THE OXIDATION OF HYDROCARBONS AT HIGH PRESSURE

D. M. NEWITT

Imperial College of Science and Technology, South Kensington, London, England

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It is the purpose of this paper to give an account of the effect of pressure upon the formation and survival of oxygenated products during the slow (isothermal) combustion of hydrocarbons in air or oxygen at high pressures, and also to consider briefly the bearing of the results upon the theory of hydrocarbon combustion generally. The data available are unfortunately by no means as comprehensive as could be desired, but sufficient work has been done to leave no doubt but that pressure plays an important part in changing or modifying the course of oxidation during both slow and explosive combustion.

THE RÔLE OF PRESSURE

It will be of interest to consider first the possible ways in which pressure may influence the course of a gaseous reaction. One of the direct consequences of raising the pressure is to increase proportionately the frequency of molecular collision; in so far as reaction velocity depends upon collision rate, it will undergo a corresponding increase with pressure. It is, therefore, frequently possible, by suitably increasing the pressure, to carry out a reaction at a temperature considerably lower than would be practicable under atmospheric conditions and by so doing to favor the survival of intermediate products which at higher temperatures would undergo rapid further oxidation or thermal decomposition.

Pressure may also modify the course of a reaction proceeding by a chain mechanism by deactivating the carriers and thus interrupting the chain. Furthermore, a sufficiently high pressure may, by forcing the molecules into close contact, produce such an alteration in their electrostatic fields as to give rise to induced or increased polarity. Lastly, pressure will influence a reversible reaction in accordance with the Le Chatelier principle of mobile equilibrium in the direction resulting in a diminution of specific volume or molecular density. Examples of all these effects are found in combustion reactions although, owing to their complex character, it is not always possible to account for the results on a quantitative basis.

APPARATUS AND EXPERIMENTAL METHODS

In carrying out pressure oxidations in a small scale plant it is usually not practicable to make provision for adequate heat exchange, and in order to ensure substantially isothermal conditions the reacting medium must be diluted with a large excess of the combustible or with an inert gas or vapor such as nitrogen or steam; even in a large scale plant it is found advantageous to work with weak mixtures containing not more than 10 to 15 per cent of oxygen.

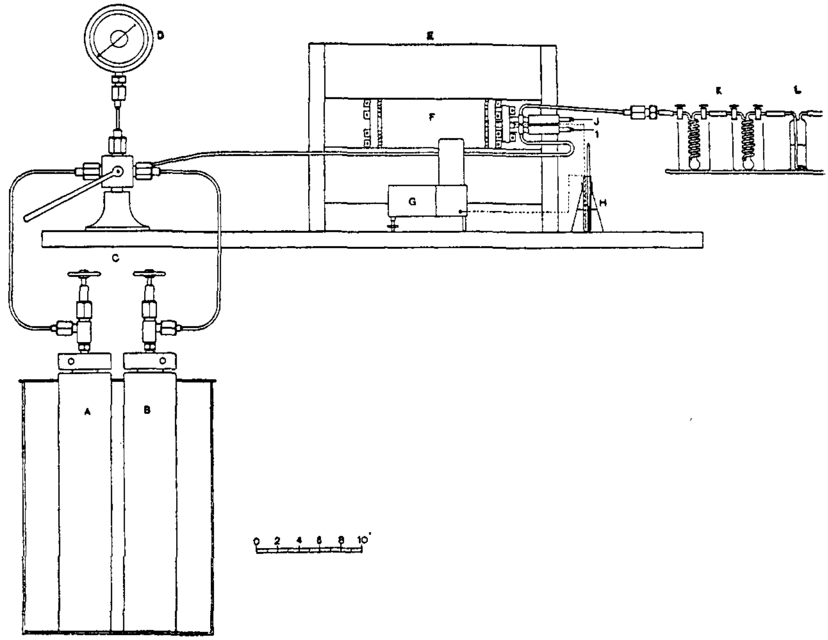


FIG. 1. Apparatus for the static method

Two methods have been generally employed: namely, (*1*) a static method in which a known quantity of the reactants is admitted into a heated reaction vessel and the progress of the reaction followed by the changes in pressure or composition of the medium, and (*2*) a flow method in which the reactants are passed at a measured velocity through a heated reaction vessel and the products are collected and analyzed.

Figure 1 shows diagrammatically an apparatus suitable for static experiments at pressures up to several hundred atmospheres. The previously mixed hydrocarbon and air or oxygen are compressed into the two steel cylinders A and B to a pressure considerably above the proposed working value, and in the case of the higher hydrocarbons the cylinders are maintained at a temperature sufficiently high to prevent any condensation taking place. The gases pass from the cylinders through the control valve C and the inlet valve I to the reaction vessel F, which is electrically heated. The inlet valve is closed, and after a time interval sufficient for the reaction to take place the contents of the vessel are released through the exit valve J and allowed to pass through a system of condensers K and absorber L, in which condensable and soluble products are removed, to a calibrated gas-holder. The initial pressure of the reacting medium is measured by the Bourdon gauge D and its temperature by a platinum-rhodium thermocouple situated in a steel tube traversing axially the reaction chamber.

