123. *The Vapour-phase Oxidation of Methyl*cyclo*pentane.*

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The pressure–temperature limits for spontaneous cool- and hot-flame ignitions of an equimolecular methyl*cyclo*pentane–oxygen mixture in a 550-c.c. quartz bulb have been determined, and the effect of the fuel : oxygen ratio has been briefly studied. The progressive changes in concentration of products or product groups in high- and low-temperature slow combustion and cool-flame reactions in the same vessel have also been investigated. Similarly, the products formed in a Pyrex-glass flow system at atmospheric pressure have been studied for different fuel : oxygen ratios and for an equimolecular mixture at varying residence times, all the reacting media being diluted with an equal volume of nitrogen. The chief stable products, apart from the oxides of carbon, are carbonyl compounds (including ketones), acids (particularly at low temperature), and unsaturated materials (particularly at high temperature). Peroxides survive in the products at low temperatures. Reaction in a flow system is initiated at an area of the reactor which has become " activated," and the position of this area varies with the flow rate.

THE increasing exploitation of petroleum as a raw material for the chemical industry has renewed interest in the homogeneous oxidation of hydrocarbons as a possible means of deriving useful intermediates. Methyl*cyclo*pentane, the subject of the present study, is available from the processing of petroleum.

Only a few chemical investigations into the vapour-phase oxidation of the cyclic paraffins generally, and of methyl*cyclo*pentane in particular, have been reported. Lewin (*Bull. Soc. chim. Belg.*, 1933, **42**, 141) studied a number of alkyl*cyclo*paraffins, including methyl*cyclo*pentane, using reaction temperatures of less than 250°, the induction period for the oxidation of methyl*cyclo*pentane then being several hours. Ivanov (*J. Gen. Chem. Russia*, 1936, **6**, 470; *Chem. Abs.*, 1936, **30**, 6344) has described the properties of the peroxides obtained by the oxidation of *cyclo*hexane with air in a flow system at 316°, and tentatively ascribes the structures $(HO{\cdot}O)_2C_6H_9{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}OH$ and $HO{\cdot}O{\cdot}C_6H_9(OH){\cdot}O{\cdot}O{\cdot}CH_2{\cdot}OH$ to the peroxides. Presumably these products are obtained by interaction of formaldehyde and *cyclo*hexyl peroxide initially formed.

Dupont and Chavanne (*Bull. Soc. chim. Belg.*, 1933, **42**, 537) studied the slow oxidation of ethyl-, butyl-, and phenyl-*cyclo*pentane, below their boiling points. From ethyl*cyclo*pentane were obtained heptan-3-one, 5-ketoheptanoic, propionic, acetic, and formic acids, as well as hydrogen and oxides of carbon. It was concluded that oxidation leads first to rupture at the tertiary carbon atom.

It is well known that in order to obtain useful yields of oxygenated intermediates by the homogeneous oxidation of hydrocarbons it is necessary to work with mixtures containing oxygen in less than stoicheiometric proportions and at temperatures and pressures somewhat below those necessary for ignition. Except for first members of homologous series the relation of pressure with temperature along the ignition limit is rarely simple. The complexities encountered are well illustrated in Newitt and Thorne's investigation (*J.*, 1937, 1656, 1669) into the oxidation of propane. It was therefore clear that, before considering the oxidation products obtainable from methyl*cyclo*pentane, it would be necessary to define the range of conditions to be covered. The ignition limits under static conditions were therefore surveyed and the progressive formation of reaction products was examined under certain typical conditions thus indicated. For the purpose of obtaining products efficiently, however, a continuous reaction system is essential, and with the knowledge obtained from " static " reactions the investigation of products was extended into a flow system.

A complex mixture of oxidation products is to be expected from a molecule of the size of methyl*cyclo*pentane. For preliminary survey, therefore, groups rather than individual compounds were in most cases determined. The work has not proceeded beyond this point, but it sets the stage for a more detailed study of individual products under selected conditions of reaction.

EXPERIMENTAL.

Materials.—Methyl*cyclo*pentane was prepared from *cyclo*hexane by isomerisation in the presence of aluminium chloride, followed by fractionation through a twenty-plate column and removal of aromatic compounds by silica gel. It was spectroscopically free from benzene but may have contained up to 5% of *cyclo*hexane.

Oxygen (99·5%), from cylinders, was stored over water in a glass gas-holder and before use was passed successively over silica gel and anhydrous magnesium perchlorate.

Apparatus and Method.—Static oxidation. The apparatus used for the "static" experiments has been described by Burgoyne (*Proc. Roy. Soc.*, 1937, *A*, **161**, 48). It consists essentially of a system for preparing a small stock of hydrocarbon–oxygen mixture (with added nitrogen if desired) of which a part can be introduced into an evacuated 550-c.c. cylindrical quartz reaction vessel at a known temperature to give the required pressure. Subsequent reaction is observed with the aid of a mercury manometer. For analysis of the products formed at intermediate stages of the reaction, the apparatus was extended by connecting to the reaction vessel, through a stopcock, a 500-c.c. bulb with a mercury manometer attached, followed by a gas burette. The bulb was evacuated and immersed in carbon dioxide–alcohol.

