41.3	41.3	125.0	40.9	40.9	123.9	41.7	41.7	126.0
Found	38.9	22.2	117.4	39.0	21.4	117.6	38.4	20.4	117.2
Diff.	2.4	19.1	7.6	1.9	19.5	6.3	3.3	21.3	8.8

The obvious explanation would be that the lines were drawn to correspond to too high an order and that the results would have agreed had the samples been timed by a slightly different set of lines. At the time when this work was being done, however, another explanation for at least part of the latter drift seemed possible. The percentage pressure changes corresponding to identical stages of the reaction vary regularly with the pressure, as mentioned previously, being greater at low than at high pressures. Thus in runs 395 - 399 the range was from 4.4 to 9.0% of the acetylene pressure. Since there are no differences in the composition of the products sufficiently marked to account for this, it seems logical to suppose that it is due to a change in the concentration of some intermediate oxygenated compound, perhaps $C_2H_2O_2$. Such a change is a reasonable one to assume since at high initial pressures the substance would be formed rapidly and would have little time to decompose, while at low ones it would be formed much more slowly and would have much more time to decompose. If it were removed by oxidation, according to the equation:

$$C_2H_2O_2 + \tfrac{1}{2}O_2 \longrightarrow 2CO + H_2O$$

there would be a marked difference in the composition of gases corresponding to the same percentage reaction. This would not be great enough, however, to account for the differences which actually occur. Moreover, there is no direct evidence in support of it from the material balances, although the accuracy attained in them might not be great enough for detecting variations in the condensable carbon compounds. Some support might be drawn from the fact that when the percentage reactions can be calculated with the 1:1 and 2:1 mixtures the drift is not as great as would be expected from the analyses in the absence of nitrogen. In view of the later work it seems possible that both factors are operating, that is, that the assumed order is slightly high and that there is a variation in the amount of the condensable carbon compounds.

In order to give more definite form to the ideas considered above, some actual calculations will be made for runs 395 and 399. To simplify the matter it will be assumed that the original mixture contained 33% C_2H_2, 66% O_2 and 1% N_2, that the sample corresponds to 50% reaction and that the changes can be represented by the over all equations:

$$(1)\quad C_2H_2 + 2\tfrac{1}{2}O_2 \longrightarrow 2CO_2 + H_2O$$

$$(2)\quad C_2H_2 + 1\tfrac{1}{2}O_2 \longrightarrow 2CO + H_2O$$

$$(3)\quad C_2H_2 + O_2 \longrightarrow C_2H_2O_2$$

which disregard the small amount of hydrogen formed.

Then if 2.8 parts acetylene react according to (1), 11.0 according to (2) and 2.7 according to (3), the pressure change will be equivalent to 1.4 parts, that is, 4.2% of $P_{C_2H_2}$ (run 395 - 4.4%) and the products after condensation of the water and $C_2H_2O_2$ should analyze: CO_2 - 6.6%, C_2H_2 - 19.4%, O_2 47.0%, CO - 25.9%, res. - 1.1%. This is in good agreement with the actual result in 395.

If, now, 1.0 part of the $C_2H_2O_2$ reacts according to

$$C_2H_2O_2 + \tfrac{1}{2}O_2 \longrightarrow 2CO + H_2O$$

the total pressure change will be 2.9 parts, that is, 8.8% of $P_{C_2H_2}$ (run 399 - 9.0%) and the product gases should analyze: CO_2 - 6.5%, C_2H_2 - 19.1%, O_2 - 45.5%, CO - 27.8%, res. - 1.1%. Thus, while such a scheme does not account for all of the difference between runs 395 and 399, it will explain considerably more than half of it. The variation in the condensable carbon would only be from 8.4% of the total at high pressures to 5% at low pressures which is not outside the limits shown in table 14 and, indeed, is about the same as that between runs 400 and 403.

The above case is by no means the most favourable one for showing this effect. For example, had 398 been calculated as above, 7.9% pressure increase (exp. - 7.7%) would have corresponded to a product of the composition: CO_2 - 6.5%, C_2H_2 - 19.2%, O_2 - 45.7%, CO - 27.4%, res. - 1.2%, which is in surprisingly good agreement with the actual result. Obviously this must be partly fortuitous since hydrogen has been neglected and since $C_2H_2O_2$ is certainly not the only condensable organic product.

However, in view of such results it seemed advisable to continue the investigation using the same diagram as before, except that the full line for the 1:1 mixture in figure 10 was used in determining when to remove the corresponding samples for analysis. The results are given in tables 15 and 16, and the material balances derived from them in table 17.

Since the results are very similar to those just discussed, they will not be considered in detail. The change in the timing with the 1:1 mixture has given values agreeing better than the previous ones, and probably within the experimental error.

It is to be noted that the first run with each mixture quite often gives an abnormally low rate. This has been a fairly general phenomenon throughout and is almost certainly connected with the fact that these runs are always the first ones of each day. In this regard some results of Kowalsky, Sadownikow and Tschirkow (104) may be quoted since they show an effect very similar to that observed here. Working with the ethane-oxygen reaction in silica bulbs, they found that marked ageing occurred. Thus, in one series $t_{\frac{1}{2}}$ changed from 760 to 375 seconds during eight runs, but went back to 455 in the ninth after standing twenty hours - behaviour identical with that mentioned above. In another series the change was twenty-fold. In a third $t_{\frac{1}{2}}$ went from 330 to 115 sec., then, when air was let in and allowed to stand for two days, the first run gave 180, the second 115--which agrees with the present observations that this disturbing effect acts only on the first run of each day. They found that

TABLE 15.

GAS ANALYSES FROM RUNS 440 - 470.

A = CO/CO_2. B = $(CO + CO_2)/C_2H_2$. C = $\%C_2H_2$ Reacted.