For the flow method a more elaborate apparatus is required, one form of which is shown in figure 2. A and B are storage cylinders containing the reactants at a suitable high pressure. From the cylinders they pass through separate pipe lines to the preheaters C and D and thence through orifice meters E and F to the premixing chamber H. From H they travel directly into the reaction chamber, which is electrically heated, and on emerging are rapidly cooled in the coil K; the condensable and soluble products are removed in the receivers L and M. The residual gases are then reduced to atmospheric pressure by the valve V and are passed through a meter R to a calibrated gas holder. Various adaptations and modifications of this apparatus can be used according to the nature of the investigation.

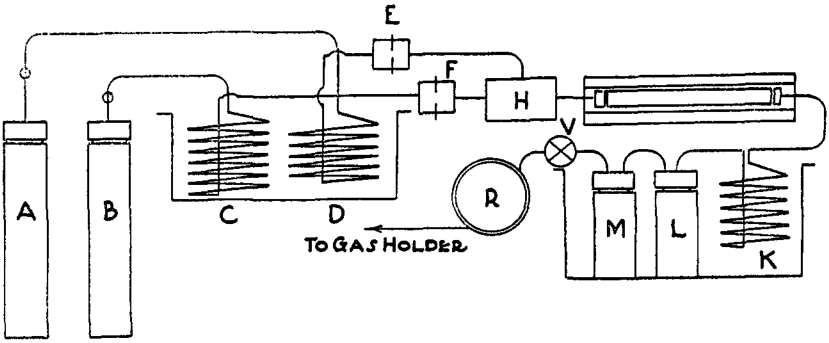


FIG. 2. Apparatus for the flow method

Of the two methods the static permits of more accurate control of experimental conditions, whilst the flow method enables larger amounts of material to be used and thus facilitates analyses of the complex mixtures of alcohols, aldehydes, and acids that are found in the products.

OXIDATION OF METHANE

General characteristics of the high-pressure reaction

When a methane–oxygen mixture containing a large excess of the combustible or of an inert gas (e.g., $8CH_4 + O_2$) is maintained at a suitable temperature for slow reaction ultimately to take place there is an "induction" period which may last many minutes, during which little or no oxidation takes place, followed by a reaction period during which the whole of the free oxygen is consumed and various intermediates and end products are formed. The temperature at which reaction first becomes noticeable is found to depend *inter alia* upon mixture composition and pressure; thus an $8CH_4 + O_2$ medium will react at comparable rates under the following conditions (5):

Temperature in °C.	*Pressure in atmospheres*
410	1
360	48
340	105
337	150

The products of the combustion are methyl alcohol, formaldehyde, formic acid, the two oxides of carbon, and steam; hydrogen is found only in exceptional circumstances when the reaction is of an explosive character. The stoichiometric equations for the formation of these compounds, namely,

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CH_3OH$$

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

$$CH_4 + 1\tfrac{1}{2}O_2 \rightarrow HCOOH + H_2O$$

indicate that whilst formaldehyde is formed with no change in volume, both methyl alcohol and formic acid result in a contraction. The proportions in which they survive depend largely upon experimental conditions and in particular upon temperature and pressure. In a static system, for example, the yields recorded in table 1 were obtained for an $8.1CH_4 + O_2$ medium at 106.4 atm. and various temperatures between 336° and 355°C.

The data in table 1 show clearly that at constant pressure there is an optimum temperature or rate of reaction for the survival of both alcohol and aldehyde, which is probably determined by their respective rates of formation and further oxidation. It is also noticeable that at the higher temperature, when reaction takes place rapidly with a comparatively large temperature rise, the yields of intermediates are considerably reduced, whilst the CO/CO_2 ratio increases.

The effect of increasing the initial pressure is to increase progressively the quantities of alcohol surviving in the products, providing always that

TABLE 1

Products from the slow combustion of an $8.1CH_4 + O_2$ *medium at 106.4 atm.* (*5*)

INITIAL TEMPERATURE	RISE IN TEMPERATURE	DURATION OF		PRODUCTS AS PER CENT OF METHANE BURNT		RATIO CO/CO_2 IN GASEOUS PRODUCTS
		Induction	Reaction	CH_3OH	HCHO	
°C.	*°C.*	*min.*	*min.*			
336	4	53	35	10.1	0.30	0.05
339	10	14	22	14.1	0.36	0.01
341	14	2.5	9.5	22.3	0.75	1.5
343	10		12	20.0	0.93	1.0
347	17	2.5	5.5	16.6	0.30	
352	26*	1	1	9.8	0.95	3.9
355	37*	0†	1	3.8	Trace	4.2

* Probable formation of flame during combustion.

† Comparable with time for filling reaction vessel.

TABLE 2

The influence of pressure upon the survival of methyl alcohol and formaldehyde in the slow combustion of an $8.1CH_4 + O_2$ *medium* (*5*)

INITIAL PRESSURE	INITIAL TEMPERATURE	DURATION OF OXIDATION	PRODUCTS AS PER CENT OF METHANE BURNT		RATIO CO/CO_2
			CH_3OH	HCHO	
atm.	*°C.*	*min.*			
10	400	10	1.1	Trace	0.06
25	385	7	4.8	0.66	0.15
40*	372	15	6.1	1.20	0.05
48	373	4	13.7	0.80	0.35
106.4	341	12	22.3	0.75	
149*	341	16	19.0	0.60	0.08

* Not quite optimum conditions.