To withdraw the products from the reaction vessel, the stopcock to the cold evacuated bulb was opened, most of the reacting mixture then flowing quickly into the bulb. The proportion removed from the reaction vessel was ascertained by an immediate reading of the reaction manometer. To obtain a suitable amount of material for analysis the reaction and the process of sampling were repeated 3—10 times, depending on the pressures of reactants which could be admitted to the bulb without causing ignition. The gas pressure in the sampling bulb at the temperature of solid carbon dioxide was then noted and a gas sample pumped out with the aid of a gas burette. The bulb was allowed to warm to room temperature and the remaining products were dissolved and washed out with water. The washings were made up to a standard volume, from which aliquot parts were withdrawn for analysis. The small amount of water-immiscible matter was dispersed by vigorous shaking before withdrawal of portions of the mixture for analysis.

Flow-oxidation apparatus. In principle the method was to pass streams of oxygen and of nitrogen, saturated with methyl*cyclo*pentane at various temperatures, by way of separate pre-heating tubes to a mixing spiral (10-ml. capacity) and 3·2-cm.-diameter cylindrical Pyrex reaction chamber (83-ml. capacity), all enclosed in an electric furnace. Immediately after leaving the furnace the gas stream passed through a water-cooled condenser into a cooled receiver.

The furnace temperature was accurately controlled by an air-bulb thermoregulator operating through a 200-watt auxiliary heater traversing the length of the furnace tube. Under steady conditions this gave control within 2°, but the regulator could only compensate to a limited extent for local temperature rises occurring in the reaction chamber. Temperatures were measured by a roving Pt/Pt–Rh thermocouple which, however, rested for the most part on top of the reaction chamber. The part of the furnace occupied by the mixer and reactor was uniform in temperature within 5°.

With this apparatus residence times of 2—40 seconds were possible, and, in the results that follow, residence time should be understood to mean that which would apply without change in volume caused by exothermic reaction or by change in the number of molecules through reaction; in most of the experiments the divergence from the true residence time did not exceed 10%. At 300° it was possible to run the system at a standard pressure of 760 mm. with the aid of an arrangement of mercury bubblers connected with a water-pump, but at higher temperatures it was necessary to work at the prevailing atmospheric pressure to avoid ignitions resulting from sharp changes in the working pressure.

On account of mist formation a receiver cooled in solid carbon dioxide was not satisfactory, and a sintered-plate bubbler containing solvent and cooled in ice was more suitable; gas samples were withdrawn after they had passed the bubbler.

In general, *iso*propanol was the best solvent for absorption of the products, including water, together with excess of hydrocarbon, but owing to interference of *iso*propanol with some of the analytical methods the products were collected in water; the aqueous and the hydrocarbon layer were separated and each made up to a definite volume (the latter with pure *cyclo*hexane). Equal proportions of each solution were then taken for each determination, excepting that of formaldehyde which was found exclusively in the aqueous part; higher aldehydes could not satisfactorily be determined owing to their presence in part in the hydrocarbon layer.

Methods of Analysis.—Gases. The gas sample was analysed in a Bone–Newitt constant-volume apparatus, using potassium hydroxide solution for carbon dioxide, alkaline pyrogallol for oxygen, mercuric perchlorate for olefins (R. A. Cox, personal communication), and ammoniacal cuprous chloride for carbon monoxide. The residue was exploded with a measured volume (A) of oxygen in excess, and the carbon dioxide (B) formed was measured. Residual oxygen (C) was then absorbed, and also the small but erratic volume of carbon monoxide (D) evolved from the pyrogallol. (B) gave the quantity of paraffinic carbon; and from the oxygen consumed, $[A - (C + D)]$, the total of paraffinic and free hydrogen was calculated, after allowance for oxygen required to form carbon dioxide.

Liquids. After considerable investigation, the following methods were adopted.

(1) Acids. Titration with N/50-alkali, to phenolphthalein or α-naphtholphthalein.

(2) Peroxides. Two iodometric methods were used together: (*a*) A 5-ml. sample was added to acetic acid (15 ml.) containing 50% aqueous potassium iodide (2 ml.) (iodine liberated by peracetic acid being removed previously with sodium thiosulphate). After at least 1½ hours, the solution was diluted with water and titrated with N/50-thiosulphate. (*b*) (Based on Clover and Houghton's method, *Amer. Chem. J.*, 1904, **32**, 43.) The sample was added to 50% potassium iodide solution (2 ml.), and the following procedures carried out: (i) the mixture was kept for 10 minutes and then titrated with sodium thiosulphate; (ii) the mixture was treated with 20% sulphuric acid, kept for a further 30 minutes and titrated again; (iii) iodine liberated after this mixture had been kept overnight was titrated; and (iv)

iodine liberated after the addition of a trace of ferrous salt was titrated. In practice no significant readings were obtained in steps (iii) and (iv), from which it was concluded that alkyl hydroperoxides and dialkyl peroxides were not present in appreciable quantity. In methods (*a*) and (*b*) closed flasks were used from which air was displaced by nitrogen.