No.	$P_{C_2H_2}$	t	Composition of Sample - %						A	B	C
	(cm.)	(min.)	CO_2	C_2H_2	O_2	CO	H_2	N_2			
Original Mixture - O_2:C_2H_2:N_2 = 1:1:1.											
440	21.3	7.0	5.9	17.8	7.1	28.7	0.7	39.8	4.87	1.94	53.3
441	17.1	10.2	6.0	17.8	6.6	29.0	0.6	40.0	4.83	1.96	53.5
442	13.7	14.7	6.1	17.6	6.5	29.5	0.7	39.6	4.83	2.02	53.5
443	11.0	21.4	6.0	17.5	6.9	28.6	0.9	40.1	4.76	1.98	54.3
444	8.8	30.9	5.9	17.6	7.1	28.2	0.6	40.6	4.78	1.94	55.9
Original Mixture - O_2:C_2H_2 = 1.											
454	21.9	6.7	9.3	30.0	11.4	46.4	2.9		4.98	1.86	-
455	17.5	9.75	9.9	29.1	11.7	46.6	2.7		4.72	1.94	-
456	14.0	14.2	9.8	28.3	9.8	49.1	3.0		5.02	2.08	-
457	11.2	20.7	9.6	28.1	9.6	49.6	3.1		5.18	2.10	-
458	8.9	30.5	9.8	27.5	9.8	50.0	2.9		5.10	2.17	-
Original Mixture - O_2:C_2H_2:N_2 = 2:1:1.											
445	15.7	12.7	5.0	13.7	32.1	20.0	0.4	28.8	4.00	1.82	49.8
446	12.6	18.7	5.3	12.5	30.9	22.0	0.6	28.7	4.15	2.18	54.7
447	10.2	26.8	5.3	12.3	30.7	21.8	0.7	29.2	4.12	2.20	56.2
448	8.1	39.4	5.5	12.8	29.7	22.4	0.5	29.1	4.07	2.18	54.3
Original Mixture - O_2:C_2H_2 = 2.											
462	21.3	7.5	6.3	19.8	45.5	26.4	2.0		4.18	1.65	-
463	17.0	11.0	6.7	18.6	44.6	28.1	2.0		4.18	1.87	-
464	13.6	16.0	6.8	18.2	43.5	29.7	1.8		4.37	2.00	-
465	11.0	23.1	6.6	17.7	42.4	31.3	2.0		4.75	2.14	-
466	8.8	33.7	6.6	17.4	42.6	31.7	1.7		4.80	2.20	-

TABLE 16.

SAME AS TABLE 15.

No.	$P_{C_2H_2}$	t	Composition of Sample - %						A	B	C
	(cm.)	(min.)	CO_2	C_2H_2	O_2	CO	H_2	N_2			
Original Mixture - O_2:C_2H_2:N_2 = 3:1:1.											
449	12.7	19.0	4.2	10.7	46.0	15.6	0.5	23.0	3.72	1.85	50.9
450	10.1	27.7	4.3	10.5	45.3	16.4	0.3	23.2	3.82	1.97	52.3
451	8.1	40.7	4.3	10.4	45.3	16.4	0.4	23.2	3.82	1.99	52.7
Original Mixture - O_2:C_2H_2 = 3.											
467	15.9	13.1	4.8	13.6	62.1	17.8	1.7		3.71	1.66	-
468	12.7	19.4	5.0	12.9	59.9	20.2	2.0		4.04	1.95	-
469*	10.3	28.8	5.3	12.5	58.7	21.7	1.8		4.10	2.16	-
470	8.2	39.7	5.4	12.5	58.1	22.1	1.9		4.10	2.20	-
Original Mixture - O_2:C_2H_2:N_2 = 5:1:1.											
452	9.1	34.6	3.0	8.1	60.9	10.7	0.2	17.1	3.57	1.69	47.0
453	7.2	51.3	3.1	7.3	60.7	11.2	0.3	17.4	3.62	1.96	53.2
Original Mixture - O_2:C_2H_2 = 5.											
459	10.5	27.0	3.5	9.0	72.4	13.6	1.5		3.89	1.90	-
460	8.5	39.1	3.8	8.8	71.4	14.3	1.7		3.76	2.06	-
461	6.8	57.6	3.9	8.6	70.7	15.0	1.8		3.84	2.20	-

* Sample should have been taken at 27.8 rather than 28.8 min.

ANALYSES OF MIXTURES.

1:1:1 C_2H_2 - 33.1, 32.9; O_2 - 32.4, 32.5; N_2 - 34.5, 34.6.

2:1:1 C_2H_2 - 25.1, 24.9; O_2 - 49.1, 48.8; N_2 - 25.8, 26.3.

5:1:1 C_2H_2 - 14.3, 14.5; O_2 - 69.6, 69.4; N_2 - 16.1, 16.1.

3:1:1 C_2H_2 - 19.9, 20.1; O_2 - 59.1, 58.8; N_2 - 21.0, 21.1.

TABLE 17.

MATERIAL BALANCES.

	440			441			442		
	C	H	O	C	H	O	C	H	O
Calc.	76.1	76.1	75.0	76.5	76.5	75.4	75.7	75.7	74.6
Found	70.2	37.0	54.7	70.6	36.8	54.2	71.0	36.8	54.7
Diff.	5.9	39.1	20.3	5.9	39.7	21.2	4.7	38.9	19.9

	443			444			445		
Calc.	76.7	76.7	75.5	77.7	77.7	76.3	55.5	55.5	108.7
Found	69.6	36.8	54.4	69.3	36.4	54.2	52.4	28.2	94.2
Diff.	7.1	39.9	21.1	8.4	41.3	22.1	3.1	27.3	14.5

	446			447			448		
Calc.	55.2	55.2	108.1	56.2	56.2	110.0	56.0	56.0	109.6
Found	52.3	26.2	94.4	51.7	26.0	93.8	53.5	26.6	92.8
Diff.	2.9	29.0	13.7	4.5	30.2	16.2	2.5	29.4	16.8

	449			450			451		
Calc.	43.9	43.9	129.3	44.2	44.2	130.4	44.2	44.2	130.4
Found	41.2	22.4	116.0	41.7	21.6	115.6	41.5	21.6	115.6
Diff.	2.7	21.5	13.3	2.5	22.6	14.8	2.7	22.6	14.8

	452			453		
Calc.	30.6	30.6	147.7	31.1	31.1	150.2
Found	29.9	16.6	138.5	28.9	15.2	138.8
Diff.	0.7	14.0	9.2	2.2	15.9	11.4

% of Total Carbon in Condensable.

Run	440	441	442	443	444	445	446	447	448	449	450	451	452	453
%	7.8	7.7	6.2	9.3	10.9	5.6	5.3	8.0	4.5	6.2	5.7	6.1	2.5	7.1

heating to high temperatures further increased the rate but that hour long pumping had no effect. In the present work the most reproducible results were obtained when no precautions at all were taken, that is, when the runs were made as quickly as was convenient, without prolonged pumping or any heat treatment between them. In the later experiments some of the reacting gas was left in the bulb over night in the hope that this would reduce the effect of standing. However, there was little action, either favourable or unfavourable.

It would appear, therefore, that the particularly low results in 445, 449, 452, 462 and 467 should be overlooked. In that case the runs with the different mixtures agree fairly well, so that the retarding effect attributed to oxygen when the lines were drawn up seems to be confirmed. As in the previous series, however, there is a slight change in going from high to low pressures, so that the order may be incorrect. The material balances again fail to establish definitely whether there is any drift in the amount of condensable carbon. In the present series of runs the drift in the $(CO + CO_2)/C_2H_2$ ratio is much more pronounced in the absence of nitrogen than in its presence. This may be only chance, in any case no explanation of it can be offered here.

As a final check on the order, a series of runs was made with a 2:1 mixture and the samples removed at times which would correspond to an order of 2.5. The reaction bulb had been removed and left open to the air for about two weeks between this and the series just discussed and, unfortunately, in that time must have undergone marked changes. Thus, when the times

TABLE 18.