TABLE 3

The influence of diluents upon the yields of methyl alcohol and formaldehyde from the combustion of a $2CH_4 + O_2$ *medium at 50 atm. pressure* (*5*)

INITIAL MIXTURE $2CH_4 + O_2 +$	TEMPERATURE	TIME OF REACTION	PRODUCTS SURVIVING, IN CC. AT N.T.P.	
			CH_3OH	HCHO
	°C.	*min.*		
$6.5N_2$	397	16	48	2.7
$6.5H_2O$	400	2	43	1.6
$6.5CO_2$	390	8	50	3.0
$6.5CH_4$	397	1	80	4.6

the reaction temperatures are so adjusted as to give comparable conditions in respect of reaction velocities. Formaldehyde, which is only found in small quantities, shows little response to pressure (see table 2).

The oxidation proceeds in a similar way when air is substituted for oxygen or when the medium is diluted with nitrogen, carbon dioxide, or steam, but in all such cases the reaction is slowed up and the yields of alcohol are diminished (table 3).

OXIDATION OF ETHANE

Ethane oxidizes rather more readily than does methane, but in other respects the characteristics of its combustion are similar; in both cases the most reactive mixture is one containing the hydrocarbon and oxygen in the ratio 2:1. The products from its slow combustion at high pressures are ethyl and methyl alcohols, acetaldehyde, formaldehyde, acetic and formic acids, the two oxides of carbon, methane, and steam (3). The proportion in which the carbon of the ethane burnt is distributed amongst these products depends upon the experimental conditions; thus, for example, in the case of an $8C_2H_6 + O_2$ medium reacting on a static system at 50 atm. the relative yields are as shown in table 4.

TABLE 4

Products from the reaction of an $8C_2H_6+O_2$ *medium at 50 atm. and various temperatures*

INITIAL TEMPERATURE	DURATION OF		PERCENTAGE OF THE CARBON OF THE ETHANE BURNT SURVIVING AS										
	Induction	Reaction	C_2H_5OH	CH_3OH	CH_3CHO	HCHO	CH_3COOH	HCOOH	CO	CO_2	CH_4	Total liquid products	Total gaseous products
°C.	*min.*	*min.*											
279.2	18.0	100.0	14.8	10.8	4.7	0.2	15.2	0.3	19.3	32.5	Nil	46.0	51.8
286.0	7.0	3.8	24.4	14.1	8.3	2.0	1.7	0.9	34.8	10.0	Nil	51.4	44.8
288.0	6.5	3.8	20.5	11.3	7.3	1.2	2.3	0.7	31.6	7.1	13.7	43.2	52.4
289.0	4.2	2.8	16.0	14.4	4.9	2.0	2.4	0.4	36.0	4.6	20.7	40.1	61.3
294.0	2.0	3.2	17.2	14.1	5.2	1.9	Nil	0.7	40.8	7.8	8.1	39.1	56.1

The results indicate that in so far as ethyl alcohol and acetaldehyde are concerned a temperature giving a medium rate of reaction is most favorable to their survival; acetic acid on the other hand requires a very slow reaction rate, whilst methyl alcohol varies little throughout the series.

The effect of increasing the pressure is favorable to these products containing two carbon atoms but reduces the yields of methyl alcohol and formaldehyde (see table 5).

From the point of view of the mechanism of hydrocarbon combustion it is important to know something of the order in which the various intermediates are formed and to distinguish between those participating in the main reaction and those resulting from secondary reactions. Some light is thrown on this matter by the results of experiments carried out by the flow method (9); if, for example, a hydrocarbon–oxygen mixture is passed through a heated zone at progressively increasing velocity, then, provided the products are rapidly chilled, those initially formed should survive in increasing amounts. In this way it has been shown that at high pressures methyl and ethyl alcohols are formed at an early stage in the oxidation of methane and ethane, respectively (7). Furthermore, when methyl and ethyl alcohols are themselves oxidized at high pressures the products include all those found in comparable reactions with the parent hydrocarbons (table 6).

TABLE 5

The influence of initial pressure on the survival of intermediate products from the reaction of an $8C_2H_6 + O_2$ *medium*

INITIAL PRESSURE	INITIAL TEMPERATURE	DURATION OF REACTION	PERCENTAGE OF THE CARBON OF THE ETHANE BURNT SURVIVING AS						
			C_2H_5OH	CH_3OH	CH_3CHO	HCHO	CH_3COOH	HCOOH	Total condensable products
atm.	°*C.*	*min.*							
15	315	3.0	16.0	19.4	1.9	4.5	Nil	Nil	41.8
50	294	3.25	17.2	14.1	5.2	1.9	Nil	0.7	39.1
75	279	2.5	18.0	16.6	6.8	0.4	3.6	0.6	46.0
100	270.5	4.5	23.6	14.0	9.7	0.1	12.5	0.5	50.4

TABLE 6

Products from the slow oxidation of ethyl alcohol at 100 atm. and 261°C.