(3) *Total carbonyl compounds.* A hydroxylamine reagent was prepared by dissolving hydroxylamine hydrochloride (10 g.) in water (100 ml.), dilution to 1 l. with alcohol, and adjustment of the pH to the dichroic neutral point of bromophenol-blue by addition of alkali. 70 ml. of the reagent with 10 ml. of sample were warmed at 50° for 30 minutes; after cooling, the mixture was treated with 1 ml. of 0·2% bromophenol-blue, and the solution titrated with N/30-alkali to the colour of a blank containing the same volume of water.

Such evidence as is available indicated that under the conditions of this determination, hydroxyperoxides, which may be formed from aldehydes and hydroperoxides in the products, dissociate into the original components. Small quantities of hydrogen peroxide were found not to interfere, and there appeared to be little reaction of organic peroxides during the period of the determination, since subsequent heating of samples containing peroxides resulted in a *slow* liberation of hydrochloric acid which required several hours for completion. No correlation was found, however, between the acid thus liberated and the quantity of peroxides determined iodometrically.

(4) *Formaldehyde.* The colorimetric test described by Steigmann (*J. Soc. Chem. Ind.*, 1942, **51**, 18) was adapted for quantitative use. The reagent consisted of an aqueous solution of magenta (Technical) (0·025% w/v), sulphuric acid (2·5% v/v), and thiolacetic acid (0·03—0·05% w/v). The acid dye solution was kept for several hours before addition of the thiolacetic acid, and the reagent was freshly prepared every few days. After an approximate determination by comparison with a series of standards in which the formaldehyde contents were in geometric progression with a ratio of 1·6, the colour developed by the appropriate volume of sample was compared after 10 minutes with that of a series of standards prepared from 5 ml. of reagent and severally 1·0, 1·1, 1·2, 1·3, 1·4, 1·5, 1·6 ml. of 0·0075M-formaldehyde. Under these conditions interference effects were least pronounced.

(5) *Higher aldehydes.* The colorimetric method using Schiff's reagent was employed, with aqueous propaldehyde as standard.

(6) *Ketones.* These were deduced by difference, *i.e.*, total carbonyl — (formaldehyde + higher aldehydes).

(7) *Unsaturation.* An excess of M/30-bromine in aqueous potassium bromide was run into the sample in about 100-ml. of water, shaken for 30 seconds, and treated with potassium iodide solution. The liberated iodine was titrated with thiosulphate. By working in dilute neutral solution and titrating the iodine promptly, peroxide interference was largely avoided, and the reaction of higher aldehydes minimised.

(8) *Alcohols.* The acetyl chloride–pyridine method of Smith and Bryant (*J. Amer. Chem. Soc.*, 1935, **57**, 61) was employed. For this analysis separate reactions were carried out and the products collected in toluene instead of water. The receivers were washed out with dioxan to remove water, and the final solution was dried with anhydrous sodium sulphate before analysis. The method was satisfactory only in the absence of peroxides.

RESULTS AND DISCUSSION.

Zones of Reaction.—The observed modes of reaction of an equimolecular methyl*cyclo*pentane–oxygen mixture in relation to temperature and pressure are set out in Fig. 1. The general form of the diagram is typical of the higher paraffins and it differs only in detail. Figures attached to points on the boundary curves represent measured delays between admission of the mixture to the reaction vessel and the occurrence of cool-flame or true ignition as the case may be.

Ignition near the limit at high temperatures was always followed by some slow combustion which increased in extent with increasing temperature. Over most of the cool-flame region three successive pulses were observed in each reaction; and in the ignition zone within the cool-flame temperature range (245—365°) two cool-flame pulses preceded each ignition.

The state of the surface of the reaction vessel exerted a strong influence on the results obtained both for delay periods and for the actual limits of cool-flame or true ignition. To standardise conditions, it was best to prepare the vessel by carrying out a few mild ignitions at high temperatures. Between tests the vessel was first evacuated roughly, then swept out with air for half a minute, and finally evacuated fully.

A few cool- and hot-flame ignition-limit determinations were made with 1 : 2 and 2 : 1 methyl*cyclo*pentane–oxygen and 1 : 1 : 4 methyl*cyclo*pentane–oxygen–nitrogen mixtures. The results are compared with data for the equimolecular mixture, taken from Fig. 1, in Table I, the nitrogen mixture being calculated to a nitrogen-free basis. It will be seen that the cool-flame limit is not greatly affected by composition but is lowered in the presence of nitrogen. The hot-flame limit rises throughout the temperature range on increasing the proportion of hydrocarbon, but is lowered in the presence of nitrogen. With the 2 : 1 mixture not more than two successive cool flames were observed in any one reaction, but with the 1 : 2 mixture as many as five successive cool flames occurred.