GAS ANALYSES FOR RUNS WITH ASSUMED ORDER 2.5

$A = CO/CO_2$. $B = (CO + CO_2)/C_2H_2$.

No.	$P_{C_2H_2}$ (cm.)	t (min.)	Composition of Sample - % CO_2	C_2H_2	O_2	CO	Res.	A	B
Samples Taken at Usual Times.									
500	19.0	8.8	2.9	28.0	56.5	10.9	1.7	3.76	0.49
501	15.4	12.0	3.1	27.7	55.4	12.0	1.8	3.86	0.54
502	12.5	16.5	3.2	27.6	55.6	12.0	1.6	3.74	0.55
503	9.9	23.1	3.0	27.7	55.4	11.9	2.0	3.97	0.54
504	7.9	32.5	3.2	27.4	56.1	11.5	1.8	3.59	0.54
505	6.3	45.3	2.5	27.5	57.5	10.8	1.7	4.32	0.48
Samples Taken After Three Times as Long.									
510	21.0	22.7	8.4	19.1	43.6	26.7	2.2	3.18	1.84
511	13.9	42.0	8.1	19.5	44.1	26.1	2.2	3.22	1.75
512	10.1	67.0	7.9	19.7	45.3	25.2	1.9	3.19	1.66

were almost identical with those of the previous runs, the percentage reaction was less than 25 compared with about 53 above. This would correspond to a four-fold change in rate. It was quite surprising, therefore, that there was no ageing effect in the results. Sometime later another group of runs was made, the samples being taken at times which were three times those which would have been used in the series just mentioned. Both are given in table 18. After the first run there were no erratic variations despite the fact that the evacuations between runs were rarely more than thirty minutes. With the short reaction times the agreement throughout the series is quite good, although at the low pressure in 505 there is somewhat less reaction. In the longer runs, which, as stated previously, are likely to be more accurate, the trend towards smaller percentage changes at lower pressures is quite definite. It is evident, therefore, that the order of the reaction is greater than 2.5.

In view of the difference between this value and that found by Spence and Kistiakowsky (89) it was of importance to determine whether the order varied with the stage of the reaction, as has often been reported for hydrocarbon oxidations. In order to avoid the effect, if any, of changing O_2:C_2H_2 ratio a 3:2 mixture was taken. This is approximately the proportion in which the gases are used up. The runs were made while the bulb was in its more reactive state and the samples were taken at periods 1/3 and 3 times those indicated by a line intermediate between the 1:1 and 2:1 lines in figure 10. The results are given in table 19. Unfortunately, during the time this work was being done there was a leak in the acetylene storage bulb so that successive mixtures contained slowly increasing amounts of nitrogen, and all of them contained much more of it than had any of the previous mixtures. Nevertheless, since these runs serve the desired purpose, they were not repeated. In the table, three different lots of the mixture are represented, the corresponding groups of runs being 475 - 7, 478 - 81 and 482 - 5.

The $(CO + CO_2)/C_2H_2$ ratio changes considerably in going from high to low pressures with both the short and long

TABLE 19.

GAS ANALYSES FOR RUNS WITH DIFFERENT REACTION TIMES.

3:2 Mixture. Temp. 320° C. Assumed order 2.6.

$A = CO/CO_2$. $B = (CO + CO_2)/C_2H_2$.

No.	$P_{C_2H_2}$ (cm.)	t (min.)	Composition of Sample - % CO_2	C_2H_2	O_2	CO	Res.	A	B
		Samples Taken at 1/3 the Standard Times.							
483	21.2	2.45	3.0	29.0	49.2	14.5	4.3	4.83	0.60
478	21.4	2.42	3.3	29.4	48.0	15.0	4.3	4.55	0.62
479	13.9	5.0	3.4	28.8	47.2	16.3	4.3	4.80	0.68
484	13.9	5.05	3.0	28.6	48.1	16.0	4.3	5.33	0.66
480	9.4	9.9	4.0	27.8	45.7	17.9	4.6	4.47	0.79
477	9.5	9.6	3.9	27.7	45.2	18.7	4.5	4.80	0.81
		Samples Taken at Three Times the Standard Times.							
482	22.1	20.4	11.3	13.5	25.3	44.7	5.2	3.96	4.15
475	22.8	19.3	12.1	14.0	21.1	48.0	4.8	3.98	4.29
476	17.1	31.7	12.9	13.2	19.3	50.0	4.7	3.87	4.75
485	14.3	43.0	11.7	12.6	21.6	48.9	5.2	4.17	4.88
481	9.3	89.0	12.4	11.7	19.3	51.7	4.9	4.17	5.48

periods of reaction. However, the relative changes are about the same. Thus, the value for run 481 divided by the average of those for 475 and 482 gives 1.30, while the average for 478 and 483 divided by that for 477 and 480 also gives 1.30. Admittedly, this is not an exact test - it would have been preferable to choose times such that the $(CO + CO_2)/C_2H_2$ ratios were constant in both sets - but it is surely sufficient to demonstrate that there is no appreciable change in order over a nine-fold difference in reacting times.

These runs also afford an opportunity for testing the method of extrapolation used in the treatment of the earlier series of experiments. Runs 482 and 483 are under almost identical conditions except for the difference in times and, therefore, according to the integrated rate equation the relation

$$(1/(a - x)^{n-1} - 1/a^{n-1}) = 9(1/(a - x)^{n-1} - 1/a^{n-1})$$

should hold for them (the 9 comes from the ratio of the two times). At the earlier stage in the reaction the percent of the total carbon in the condensable matter will probably be higher than in the corresponding runs for which the carbon balances have been given in table 17. Nevertheless, as an approximation we may assume that in 483 it is 8%. This gives the percentage reaction in that run as 28.8. Substituting this in the above equation and putting $x = ya$ and $n = 2.6$, we get

$$1/(1 - y)^{1.6} - 1 = 9(1/0.712^{1.6} - 1)$$

On solving, this gives $y = 0.716$, that is, the percentage reaction in run 482 should be 71.6. If 5% of the total carbon in that case is in the condensate the actual value is 69.0%, which is in fairly good agreement. For the 3:1 ratio of times the percentage reaction is calculated to be 51.3. This is approximately what would be expected since in run 440, table 15, the value was 53.3%, while in the present case the presence of nitrogen in the acetylene would reduce the concentration somewhat and, therefore, decrease the percentage reaction.

Runs 480 and 481 can be treated in the same manner. With the same assumptions as above, the percentage reaction in the former of these is 33.6 and in the latter is 74.5. The calculated value is 75.1. The intermediate one works out to 56.0 which, while rather high, is certainly not unreasonably so. Similar calculations should have been possible in the case of the runs in table 18. However, between the two series shown there, there had been an explosion in the bulb and it had been removed and open to the air for a time. Changes in activity were, therefore, quite possible and, indeed, there was direct evidence that they had occurred, the rate being greater after than before the explosion. In accordance with this the actual percentage reaction is somewhat greater than the calculated. It is evident, therefore, that, within the experimental error, the reaction follows an order of 2.6 over at least 75% of its course and that extrapolations based on this assumption are justified.