PARTIAL PRESSURE OF REACTANTS IN ATMOSPHERES			INITIAL TEMPERATURE	PRODUCTS AS PERCENTAGE OF THE ALCOHOL OXIDIZED OR DECOMPOSED								
C_2H_5OH	O_2	N_2		CH_3CHO	CH_3COOH	$CH_3COOC_2H_5$	CH_3OH	HCHO	HCOOH	CO_2	CO	CH_4
			°*C.*									
20	4	76	261	32.8	0.8	39.9	7.5		0.5	5.1	13.6	
20	10	70	261	20.7	2.4	36.2	13.5	0.2	0.3	20.4	3.6	2.6
10	10	80	261	10.4	1.4	35.6	8.2		0.4	27.6	12.5	
5	10	85	261	3.4	1.7	19.4	4.3	Trace	0.3	63.0	7.9	

OXIDATION OF PROPANE

Propane occupies a very important position between the lower and higher members of the paraffin series, for whilst its properties show certain resemblances to those of methane and ethane its reaction with oxygen is characterized by features peculiar to the higher hydrocarbons. The work of Prettre (10) and of Beatty and Edgar (1) has shown that during its slow combustion luminescence may be observed and in certain circumstances cool flames may be formed, whilst Townend and Chamberlain (12) have mapped out its upper and lower regions of inflammability.

The reaction at high pressures

When propane is oxidized at high pressures the products contain not only most of those intermediate substances found in the low-pressure reaction,—namely, propyl, ethyl, and methyl alcohols, propionaldehyde, acetaldehyde, and formaldehyde, and propionic, acetic, and formic acids,—but also isopropyl alcohol and acetone arising probably from some initial oxidation at the center —CH_2 group (6). The rôle of pressure in inducing such a change in the primary process is by no means clear, but evidence suggests that it may be due to a change in polarity of the hydrocarbon molecule altering the ratio of the collision period leading to activation and the vibrational periods of the C—C or C—H linkages.

TABLE 7

Products from the reaction of a 1:3.6 propane–air medium at 1, 20, 60, and 100 atm.

	Pressure in atmospheres	1	20	60	100
	Reaction temperature in °C	373	281	252	250
	PRODUCTS	PERCENTAGES OF THE CARBON OF THE PROPANE BURNT			
A	Total aldehydes	20.5	21.8	13.5	13.7
	Normal alcohols	19.7	21.0	17.5	15.2
B	Isopropyl alcohol	1.3	2.8	6.2	16.0
	Acetone	0.5	4.3	12.5	7.9
	Acids	4.3	17.0	19.0	18.9
	Carbon dioxide	7.3	17.1	21.4	20.6
	Carbon monoxide	21.3	16.0	9.9	7.7
	Propylene	25.1	Nil	Nil	Nil
	Ratio A/B	22.3	6.0	1.7	1.2

The effect of a progressive increase of pressure upon the distribution of products is well brought out by the data summarized in table 7, which relate to the reaction of a 1:3.6 propane–air medium at four pressures in the range 1 to 100 atm.

The most noticeable feature of these results is the absence of peroxidic bodies and of propylene in the high-pressure experiments and the increasing amount of isopropyl alcohol and acetone surviving as the pressure increases. If the sum of the total aldehydes and normal alcohols, A, and of the isopropyl alcohol and acetone, B, be taken as a rough measure of the tendency for oxidation to take place at a terminal methyl group and the central —CH_2 group, then the progressive decrease in the ratio A/B indicates that the latter process is favored by pressure.

It has been shown that in the case of methane and ethane an increase in the concentration of the hydrocarbon favors the survival of liquid products, and propane behaves in a similar manner. Thus when a series of propane–air mixtures in which the proportion of propane is varied from 1:20 to 1:0.5 react at 30 atm. pressure and 275°C. in a static system, the results given in table 8 are obtained. The total condensable products increase from 47.6 per cent for a 1:20 mixture to 85.5 per cent for a 1:0.5 mixture.

TABLE 8

Products from the reaction of various propane–air mixtures at 30 atm. pressure and 275°C.

	Propane: air ratio	1:20	1:5	1:3.6	1:1.25	1:0.5
	PRODUCTS	PERCENTAGES OF THE CARBON OF THE PROPANE BURNT				
A	Total aldehydes	12.5	8.8	12.0	16.1	16.7
	Normal alcohols	17.3	25.5	23.0	33.1	34.5
B	Isopropyl alcohol	2.7	6.9	5.2	5.2	14.4
	Acetone	1.2	1.4	1.3	0.3	7.4
	Acids	13.9	13.4	15.2	8.9	12.5
	Carbon dioxide	31.5	25.0	22.1	10.5	7.0
	Carbon monoxide	20.9	19.0	21.3	25.9	8.0
	Total condensable products	47.6	56.0	56.7	63.6	85.5
	Ratio A/B	7.6	4.1	5.4	9.0	2.4

The distribution of alcohols

The normal alcohols formed during the slow combustion consist of methyl, ethyl, and propyl alcohols, methyl alcohol usually being present in excess (Pease (8)); the proportions in which they survive, however, depend upon the pressure, increasing amounts of propyl alcohol being found at the higher pressures. Thus, for example, Wiezevich and Frolich find that for an 11:1 propane–oxygen mixture, reacting at 170 atm. and 350°C., methyl, ethyl, and propyl alcohols are found in the approximate ratio 13.4:8:5.2, whilst Newitt and Schmidt (6) working with a propane–air mixture at pressures between 5 and 65 atm. obtained the data given in table 9.