TABLE I.

Cool- and hot-flame ignition limits (mm.) for C_6H_{12}–O_2 *mixtures.*

(H.F. = hot flame; C.F. = cold flame.)

Ratio $C_6H_{12} : O_2$.

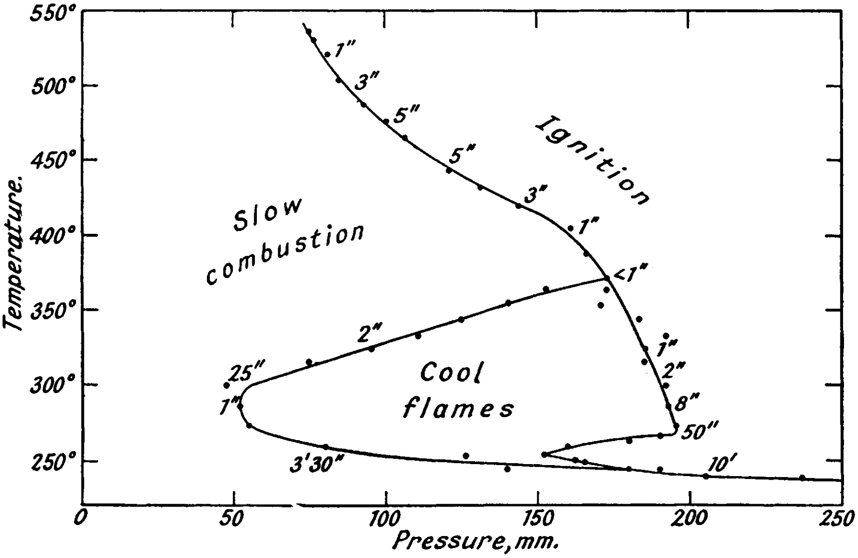
	1 : 2.		1 : 1.		2 : 1.		1 : 1(+4N_2).*	
Temp.	H.F.	C.F.	H.F.	C.F.	H.F.	C.F.	H.F.	C.F.
509°	53	—	75	—	†	—	52	—
450	87	—	105	—	†	—	74	—
420	†	—	130	—	156	—	†	—
380	148	—	165	—	205	—	138	125 (?)
340	†	128	183	124	†	138	†	97
315	175	†	195	75	†	73	147	61
274	167	54	195	55	212	62	150	48
255	102	96	152	126	165	124	129	89

* Calc. as partial pressure of the $C_6H_{12} : O_2$ mixture.
† Not determinable owing to shortness of lags.

Products of Reaction in a Static System.—Consideration of Fig. 1 suggests that there are three zones of reaction requiring study, namely, the cool-flame region and the regions of slow combustion at lower and higher temperatures. Accordingly, conditions of reaction were selected to typify these three zones, and for each condition the progressive formation of products throughout the reaction was followed. The results are presented in Tables II—IV and in Figs. 2—7.

FIG. 1.

*Combustion diagram for equimolecular methyl*cyclo*pentane–oxygen mixture in quartz bulb.**



Yields of products are expressed directly in terms of the number of moles of each obtained from 100 moles of starting material (either methyl*cyclo*pentane or oxygen, the mixture being equimolecular). Since it was impracticable to determine the amount of unchanged hydrocarbon, and the precise nature of the individual products was unknown, carbon balances could not be calculated. An oxygen balance can, however, be obtained if the following overall reactions are assumed irrespective of the actual mechanism :

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* *Added in Proof.*—In the light of a recent paper by Malherbe and Walsh (*Trans. Faraday Soc.*, 1950, **46**, 835) we are inclined to believe that the deviations of the experimental points from the smooth limit curves at temperatures below 400° are to some extent significant. Thus pressure minima in the ignition limit are indicated at about 350° and 310° as well as the one shown at about 255°; and the cool flame limit appears to show corresponding features.

$$\begin{aligned}
\mathrm{CH_2 + 1\tfrac{1}{2}O_2} &= \mathrm{CO_2H + H_2O} \\
\mathrm{CH_2 + O_2} &= \mathrm{CO + H_2O} \\
\mathrm{CH + O_2} &= \mathrm{CO_2H} \\
\mathrm{CH + \tfrac{1}{2}O_2} &= \mathrm{C{\cdot}OH} \\
\mathrm{CH{\cdot}CH + \tfrac{1}{2}O_2} &= \mathrm{C{:}C + H_2O}
\end{aligned}$$

$$\mathrm{R{\cdot}CO_2H = RH + CO_2}$$

$$\mathrm{R{\cdot}CHO = RH + CO}$$

These equations do not, however, take into account the fission of C–C bonds, which would be equivalent to oxidation.

High-temperature Reaction (450° and 100 mm.) (see Table II and Figs. 2 and 3).—Observable

FIG. 2.