Temperature Coefficient.

In view of the wide difference between the value found for the temperature coefficient of the reaction from the results in the presence of P_2O_5 (20,000 cals.) and that reported by Spence and Kistiakowsky (34,700 cals.) it was of considerable importance to check the value by the present method. Since it was apparent from the first run that the results here would correspond to a value nearer the 34,700, the times for taking the samples have been calculated on the basis of a value of 35,000. The results are given in table 20. Because of the

TABLE 20.

TEMPERATURE COEFFICIENT.

A = CO/CO_2.   B = $(CO + CO_2)/C_2H_2$.

No.	Temp. °C.	$P_{C_2H_2}$ (cm.)	t (min.)	Composition of Sample - % CO_2	C_2H_2	O_2	CO	Res.	A	B
473	280	12.4	140	6.5	18.8	47.3	24.6	2.8	3.79	1.65
472	300	12.9	46.3	6.8	17.9	44.5	28.1	2.7	4.13	1.95
471	320	13.3	16.5	6.3	17.9	45.7	27.5	2.3	4.36	1.89
474	340	13.3	6.6	5.7	18.9	46.8	26.0	2.6	4.55	1.68

rapid change of rate with concentration it is important that the comparisons be made at constant concentration rather than at constant pressure. Allowance has been made for this. Thus, in the case of run 474, the time has been increased by the amount necessary to neutralize the decrease in concentration. While the agreement among the whole four is by no means entirely satisfactory, that between the pairs of analyses for 300° and 320° and for 280° and 340° is very good. The coefficient, therefore, cannot be more than one or two thousand calories off from 35,000 cals.

A second series of runs was made with the same bulb at a later stage when it was giving a much slower rate. However, the results were not very satisfactory. With reaction proceeding so slowly it was impractical to go below 300° and at 360°, although calculation indicated that several minutes should have been required for fifty percent reaction - a much slower rate than others previously realized - there was an almost immediate explosion. No carbon was deposited. The three values obtained at other temperatures were quite erratic and, while not supporting this value, at least did not support any other. They will not be reproduced here. Since the exact magnitude of the temperature coefficient is not of great importance, no further attempt was made to determine it accurately.

Effect of Packing.

Since it was not convenient to pack the spherical silica bulb used in the above experiments, the effect of an increase in surface was investigated in a cylindrical silica bulb of about 125 cc. capacity. The packing consisted of several lengths of quartz capillary and was rather loose, the top quarter of the bulb being entirely unaffected. The results are shown in table 21 and figure 11. The points in the figure only indicate the times when the samples were taken and acquire significance only when considered in connection with the corresponding analyses. The lines, which represent equal reaction, are drawn in what seemed the most likely position on the basis of the data given. Neither of them may be entirely correct, but they certainly show the general relation between the two series. It will be noted that the rate in this open bulb is much less than that in most of the runs in the spherical bulb and is more closely comparable with runs 500 - 505 in table 18.

The effect obtained is somewhat surprising since the rate is decreased at high pressures and increased at low pressures. It would appear that this was actually due to a variation in the relative importance of two effects - a decrease in the rate of formation of carbon monoxide and an increase in that of

TABLE 21.

EFFECT OF PACKING.

A : CO/CO_2. B = $(CO + CO_2)/C_2H_2$.

D : No. of Corresponding Point in Figure 11.

No.	D	$P_{C_2H_2}$	t	Composition of Sample - %					A	B
		(cm.)	(min.)	CO_2	C_2H_2	O_2	CO	Res.		
				Packed Bulb.						
486	1	22.8	25.0	7.1	27.0	53.1	11.1	1.7	1.56	0.67
487	2	19.9	30.6	8.8	26.4	52.4	10.7	1.7	1.21	0.74
488	3	17.4	30.8	8.7	27.2	52.8	9.4	1.9	1.08	0.67
489	4	10.1	47.0	13.9	25.5	50.4	8.0	2.2	0.58	0.86
490	5	12.7	36.4	10.9	26.8	52.4	7.7	2.2	0.71	0.69
491	6	12.3	36.0	11.4	26.7	52.3	7.4	2.2	0.65	0.70
492	7	9.4	39.3	13.0	26.7	51.9	6.1	2.3	0.47	0.71
				Open Bulb.						
494	8	19.8	16.0	4.7	27.0	55.7	10.9	1.7	2.32	0.58
495	9	17.0	30.5	5.9	25.4	52.9	14.0	1.8	2.37	0.78
496	10	14.6	29.2	5.0	26.4	54.5	12.4	1.7	2.48	0.66
497	11	12.5	34.0	4.9	26.0	55.4	12.2	1.5	2.49	0.66
498	12	22.5	19.7	5.9	25.6	52.0	14.9	1.6	2.52	0.81
499	13	11.3	38.8	4.9	26.9	53.9	12.6	1.7	2.57	0.65

carbon dioxide. Since the order of the reaction in the packed bulb approaches one as the carbon dioxide formation becomes predominant it would be natural to conclude that it was formed by a first order surface reaction which was quite distinct from that giving the carbon monoxide. The latter, since it