The formation of a series of normal alcohols from propane suggests that initial oxidation occurs at an end methyl group giving propyl alcohol, which then undergoes further oxidation *via* propionaldehyde to give in turn ethyl and methyl alcohols. In support of this view is the fact that propyl alcohol on oxidation at 240°C. and 56 atm. yields propionaldehyde, acetaldehyde, ethyl alcohol, and propionic and acetic acids, whilst ethyl alcohol at 280°C. and 50 atm. gives acetaldehyde, methyl alcohol, and acetic and formic acids. Propyl and ethyl alcohols are, however, more easily oxidized than is methyl alcohol, and consequently the latter would be expected to, and in fact does, survive in large quantities in the product.

The increasing amounts of isopropyl alcohol and acetone found in the products as the combustion pressure is raised have been attributed to oxidation at the —CH_2 group. An alternative view is that isopropyl alcohol might arise from hydration of propylene which occurs in large quantities during the low-pressure combustion. The reaction

TABLE 9

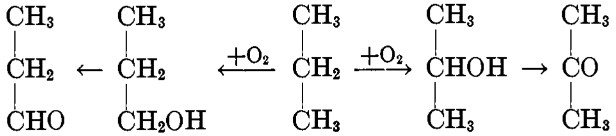
Relative quantities of alcohols surviving from the slow reaction of a 1:3.6 propane-air medium

Pressure in atmospheres	5	30		65
PRODUCTS	PER CENT			
Methyl alcohol	76.3	58.0	55.3	50.1
Ethyl alcohol	19.1	17.6	13.2	9.8
Propyl alcohol	4.6	4.3	7.3	12.2
Isopropyl alcohol		20.0	24.2	27.9

$$C_3H_6 + H_2O \rightleftharpoons (CH_3)_2CHOH$$

however, requires the presence of a catalyst and the value of its equilibrium constant at 300°C. indicates that a considerable amount of propylene should be present in the system at equilibrium, whereas it is almost entirely absent in the high-pressure experiment.

It may therefore be concluded that the propane molecule can undergo oxidation in two ways according to the following scheme,



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CHO \end{array} \leftarrow \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2OH \end{array} \xleftarrow{+O_2} \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} \xrightarrow{+O_2} \begin{array}{c} CH_3 \\ | \\ CHOH \\ | \\ CH_3 \end{array} \rightarrow \begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array}$$

the proportions in which the oxygen is distributed depending upon the temperature, pressure, and the concentration of the reactants.

OXIDATION OF BUTANE

The products from the high-pressure oxidation of butane are too complex to admit of accurate quantitative analysis. Wiezevich and Frolich (14) have, however, identified acetaldehyde, propionaldehyde, acetone, acetic acid, propyl acetate, and methyl, ethyl, isopropyl, *n*-propyl, and isobutyl alcohols and give the data presented in table 10 to show the effect of pressure upon the types of products produced. Low pressure tends to favor the formation of lower alcohols and acids, and high pressure the formation of higher alcohols and aldehydes. The data are not sufficiently detailed to afford any indication as to the point of initial oxygen attack, although the presence of isobutyl alcohol shows that some oxidation takes place at the —CH_2 groups.

TABLE 10

Products obtained in high-pressure oxidation of butane

INLET OXYGEN GOING TO	PER CENT OF OXYGEN AT	
	33 atm.	133 atm.
Acetone	1.4	0.7
Methyl alcohol	15.0	8.4
Ethyl alcohol	2.5	6.3
Propyl alcohols	3.2	8.9
Butyl alcohols	0.6	2.5
Aldehydes	6.9	15.9
Acids	16.7	4.6
Carbon dioxide	9.4	6.1
Carbon monoxide	3.8	9.4

OXIDATION OF THE AROMATIC HYDROCARBONS

Although the controlled slow oxidation of the aromatic hydrocarbons forms the basis of a number of industrial processes such as, for example, the production of phthalic acid from naphthalene and of maleic acid from benzene, the actual mechanism by which ring cleavage occurs is still a matter of surmise. By carrying out such oxidations in the vapor phase at high pressure (4), however, comparatively low reaction temperatures can be employed and enhanced yields obtained of those nuclear derivatives formed in the primary processes before the ring breaks; in this way the successive steps in the initial phase of the oxidation of benzene, toluene, and ethylbenzene have been identified.

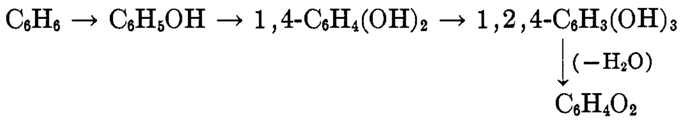
Benzene

The principal products from the oxidation of an excess benzene–oxygen medium in a static system at pressures of the order of 50 atm. are phenol, the two oxides of carbon, and steam. Smaller quantities of hydroquinone, quinone, maleic acid, and formaldehyde are also found, together with biphenyl, arising from the direct pyrolysis of the benzene. Unlike the reaction in the case of the aliphatic hydrocarbons, that of benzene is not preceded by any marked induction period and cool flames are not observed.