*Gaseous products from equimolecular methyl*cyclo*pentane–oxygen mixture at* 450° *and* 100 *mm.*

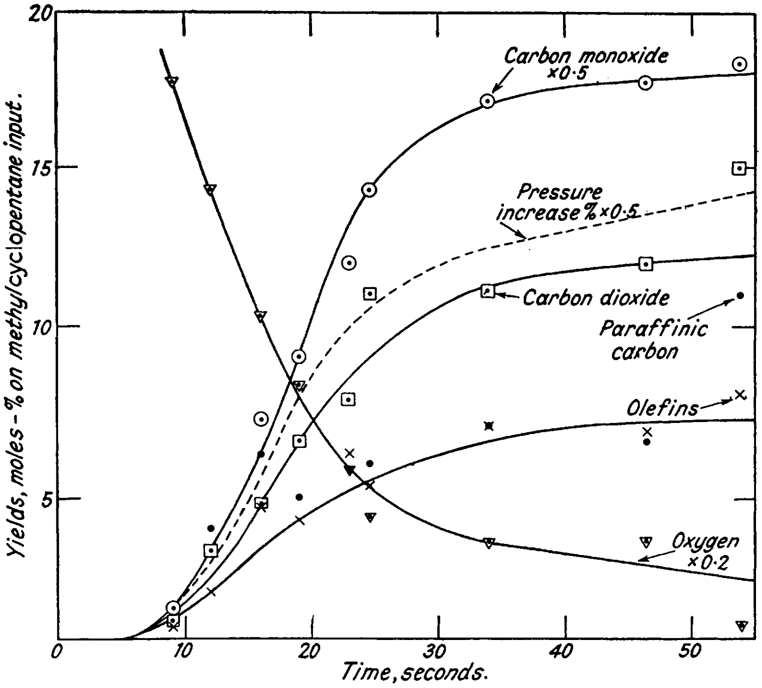


TABLE II.

High-temperature reaction at 465° *and* 100 *mm.*

	Products in moles per 100 moles of O_2 (or C_6H_{12}) input.									
Mean initial pressure, mm.	93	101	101	96	97	104	96	97	104	109
Time, secs.	9	12	16	19	23	24·5	34	46·5	54	75
Pressure increase (% of initial)	2	5	10	15	20	21·5	25	27·2	28·4	30
Carboxyl	0·25	0·3	0·5	0·7	0·75	0·75	0·85	1·05	0·65	0·6
Carbonyl total	2·6	5·4	11·0	13·4	16·0	16·25	17·85	16·9	17·0	14·9
Formaldehyde	1·4	1·8	2·7	3·8	4·1	4·2	5·2	5·45	5·8	—
Higher aldehyde	1·5	2·5	4·9	6·0	7·3	6·7	8·9	7·7	5·55	—
Ketone	(—0·5)	1·2	3·4	3·4	4·6	5·4	3·8	3·8	5·6	—
Unsaturation	1·0	2·9	4·2	4·85	5·55	6·4	6·05	5·6	5·55	5·15
Hydroxyl	—	1·2	2·9	2·1	—	—	2·2	—	—	1·9
CO	1·85	5·55	14·05	18·0	24·0	28·3	34·3	35·6	36·75	37·6
CO_2	0·055	2·8	4·3	6·3	7·6	10·9	11·05	12·05	15·1	14·3
Olefins	0·55	1·5	4·2	3·7	5·85	4·85	6·8	6·55	7·35	7·6
Paraffinic C	—	3·5	5·9	4·5	5·35	5·6	6·8	6·3	10·9	13·0
Paraff. and free H	—	6·95	21·4	21·3	25·0	25·1	32·3	32·8	40·5	51·2
Paraff. C/H ratio (from graph)	—	2·0	3·35	4·0	4·0	5·1	4·5	4·65	4·65	4·0
O_2, unconsumed	88·8	72·0	51·6	40·6	27·0	19·7	15·5	15·4	2·15	3·94
O_2, accounted for	95·7	90·5	89·05	87·9	86·2	85·8	93·1	86·3	87·0	86·2

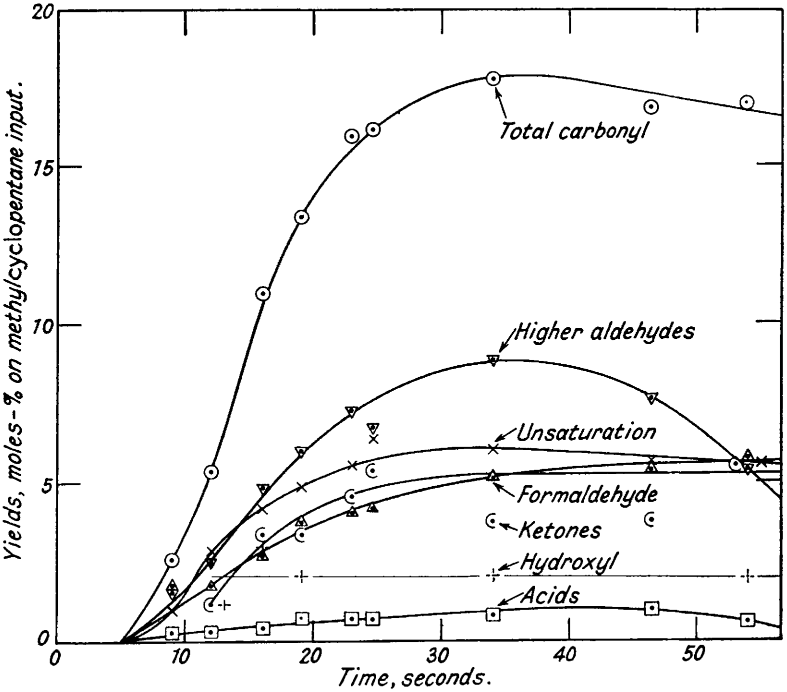
reaction commenced after about 5 seconds, and in the following 20 seconds 50% of the available oxygen was consumed in a relatively fast reaction. Completion of the reaction required a further 50 seconds.