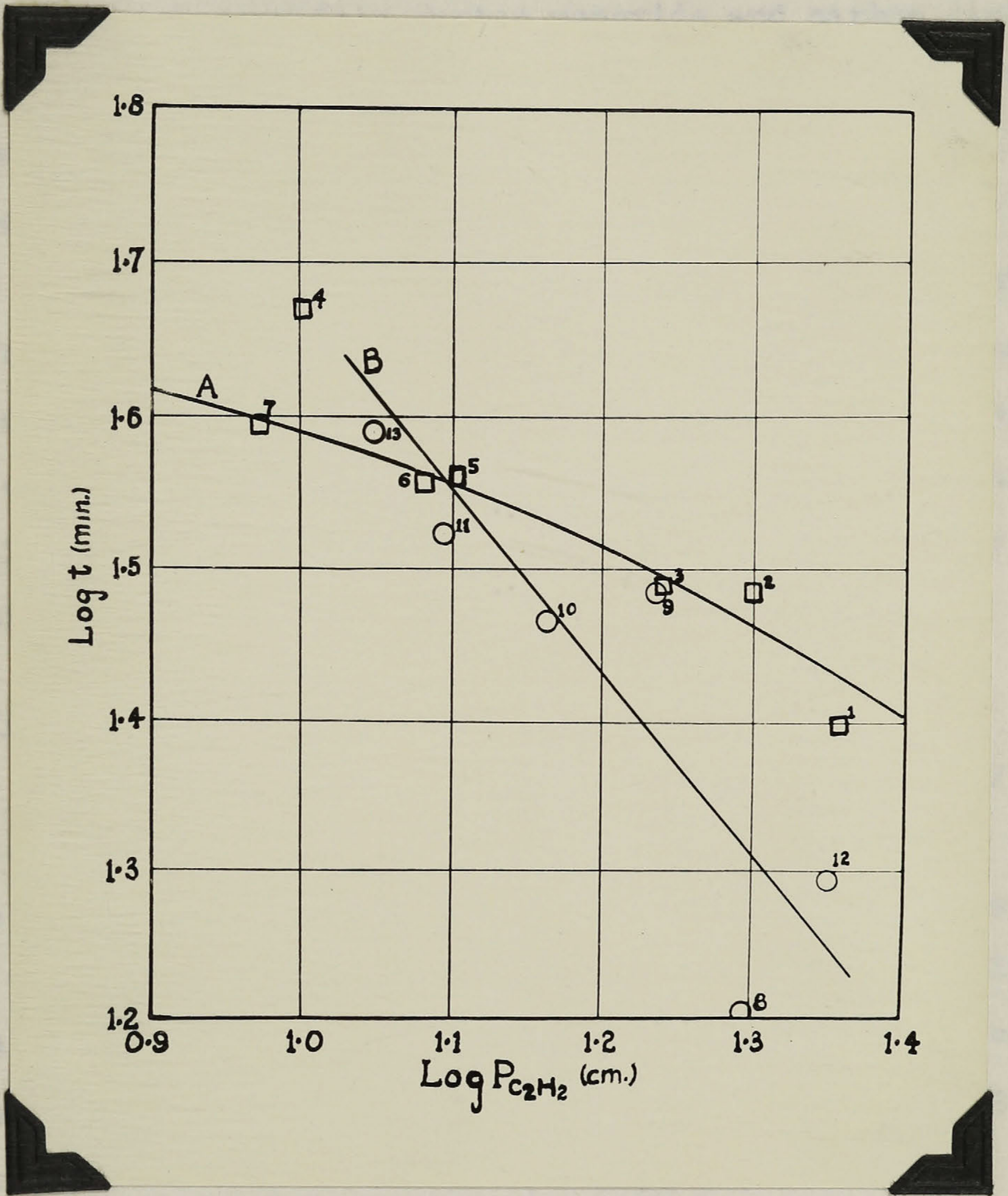


FIGURE 11.

EFFECT OF PACKING.

A - Packed bulb. B - Unpacked bulb.

Numbering of points as indicated in table 21.

was retarded by packing, must have been a chain reaction. However, there are reasons for rejecting any explanation of the results which considers carbon monoxide and carbon dioxide formation as two separate processes. Since these will be brought forward in the discussion, the matter will not be gone into any more thoroughly here.

It will be observed that the line for the unpacked bulb corresponds to an order of 2.2, which is lower than that found in the other bulbs. This may be partly due to error in placing it, although the pronounced shift in its position which would be required to give an order of 2.6 would hardly be compatible with the results.

Effect of Additions of Glyoxal.

Since glyoxal has often been assumed to play an important part in the oxidation of acetylene (88, 89, 29e), it was of interest to investigate the effect of additions of it on the rate of reaction. As has been pointed out by Steacie and Plewes (85), any substance which acts as a chain carrier must greatly increase the rate when added to the reaction mixture. The results obtained with glyoxal are shown in table 22. Before the series was begun, about 15 cm. of acetylene was let into the reaction bulb and then about 10 cm. of oxygen was added, the intention being to eliminate the effect of a low rate in the first run of the series, which had been so often encountered previously. Surprisingly enough, there was an immediate inflammation with a lurid flame and deposition of carbon in

TABLE 22.

EFFECT OF GLYOXAL.

C = % of C_2H_2 Reacted.   E = P_{CHOCHO}.

No.	$P_{C_2H_2}$	E	t	Composition of Sample - %						C
	(cm.)	(cm.)	(min.)	CO_2	C_2H_2	O_2	CO	H_2	N_2	
514	15.7	-	12.1	2.4	19.7	42.0	8.0	0.2	27.9	23.0
515	12.4	1.1	17.7	3.3	19.4	40.0	9.4	0.3	27.6	23.6
516	9.6	2.55	26.5	5.8	18.1	33.5	15.7	0.3	26.6	25.8
517	8.2	-	35.7	2.6	19.8	41.9	7.5	0.4	27.8	22.6

the capillary and, presumably, in the reaction bulb. It is to be emphasized that these were only the normal reactants without addition of glyoxal, the result being mentioned here since, because of it, the subsequent runs might have been affected by the presence of carbon. It should also be noted that had the gases been mixed previously, it would have taken at least 12 minutes for 25% reaction.

The glyoxal used was prepared by warming a mixture of paraglyoxal and phosphorus pentoxide and was kept in CO_2-acetone cooling mixture. It was admitted directly to the reaction bulb and the mixture of oxygen and acetylene was then added. At 320° glyoxal does not decompose appreciably (93), so that there was no possibility of its destruction before the other gases were let in. In order to permit the calculation of the percentage reaction for the acetylene all runs were made in the presence of a known amount of nitrogen, the original mixture analyzing - C_2H_2 - 24.7%, O_2 - 48.4%, N_2 - 26.9%.

Due to the oxidation of the glyoxal, the pressure change curves were entirely different from the normal ones and, of course, the composition of the products was also affected.

The samples were removed at times arrived at on the assumption of an order of 2.6 with respect to the acetylene and oxygen pressure. The agreement between runs 514 and 517 is sufficient justification for this procedure. The results indicate that glyoxal at a concentration of 9.0% of the acetylene has no appreciable effect. At 26.5% of the acetylene pressure it increases the rate slightly, but this is probably to be explained merely as a disturbance of the normal energy distribution due to the energy liberated by the glyoxal oxidation. In any case, the additional amount of acetylene which reacts is only about one molecule for every ten of glyoxal.

In this series the samples have been taken at an early stage since, had the additions had any effect, it would have been most pronounced before they had been entirely removed. From the pressure change data it seems probable that a little glyoxal was still present in each case, but this is not certain.

The results show beyond reasonable doubt that glyoxal is not a chain carrier in the acetylene oxidation.

Discussion.

Despite the difficulties experienced in obtaining reproducible results this investigation has succeeded in its main purpose, that is, in providing by the static method data which will permit a more exact treatment of the kinetics of the acetylene oxidation. It now remains to collect and correlate that data.