The yields of phenol from experiments at 312°C. with a series of mixtures in which the benzene–oxygen ratio was varied between 20:1 and 1.9:1, the partial pressure of the hydrocarbon being kept constant at 20 atm., are as follows (4):

Ratio $C_6H_6:O_2$	*Per cent of the* C_6H_6 *burnt surviving as phenol*
1.9	12.8
3.7	37.7
9.9	24.9
20.0	38.3

It is clear that an excess of the hydrocarbon is favorable to the survival of phenol. Similar results are obtained with benzene–air media, the products from a 4:1 mixture at 50 atm. and 362°C. being as given in table 11. The phenol recovered from this experiment represents upwards of 50 per cent of the benzene burnt. It is noteworthy that aromatic products other than phenol seldom survive in anything but traces in the homogeneous vapor-phase reaction; nevertheless the presence of hydroquinone and quinone (13) is significant in that it affords evidence that oxidation of the nucleus proceeds by successive stages of hydroxylation, as represented by the following scheme:



$$\begin{tikzcd} C_6H_6 \arrow[r] & C_6H_5OH \arrow[r] & 1,4\text{-}C_6H_4(OH)_2 \arrow[r] & 1,2,4\text{-}C_6H_3(OH)_3 \arrow[d, "(-H_2O)"] \\ & & & C_6H_4O_2 \end{tikzcd}$$

Toluene and ethylbenzene

The products of the oxidation of the simple alkyl derivatives of benzene may be divided into three groups, according as they result from oxidation of the nucleus, of the side chain, or of the fragments resulting from ring cleavage. The relative proportions in which each group survives depend *inter alia* upon temperature, pressure, and mixture composition. In the case of toluene the principal products are: (*1*) From side-chain oxidations,—benzyl alcohol, benzaldehyde, and benzoic acid; (*2*) from nuclear oxidation,—*p*-cresol and 2,4-dihydroxytoluene; (*3*) from ring cleavage,—aliphatic acids, formaldehyde, the two oxides of carbon, and steam. In addition bibenzyl is formed by the pyrolysis of toluene and small quantities of benzene from the decarboxylation of benzoic acid (4).

The proportions in which the more important of these substances are found in the products from a series of toluene–oxygen mixtures at 20 atm. reacting in a static system are shown by the results in table 12. It is evident that the course of the combustion and particularly the extent to which the side chain undergoes oxidation are influenced to a very marked degree by the composition of the medium. Thus whilst the comparatively rich 1:1 toluene–oxygen mixture gave 59.3 per cent of benzoic acid in the products and only 3 per cent of benzaldehyde and less than 1 per cent of benzyl alcohol, the 30:1 mixture gave 6.2 per cent of benzyl alcohol, 50.6 per cent of benzaldehyde, and only 16.3 per cent of benzoic acid. In the case of the latter mixture no less than 83 per cent of the carbon of the toluene burnt appeared as aromatic intermediates in the products.

TABLE 11

Oxidation of a 4:1 mixture of benzene and air at 50 atm. and 362°C.

PRODUCTS	PERCENTAGE DISTRIBUTION OF OXYGEN
Phenol	10.6
Hydroquinone and quinone	Trace
Maleic acid	2.8
Formaldehyde	3.0
Carbon monoxide	26.2
Carbon dioxide	29.8
Water	27.6

TABLE 12

Products from the reaction of various toluene–oxygen mixtures at 20 atm.

INITIAL MIXTURE $C_6H_5CH_3$: O_2	REACTION TEMPERATURE IN °C.	PRODUCTS AS PERCENTAGES OF THE CARBON OF THE TOLUENE BURNT						PERCENTAGE DISTRIBUTION OF OXYGEN IN	
		Benzyl alcohol	Benzaldehyde	Benzoic acid	2, 4-Dihydroxytoluene	CO_2	CO	Side chain	Nucleus
30*	337	6.2	50.6	16.3	9.9	5.2	5.4	81.5	18.5
20*	276	5.9	36.1	12.1	14.7	3.0	1.4	71.0	29.0
3.7	250	2.8	21.9	26.2	6.1	17.9	6.0	86.5	13.5
3.2	250	1.6	18.1	53.0	6.3	18.3	4.7	91.0	9.0
1.5	250	1.2	8.6	47.1	5.1	19.6	3.3	91.0	9.0
1.0	250	0.7	3.0	59.3	7.1	25.8	3.8	89.5	10.5

* These mixtures contained 3.76 atm. of nitrogen.

The reaction temperature has also a considerable influence upon the distribution of the products, as may be seen from the data in table 13, relating to two mixtures containing toluene and air in the proportions of 20:5 and 30:5, respectively, the partial pressure of oxygen being 1 atm. An important feature of these results is the progressive increase in the amount of benzyl alcohol surviving with increase of temperature, together with a corresponding decrease in benzoic acid. It is evident that by suitably adjusting the temperature and the hydrocarbon–oxygen ratio any one of the three side-chain derivatives can be obtained in high yields relative to the amount of hydrocarbon consumed.

TABLE 13

Products from the combustion of 20:5 and 30:5 toluene–air mixtures at various temperatures

TEMPERATURE IN °C.	PRODUCTS AS PERCENTAGES OF THE CARBON OF THE TOLUENE BURNT					
	Benzyl alcohol	Benzaldehyde	Benzoic acid	2, 4-Dihydroxytoluene	CO_2	CO
			$20\ C_6H_5CH_3 + 5$ air			
276	5.9	36.1	12.1	14.7	3.0	1.4
304	5.6	38.6	17.7	15.0	3.5	3.0
331	6.0	4.04	19.4	17.9	4.5	3.8
375	15.8	30.0	10.2		14.4	5.3
400	31.1	30.1	8.1	10.2	14.7	4.2
			$30\ C_6H_5CH_3 + 5$ air			
337	6.2	50.6	16.3	9.9	5.2	5.4
358	8.3	45.4	10.6	10.7	4.0	5.5
391	16.6	31.0	9.7	9.3	4.2	3.9
503*	6.6	3.2	3.6	3.9	3.5	9.8

* Inflammation occurred with carbon deposition.