The principal condensable products are carbonyl compounds which reach a maximum concentration, equivalent to 15% of the hydrocarbon input, towards the end of the rapid part of the reaction. The maximum appears to be due to higher aldehydes, for the formaldehyde and ketones, which accumulate during the rapid reaction, remain unchanged or increase slightly throughout the later stages.

The correlation between higher aldehyde concentration and overall reaction rate is consistent with the view that the higher aldehydes are intermediate products in consecutive reactions, though at this temperature there was probably also some pyrolysis. The trends in the ketones, hydroxyl compounds, unsaturated compounds, and (less definitely) acids suggest that they, like the more obvious end-products carbon monoxide and dioxide and gaseous olefins, are not intermediates but rather end-products of side reactions.

Fig. 3.

*Condensed products from equimolecular methyl*cyclo*pentane–oxygen mixture at* 450° *and* 100 *mm.*



The oxygen balance (Table II) shows that the products analysed account for 85—90% of the oxygen originally introduced. The discrepancy tends to increase slightly throughout the reaction, however, suggesting that there is some product not taken into account. It will be noted that peroxides were not found in the products of this reaction.

Low-temperature Reaction (232° and 400 mm.) (see Table III and Figs. 4 and 5).—At temperatures below the cool-flame range the slow reaction was preceded by a lengthy induction period that was sensitive to temperature and to the condition of the surface of the reaction vessel. For the reaction in question it varied between 10 and 15 minutes, and there were also some variations in the reaction rate. The results given were related to pressure change and thence to time through a standard pressure–time curve typical of the reaction.

An important feature of the results is that half the oxygen is consumed without much pressure increase and practically all is consumed before the pressure increase is more than half complete. In such circumstances the pressure change cannot be taken as a measure of the extent of the reaction (*e.g.*, for kinetic measurements).

The latter part of the reaction must be largely decomposition rather than oxidation, and in the earlier part (induction period) oxygen is apparently reacting without increasing the number of molecules.

When the pressure begins to rise, carbonyl compounds and acids are already present in considerable amount, together with smaller quantities of other products. Comparison with the

FIG. 4.

*Gaseous products from equimolecular methyl*cyclo*pentane–oxygen mixture at* 230° *and* 400 *mm.*

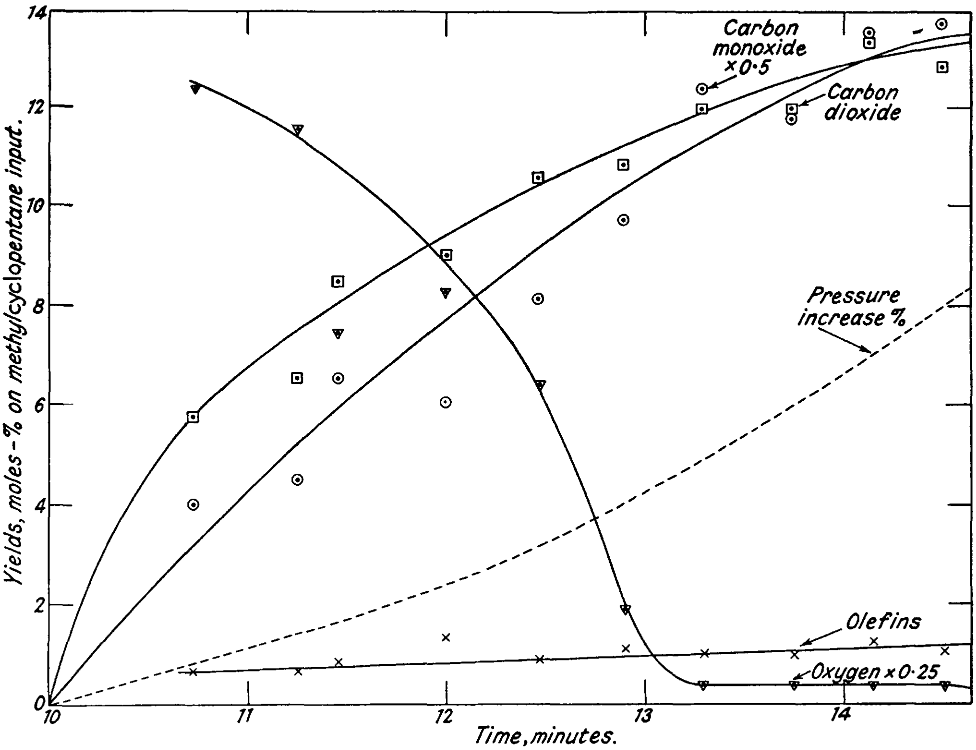


TABLE III.