It has been evident throughout the investigation that the order of reaction was between two and three, and a great deal of effort has been expended in determining it more exactly. The extreme values indicated in the different figures for spherical bulbs have been 2.4 and 2.85. The most probable value might, therefore, be considered to be 2.6 and, indeed, the later and more satisfactory work favours that value. On the basis of it the order would be 2.6 ± 0.1, and this will be adopted here. Over the range of concentrations studied, oxygen exerts a slight retarding effect corresponding to a negative order not greater than 0.1. The rate equation may therefore be written

$$-d[C_2H_2]/dt = K\frac{[C_2H_2]^{2.7}}{[O_2]^{0.1}}$$

From the results with the packed bulb which seemed to indicate that CO_2 was formed by a first order surface reaction, it would appear possible that the above order was the resultant of a higher one for the main reaction and this lower one. Actually, however, there is a great deal of evidence opposing this view. If part of the CO_2 were formed in a reaction quite distinct from the main one, the CO/CO_2 ratio would be dependent on the relative rates of the two reactions. If, as would be indicated in the present case, the rate of CO_2 formation was directly dependent on the pressure while that of CO formation was dependent on the 2.6th power of the pressure, a change reducing the latter 17 times would only reduce the former 3 times. Even if only 20% of the CO_2 were formed at the surface at the higher pressure, the CO/CO_2 ratio in these experiments should, then, drop from about 4 to about 2 in going from acetylene pressures of 21 cm. to ones of 7 cm. A consideration of the tables will show that it is, instead, remarkably constant. If there is any trend it is in the opposite direction.

By analogous reasoning it can be shown that if separate reactions of the above type were involved the CO/CO_2 ratio should decrease throughout the course of the reaction. This apparently does occur to a limited extent in the present work and Bone (27e), on varying the times from one hour to seven days with similar mixtures in sealed bulbs, observed that this ratio varied as widely as from 20 to 2. By shortening the contact times in their flow experiments Lenher and Kistiakowsky (88) obtained much the same results. However, these can be satisfactorily explained on the basis of secondary reactions of the intermediate products and so are not so important as the absence of effect with varying initial pressure.

Finally, it would hardly be expected that both rates would vary to the same degree when bulbs aged, yet the CO/CO_2 ratio is reasonably constant throughout.

It may be concluded, therefore, that only one initial reaction is involved and that the CO_2 is derived from some substance formed in the course of the acetylene oxidation. Presumably, the increase in its amount in a packed bulb would indicate that packing shifted the balance in favour of oxidation rather than decomposition of the substance. An increase in the oxygen would seem to have the same effect - as would be expected. It will be noted that in tables 15 and 16 the CO/CO_2 ratio is less in the presence of nitrogen. This may be only chance, in any case, there is no obvious explanation for it.

The most apparent difference between the results of this and previous investigations has been with regard to the order, the highest one considered elsewhere (88, 89, 95) having been two. This may be due to their use of the flow method, for Kowalsky, Sadownikow and Tschirkow (104) investigating the CH_4 - O_2 reaction by this method found that the rate of water formation was constant and commented on the fact that Spence and Kistiakowsky had obtained similar results with C_2H_2 - O_2. They conclude "we see, therefore, that no stationary process takes place in the gas stream and that it is impossible to carry out the calculation in the same way as for a closed vessel. For that reason the flow method cannot be used for the investigation of this process" (translated from the German). However, the results with the packed bulb suggest another explanation. If the reduction in effective diameter realized there can reduce the order practically to unity, it is possible that even static experiments in a narrow tube, such as was used in the flow method, might show an order as low as two. Presumably, if that were the correct explanation, the CO/CO_2 ratio should be lower in their work but, unfortunately, none of the data which they give is strictly comparable to that from the present investigation. On the whole, then, there is nothing surprising in these differences in order.

The results in the presence of P_2O_5 are much more difficult to correlate with the later ones. Since they were very erratic and the conclusions rather uncertain, it is hardly worthwhile to spend much time on them. If the higher order were conditional on the accumulation of some intermediate compound which was removed by diffusion to the P_2O_5, the results would be similar to those actually obtained. However, it is not very clear how that could be the case. It is interesting, though, that in the flow method, where such substances would be frozen out in the traps and in the runs with the packed bulb, where they could be oxidized at the surface, the orders are also low. The difference in the temperature coefficients in the two arrangements might perhaps be explained by the assumption that in the special bulb, the temperature coefficient of diffusion was partly responsible for the final result.

Since the appearance of any retardation on packing is an indication of a chain mechanism, there can be no doubt that the oxidation of acetylene is a chain reaction. However, if the conclusions reached above with regard to the CO_2 formation are accepted, it necessarily follows that the chains are started at the surface, since packing may actually have an accelerating effect at low pressures. Moreover, since if the chains were all broken at the surface, any kind of packing must cause retardation - as pointed out in the general introduction - it also follows that most of the chains must be broken in the gas. This finds support in the observation that addition of nitrogen has no appreciable effect on the rate. It would seem that these conclusions constituted an anomaly, since they would appear to require that the effect of surface in chain breaking become relatively less at low pressures (since the retardation is at high pressures) where chains reached the surface most readily. However, it is possible to overcome this difficulty if it is assumed that chain breaking in the gas phase occurs by spontaneous rearrangement or decomposition of the chain carriers between collisions and that most chains are reflected from the surface without being broken. Neither concept is in any regard new. The former is essentially that involved in the theory of unimolecular reactions and applied to the present case it would result in an increase in gas phase deactivation as the pressure decreases, which is what is required. The second concept has been suggested by Sadownikow (105) to explain the results he obtained with the ethane oxidation, where he found that treatment of the bulb with HF made it possible to obtain reproducible results for at least six months, and eliminated entirely the retarding effect of packing.

With the chains being initiated at the surface and a part of them broken there, it is not surprising that the measured rates were very erratic. It is ,of course, impossible to say which of the two processes was responsible for the variations, although if surface deactivation accounts for only a small part of the total chain breaking, changes in it could hardly cause three or four-fold changes in the rate.

Since the first run of each day was often slow, it would appear that some of the variable effects were due to substances adsorbed on the wall. Possibly these are reaction products, although that remains to be proven.

The inflammation observed when acetylene alone was admitted first to the reaction bulb (page 162) suggests an interesting line for further investigation. Since the previous workers have covered fairly thoroughly the various mixture compositions, without obtaining ignition at 320°, it can hardly be explained on the assumption that interdiffusion of the gases resulted in concentration conditions favourable to rapid reaction in one particular zone. Rather, it must have resulted from an action of the acetylene on the vessel walls. At present it is tempting to assume that, under normal conditions, oxygen is so strongly adsorbed as to prevent many chains starting from the wall, but that, in this particular case, the acetylene was able to clean it off and then, when the oxygen was added, surface initiation was so rapid as to give an explosion. A theory can hardly be based on one result but, since it should be easy to check it, it has been mentioned here.

The development of mechanisms with which to fit their experimental results continues to be a favourite mental relaxation for those who are in any way concerned with chain reactions in general, or with hydrocarbon oxidations in particular. So long as each worker feels called upon to suggest his own mechanism, forsaking all others, there seems little hope for any great progress in this direction. Nevertheless, in deference to custom, such a treatment of the acetylene oxidation will be introduced here. Before proceeding with it, however, it will be of advantage to collect all of the facts from this or other investigations which have a bearing on the subject.