Ethylbenzene

In the liquid phase ethylbenzene combines readily with oxygen at temperatures of 100–120°C. giving acetophenone and the oxides of carbon but no alcohol or aldehyde (11); in the presence of a manganese oxide catalyst, however, methylphenylcarbinol, benzoic acid, and formaldehyde are found in addition to the above products (2). In discussing the mechanism of the reaction Stephens concludes that the hydrogen attached to the carbon atom in the alpha position is first removed and that oxygen tends to substitute in the same position as do the halogens, giving acetophenone; the alcohol is regarded as arising from some independent secondary reaction.

Newitt and Burgoyne, on the other hand, have studied the vapor-phase combustion and show that reaction in these circumstances takes place by successive hydroxylations of the hydrogen attached to the carbon atom in the alpha position, yielding as a primary product methylphenylcarbinol, which in turn gives acetophenone. The further oxidation of acetophenone occurs by hydroxylation of the hydrogen attached to the carbon in the beta position, giving benzaldehyde and benzoic acid. At the same time some direct oxidation of the nucleus takes place, giving as the main product 2,4-dihydroxyethylbenzene.

As an example of their results the data of table 14 relating to a 20:7.5 ethylbenzene–air mixture reacting at 27.5 atm. and 322°, 385°, and 437°C., respectively, may be given. The increase in the methylphenylcarbinol with increase of reaction temperature affords evidence that it constitutes the initial product of the oxidation. The above experiments also show that with rise of temperature there is an increasing tendency for the nucleus to undergo direct oxidation, the distribution of oxygen between the side chain and the nucleus at the three temperatures being as follows:

TABLE 14

Products from the combustion of a 20:7.5 ethylbenzene–air medium at 27.5 atm.

Reaction temperature in °C.	322	285	437
PRODUCTS	AS PERCENTAGES OF THE CARBON OF THE ETHYLBENZENE BURNT		
Methylphenylcarbinol	8.9	11.5	27.7
Acetophenone	13.4	Trace	Trace
Benzaldehyde	54.0	52.3	23.6
Benzoic acid	6.4	8.9	8.7
2,4-Dihydroxyethylbenzene	10.3	9.2	6.8

TEMPERATURE IN °C.	PER CENT DISTRIBUTION OF OXYGEN IN	
	Side-chain products	Nuclear products
322	77.0	23.0
385	75.0	25.0
437	69.0	31.0

Although the formation of benzaldehyde and benzoic acid has been attributed to further oxidation of acetophenone, they might equally well arise from ethylbenzene by successive hydroxylations of the hydrogen attached to the carbon in the beta position. In this event phenylethylalcohol should be the first step in the oxidation and should be detectable in the products; no trace of it, however, has ever been found, whilst experiments with acetophenone show that on oxidation considerable amounts of benzaldehyde and benzoic acid are formed. The intermediate stages in the oxidation of ethylbenzene would therefore appear to be:

$$\begin{array}{r}C_6H_5CH_2CH_3 \rightarrow C_6H_5CH(OH)CH_3 \rightarrow C_6H_5C(OH)_2CH_3 \rightarrow C_6H_5COCH_3\\ \swarrow \quad\\ C_6H_5COOH \leftarrow C_6H_5CHO \leftarrow C_6H_5COCH(OH)_2 \leftarrow C_6H_5COCH_2OH\end{array}$$

SUMMARY AND CONCLUSIONS

A general survey of the experimental data relating to the combustion of both the aliphatic and the aromatic hydrocarbons makes it clear that pressure exerts a well-defined influence on the course of the reactions involved. It has been shown in the foregoing pages that it accelerates the rate of reaction, exerts a directive action on the primary oxidation process, and influences to a marked degree the distribution of the oxygen in the products. In all cases of pressure oxidation in which oxygen is in defect the products have been shown to contain large quantities of normal alcohols or phenolic derivatives arising at some early stage of the oxidation. Thus it is possible to burn methane under conditions which give yields of methyl alcohol of upwards of 50 per cent, and similar results are obtained with ethane, propane, benzene, and toluene.

TABLE 15

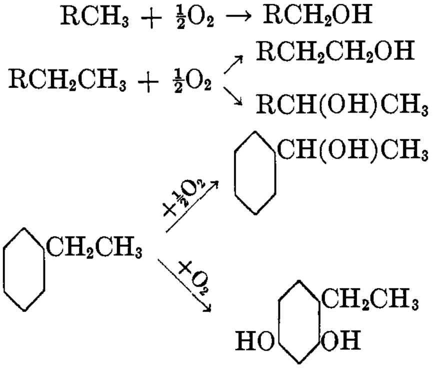
Effect of pressure upon the rate of reaction

HYDROCARBON	TEMPERATURE AT WHICH OXIDATION IS FIRST DETECTABLE WHEN THE PRESSURE IS			
	1 atm.	50 atm.	100 atm.	150 atm.
Methane	420	350	330	320
Ethane	285	276	260	
Propane	270	255	245	232
Butane		248	220	210
Benzene		270	260	
Toluene		210	195	

With the higher aliphatic hydrocarbons another pressure effect of importance is the change in the point of oxygen attack on the molecule; there is an increasing tendency with rise of pressure for direct oxidation to occur at some midpoint in the chain giving iso-alcohols and ketones, the change being probably attributable partly to the increase in the collision factor and partly to a change in the polarity of the molecule due to close packing.