Low-temperature reaction at 232° *and* 400 *mm.*

	Yields in moles of product per 100 moles of O_2 input.									
Pressure increase (% of initial) ...	$\frac{3}{4}$	$1\frac{1}{4}$	$1\frac{1}{2}$	$2\frac{1}{4}$	3	4	5	6	7	8
Time, min.	10·8	11·25	11·45	12·0	12·4	12·9	13·3	13·75	14·15	14·5
Mean initial pressure, mm.	398	400	392	401	367	386	397	398	399	402
Carboxyl	5·13	5·8	7·55	7·9	9·9	10·65	11·45	10·45	11·2	11·0
Carbonyl	12·2	13·8	18·93	18·7	22·85	22·9	25·67	23·77	24·9	26·05
Formaldehyde	2·1	2·5	3·0	3·2	4·0	4·6	5·2	4·6	5·3	5·8
Higher aldehydes	4·0	6·3	7·5	6·8	8·7	8·7	8·7	8·2	10·1	8·8
Ketones	6·1	5·0	8·5	8·7	10·1	9·6	11·8	10·9	9·5	12·4
Unsaturation	2·4	1·55	1·85	2·35	2·15	2·15	4·0	2·15	2·85	2·7
Peroxide (*a*)	1·05	1·25	1·3	1·05	1·5	1·65	1·5	1·15	1·15	0·95
(*b*) (i)	0·35	0·45	0·45	0·25	0·3	0·5	0·45	0·2	0·2	0·15
(ii)	0·75	0·75	0·9	0·85	1·15	1·15	1·15	1·0	1·0	0·8
(iii)	0·1	0·1	0·15	0·15	0·2	0·15	0·1	0·15	0·1	0·1
CO	8·25	9·35	13·25	16·95	19·55	24·9	23·7	27·15	27·35	27·35
CO_2	5·85	6·6	8·6	9·05	10·65	10·9	12·05	12·05	13·6	12·8
Olefins	0·7	0·7	0·85	1·35	0·9	1·1	1·0	1·0	1·3	1·1
Paraffinic C	1·9	1·3	1·8	1·3	1·05	0·9	1·85	1·5	2·6	1·75
Paraff. and free H	4·5	3·6	5·1	3·2	3·5	2·5	6·6	4·4	9·0	9·4
O_2, unconsumed	49·85	46·5	30·1	32·95	26·95	7·7	1·55	1·5	1·6	1·45
O_2, accounted for	89·4	90·7	89·1	92·0	100·7	85·7	91·4	85·5	94·2	93·5

results of high-temperature reactions shows ketones and especially acids to be relatively more prominent, whilst unsaturated compounds are in much lower concentration. Peroxides appear in the products in concentration related to the rate of oxygen consumption, and appear to consist chiefly of alkyl hydroperoxides and hydrogen peroxide.

FIG. 5.

*Condensed products from equimolecular methyl*cyclo*pentane–oxygen mixture at* 230° *and* 400 *mm.*