The main products of the complete reaction are CO, CO_2 and water. Hydrogen is formed only in traces. The CO/CO_2 ratio in unpacked bulbs is about four for intermediate stages but is higher in the first few moments (88, 27e) and may fall off in the later stages (27e). It is decreased by packing. Glyoxal, formaldehyde and formic acid are formed as intermediate products (88, 89). A peroxide may be isolated under proper conditions (73).

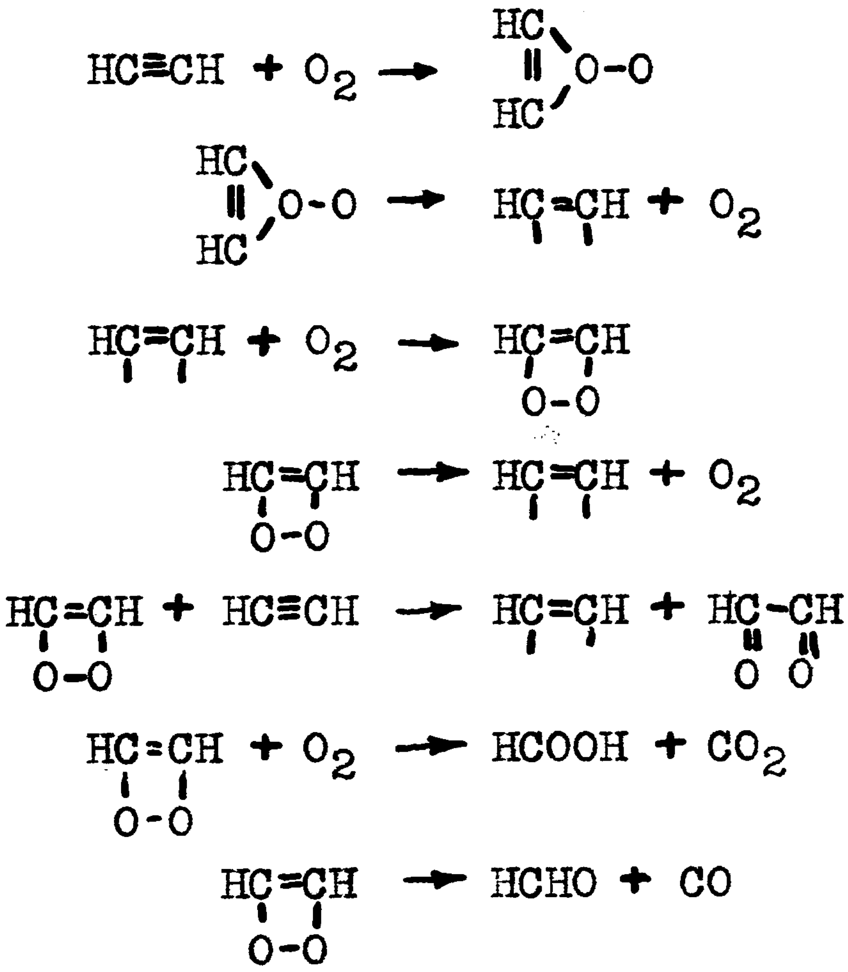
The order is about 2.6, being made up of an order of 2.7 with respect to acetylene and a negative one of 0.1 with respect to oxygen. It is independent of the stage of the reaction over a considerable range and the percentage reaction-time curves appear to be concordant with it. The order may be less under other experimental conditions. It is decreased by packing, at the same time as the reaction is retarded if the pressure is high or accelerated if it is low. Nitrogen has little effect on the rate, which is erratic under all conditions.

The temperature coefficient is about 35,000 cals., rather low if the rate determining step is a unimolecular reaction. It is apparently less in the presence of P_2O_5.

In the static experiments there was no evidence of a true induction period, although the pressure change started as a decrease and ended as an increase. The flow experiments show that there is an induction period of a few seconds (89, 92).

The chains appear to be started at the surface and mostly broken in the gas. The chain breaking step there is believed to be of a unimolecular type. Glyoxal is not the chain carrier.

The Bodenstein mechanism for hydrocarbon oxidations (see page 88) has proved more useful than any other and it is therefore advisable to retain as much of it as possible in any new one which is advanced. With that in mind the following one has been developed:-



(1) $HC\equiv CH + O_2 \rightarrow \begin{matrix}HC\diagdown\\ \| \quad O-O\\ HC\diagup\end{matrix}$ (At surface)

(2) $\begin{matrix}HC\diagdown\\ \| \quad O-O\\ HC\diagup\end{matrix} \rightarrow \underset{|}{HC}=\underset{|}{CH} + O_2$

(3) $\underset{|}{HC}=\underset{|}{CH} + O_2 \rightarrow \underset{O-O}{HC=CH}$

(4) $\underset{O-O}{HC=CH} \rightarrow \underset{|}{HC}=\underset{|}{CH} + O_2$

(5) $\underset{O-O}{HC=CH} + HC\equiv CH \rightarrow \underset{|}{HC}=\underset{|}{CH} + \underset{\underset{O}{\|}}{HC}-\underset{\underset{O}{\|}}{CH}$

(6) $\underset{O-O}{HC=CH} + O_2 \rightarrow HCOOH + CO_2$ (Surface deactivation)

(7) $\underset{O-O}{HC=CH} \rightarrow HCHO + CO$ (Gas phase deactivation)

It will be evident that this is identical with the Bodenstein scheme once the active acetylene molecule $\underset{|}{HC}=\underset{|}{CH}$ has been formed, except that reaction (6) above is specified to be a surface one.

The most obvious objections to his scheme were that the initial step was essentially a unimolecular gas reaction, which did not accord with the low temperature coefficient, and that it did not lead to an induction period unless negative catalysts were present. Moreover, it falls down completely when called on to explain surface initiation of chains, as required here. The above mechanism seems to meet all three objections, for initiation takes place at the surface and might, therefore, have a low temperature coefficient, while an induction period would be expected as the concentration of $H\underset{|}{C}=\underset{|}{C}H$ was building up to its maximum value. The actual chemical formulae assigned to the intermediate substances in this scheme are not of great importance for the present purpose, the sequence and formulation of the reactions being the important factor. The primary product has been given a formula analogous to that suggested by Lenher (75) for the ethylene oxidation. He assumed that such a substance might be formed without preliminary loosening of the hydrocarbon bond and might break down to give an activated hydrocarbon in exactly the same way as suggested here.

In order to avoid making the rate proportional to the oxygen concentration, it becomes necessary to assume that the initial surface reaction is also independent of oxygen in the pressure range studied. This is not improbable since, as pointed out earlier in the discussion, oxygen may possibly be adsorbed so strongly as to retard chain initiation. Reaction (7) would satisfy the requirements, brought out above, for gas phase deactivation by spontaneous rearrangement or decomposition of the chain carrier. In accordance with experiment the scheme provides for the formation of glyoxal, formaldehyde, formic acid and a peroxide.