The alkyl derivatives of benzene show a somewhat similar behavior, for whilst the side chains are more open to attack and at atmospheric pressure appropriate all the oxygen, at high pressures the nucleus and side chains undergo simultaneous oxidation.

Without entering into any discussion involving the kinetic aspects of the various oxidations, there is evidence from the analytical results that the initial stages of the process taking place at high pressures are represented by the following scheme:



$$RCH_3 + \tfrac{1}{2}O_2 \rightarrow RCH_2OH$$

$$RCH_2CH_3 + \tfrac{1}{2}O_2 \left\langle \begin{array}{l} \nearrow RCH_2CH_2OH \\ \searrow RCH(OH)CH_3 \end{array} \right.$$

The effect of pressure is generally to increase the rate of reaction, as may be seen from the comparative figures in table 15.

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DISCUSSION[1,2]

BERNARD LEWIS AND GUENTHER VON ELBE: Dr. Newitt has interpreted his results in terms of initial hydroxylation. It appears to us that a

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[2] Received September 25, 1937.

scheme based on a chain mechanism involving chain carriers of the peroxide type would do more justice to his results. This has already been outlined by us in the case of the oxidation of methane and ethane at high pressures (J. Am. Chem. Soc. **59**, 976 (1937); *Combustion, Flames and Explosions of Gases*, Cambridge University Press (1938)). In particular, the radical chain allows a ready interpretation of the yields of methyl and ethyl alcohols in the oxidation of ethane. It is not difficult to account for all the observed products and the trends of their yields with varying temperature, pressure, and mixture composition.

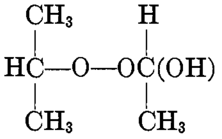
Among his newer results on the oxidation of propane we note, in particular, the simultaneous appearance of isopropyl alcohol, acetone, and acids and the disappearance of propylene and peroxides as the reaction temperature is lowered and the pressure increased. This reaction may be understood from our previously proposed formation of oxy-alkyl peroxides and olefins by reactions between peracids or their radicals and paraffins. At lower temperatures this reaction is easily conceived to take a somewhat different course than at higher temperatures. Thus, at high temperatures the following reaction might be favored:

$$CH_3CH_2CH_3 + CH_3CO(OOH) \rightarrow CH_2{=}CHCH_3 + CH_3CH(OH)OOH$$

Low temperatures would favor

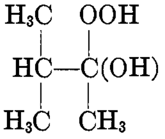
$$CH_3CH_2CH_3 + CH_3CO(OOH) \rightarrow CH_3CH(OH)CH_3 + CH_3COOH$$

It is possible that the primary step in the above two reactions is a condensation of the hydrocarbon and peracid to form



$$\begin{array}{ccc} CH_3 & & H \\ | & & | \\ HC & \!-\!O\!-\!O\! & C(OH) \\ | & & | \\ CH_3 & & CH_3 \end{array}$$

or

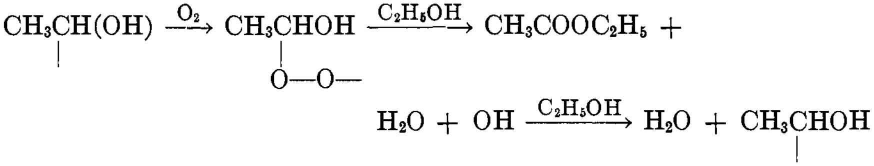


$$\begin{array}{ccc} H_3C & & OOH \\ | & & | \\ HC & \!-\! & C(OH) \\ | & & | \\ H_3C & & CH_3 \end{array}$$

which then split up into the products noted at different temperatures.

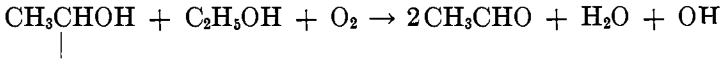
The acetone could be formed in a subsequent step from isopropyl alcohol, for example, by a reaction with a peroxide.

Another example that may be mentioned is the oxidation of ethyl alcohol at high pressures. The lower the percentage of oxygen in the mixture, the larger the yields of acetaldehyde. The yield of ethyl acetate, which is one of the main products, is much less susceptible to change in mixture composition. The formation of the latter substance is readily represented by a radical chain, viz.



$$\mathrm{CH_3\underset{|}{C}H(OH) \xrightarrow{O_2} CH_3\underset{\underset{O—O—}{|}}{C}HOH \xrightarrow{C_2H_5OH} CH_3COOC_2H_5 + H_2O + OH \xrightarrow{C_2H_5OH} H_2O + CH_3\underset{|}{C}HOH}$$

If at constant pressure the percentage of oxygen is decreased, the number of binary collisions between alcohol *radical* and oxygen should decrease relative to the number of ternary collisions



$$\mathrm{CH_3\underset{|}{C}HOH + C_2H_5OH + O_2 \rightarrow 2CH_3CHO + H_2O + OH}$$

thus leading to larger yields of acetaldehyde.

Regardless of the correctness of these particular schemes, we believe that a consistent interpretation of the oxidation of hydrocarbons is possible only along these lines.