While the form of the rate equation resulting from this mechanism should be evident from that derived by Bodenstein, the calculation will be given here. In it, the rate constants for the individual reactions are designated by k's with subscript numerals corresponding to the number of the step as shown above. Reactions (1) and (6) will each be treated as independent of oxygen concentration, although the latter can be introduced later, if required. The condition that k_7 varies inversely as $[C_2H_2]$ will only be introduced in the final equation. The treatment is dependent, as is usual, on the assumption that the concentrations of the active substances become practically constant and, therefore, that their time differentials may be equated to zero.

(a) $$-d[C_2H_2]/dt = k_1[C_2H_2] + k_5\Big[\underset{\text{O-O}}{\underset{|\ \ \ |}{\text{HC=CH}}}\Big][\text{HC}\equiv\text{CH}] .$$

$$d\left[\begin{matrix}\text{HC}\diagdown & \\ \| & \text{O-O}\\ \text{HC}\diagup & \end{matrix}\right]/dt = k_1[C_2H_2] - k_2\left[\begin{matrix}\text{HC}\diagdown & \\ \| & \text{O-O}\\ \text{HC}\diagup & \end{matrix}\right] = 0 .$$

Therefore, $$\left[\begin{matrix}\text{HC}\diagdown & \\ \| & \text{O-O}\\ \text{HC}\diagup & \end{matrix}\right] = \frac{k_1}{k_2}[C_2H_2] .$$

(b) $$d\Big[\underset{|\ \ \ |}{\text{HC=CH}}\Big]/dt = k_2\left(\frac{k_1}{k_2}[C_2H_2]\right) + k_4\Big[\underset{\text{O-O}}{\underset{|\ \ \ |}{\text{HC=CH}}}\Big] - k_3\Big[\underset{|\ \ \ |}{\text{HC=CH}}\Big][O_2]$$
$$+ k_5\Big[\underset{\text{O-O}}{\underset{|\ \ \ |}{\text{HC=CH}}}\Big][\text{HC}\equiv\text{CH}] = 0 .$$

$$(c)\quad d[\underset{\text{O-O}}{\text{HC=CH}}]/dt = k_3[\underset{|\;\;|}{\text{HC=CH}}][O_2] - k_4[\underset{\text{O-O}}{\text{HC=CH}}] - k_5[\underset{\text{O-O}}{\text{HC=CH}}][\text{HC}\equiv\text{CH}]$$

$$- k_6[\underset{\text{O-O}}{\text{HC=CH}}] - k_7[\underset{\text{O-O}}{\text{HC=CH}}] = 0 .$$

Adding (b) and (c),

$$k_1[C_2H_2] - k_6[\underset{\text{O-O}}{\text{HC=CH}}] - k_7[\underset{\text{O-O}}{\text{HC=CH}}] = 0 .$$

Therefore,

$$[\underset{\text{O-O}}{\text{HC=CH}}] = \frac{k_1[C_2H_2]}{k_6 + k_7} .$$

Substituting in (a),

$$-d[C_2H_2]/dt = k_1[C_2H_2] + \frac{k_1 k_5[C_2H_2]^2}{k_6 + k_7} .$$

(If k_6 is replaced by $k_6[O_2]$, this is Bodenstein's equation.)

The first term represents chain initiation, the second chain propagation. If the chains are long the expression therefore reduces to:-

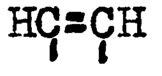
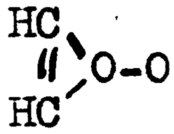
$$-d[C_2H_2]/dt = \frac{k_1 k_5[C_2H_2]^2}{k_6 + k_7} .$$

Introducing $k_7 = K/[C_2H_2]$, gives:-

$$-d[C_2H_2]/dt = \frac{k_1 k_5[C_2H_2]^3}{k_6[C_2H_2] + K} .$$

This will give an order something less than three with respect to acetylene and can explain retardation by packing at high pressures and acceleration by it at low pressures.

The retarding effect of oxygen may be introduced by assuming actual retardation in (1) or that (6) is proportional to the oxygen pressure. At very low $[O_2]$ the rate in (1) must be proportional to it and the over all rate would, therefore, become proportional to oxygen as is required by experiment (88, 89). The Spence mechanism (see page 91), despite marked superficial differences, is essentially a modification of Bodenstein's and, if necessary, could be superimposed on this one as well. Since it is designed to explain certain special observations of his, it will not be dealt with here.

There are objections to the above scheme from the point of view of the limitations imposed on the reactions of  $\underset{|}{\text{HC}}=\underset{|}{\text{CH}}$ and  $\begin{array}{l}\text{HC}\diagdown\\ \|\;\;\;\text{O-O}\\ \text{HC}\diagup\end{array}$, but they seem no greater than those which can be brought against any other mechanism. On the other hand, this one certainly accords better with the experimental results. Until more evidence is available it is, therefore, considered the most satisfactory one.

It is not apparent how it would reduce to an order of about one as required for the runs in the packed bulb and in the presence of P_2O_5. However, in the first case, it is useless to attempt to fit the results until it has been determined whether the decrease in order is due to a decrease in the effect of acetylene or to an increase in the retarding effect of oxygen. In the other case, a study of the reaction by gas analyses rather than by pressure change might give somewhat different results. It is suggested that each of these could, with advantage, be made the subject of further research.

SUMMARY.

The work reported in Part 2 of this thesis constitutes the first detailed study by the static method of the kinetics of the acetylene-oxygen reaction. The results may be summarized as follows:-

1. By using a special reaction bulb with a side-neck containing P_2O_5 it is possible to follow the reaction by measurements of pressure changes. In an ordinary reaction bulb it is necessary to use gas analyses. The rates are erratic under all conditions.

2. In the special bulb the order of the reaction is only slightly greater than one. Oxygen has no apparent effect on the rate. Packing the bulb reduces it by a relatively small amount.

3. In ordinary 200 cc. spherical bulbs of pyrex, coated pyrex or silica the order is about 2.6, the rate equation being:-

$$-d[C_2H_2]/dt = K \frac{[C_2H_2]^{2.7}}{[O_2]^{0.1}}$$

The order appears to be less in a cylindrical silica bulb and is certainly less in a packed bulb.

4. With rather loose packing the rate, relative to that in the open bulb, may be decreased at high pressure or increased at low pressure.

5. The temperature coefficient is about 20,000 cals. in the special bulb and about 35,000 cals. in the ordinary bulb.

6. Glyoxal has no appreciable effect on the rate.

7. A suitable mechanism has been developed by modifying that proposed by Bodenstein so as to give surface initiation of chains, with chain breaking mostly in the gas phase.

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