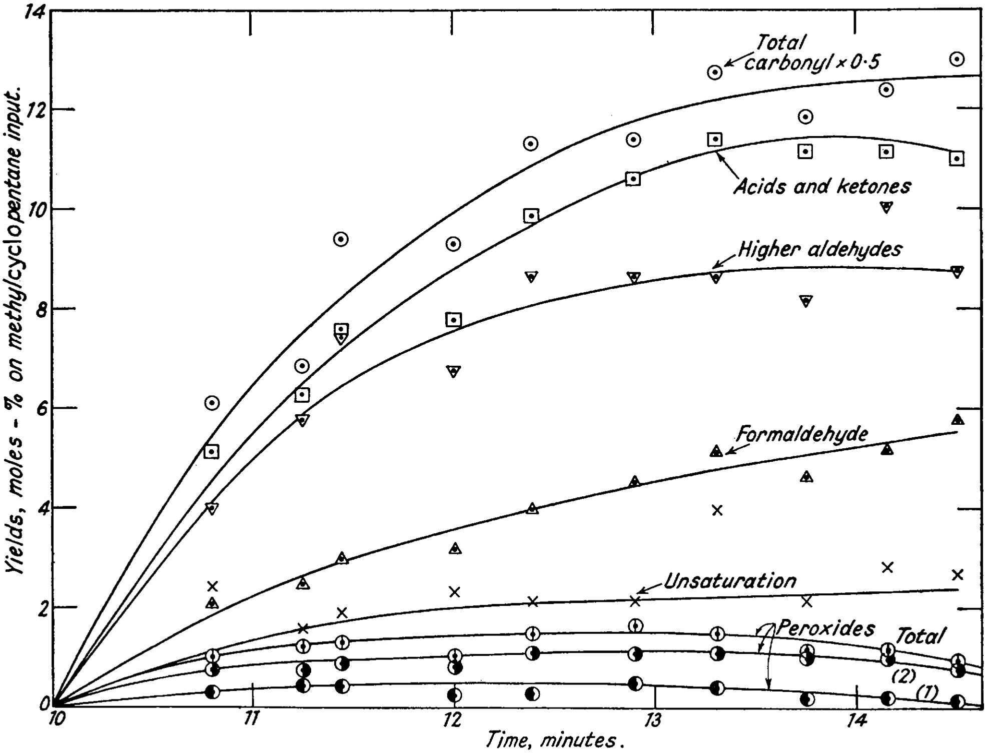


TABLE IV.

Cool-flame reaction at 275° *and* 155 *mm.*

	Yields in moles of product per 100 moles of O_2 input.					
Pressure increase (% of initial)	4·7	13·6	15·8	20·5	22·1	26·8 *
Time, min.	2·03	2·1	2·4	2·5	3·5	0·55
Mean initial pressure, mm.	153	156	158	156	156	172
Carboxyl	1·3	2·0	2·7	3·4	3·9	2·3
Carbonyl	6·6	18·2	23·7	27·8	27·2	26·6
Formaldehyde	1·4	4·6	5·2	7·3	8·7	8·5
Higher aldehydes	5·2	7·0	6·0	8·0	9·5	11·0
Ketones		6·5	12·5	12·5	9·0	7·0
Unsaturation	2·3	3·7	3·6	4·0	4·2	4·9
Peroxide (*a*)	1·1	3·2	3·9	3·2	1·1	0·9
(*b*) (i)	0·5	0·6	1·2	1·5	0·3	0·2
(ii)	0·3	0·4	0·7	0·7	0·6	0·9
(iii)	—	—	—	—	—	—
CO	5·1	17·9	21·9	32·9	38·1	39·6
CO_2	2·1	4·9	5·8	7·6	10·9	11·9
Olefins	0·7	2·2	2·8	3·6	3·5	3·6
Paraffinic C	—	3·2	1·9	3·5	4·1	2·5
Paraff. and free H	—	9·6	8·1	11·2	14·1	10·3
O_2 unconsumed	83·7	42·0	31·9	8·5	1·8	2·1
O_2, accounted for	103·0	94·6	97·4	97·5	94·3	94·7

* Products at end of reaction at 300°.

The continued pressure increase in the later stages of reaction is clearly associated with the formation of oxides of carbon, but apart from a limited disappearance of peroxides and perhaps acids and ketones there is no definite indication of the source of carbon monoxide and dioxide at this stage. The higher aldehydes survive a great deal better than at high temperatures.

Generally speaking (see Table III) 90% or more of the oxygen introduced is accounted for in the products analysed, and the balance tends to improve in the later stages of the reaction.

Cool-flame Reaction (275° and 155 mm.) (see Table IV and Figs. 6 and 7).—Under these conditions an induction period of about 110 seconds is followed by 15 seconds of slow combustion with very little pressure change, terminating in two cool flames in quick succession; after a further 20 seconds a feebler cool flame is propagated and this is followed by a final stage of slow combustion. It was not possible to interrupt the reaction between the first and second cool flames.

FIG. 6.

*Gaseous products from equimolecular methyl*cyclo*pentane–oxygen mixture at* 275° *and* 160 *mm.*

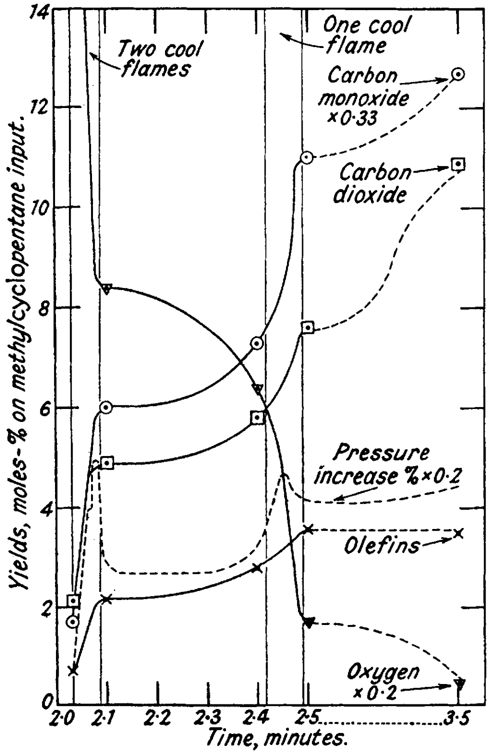
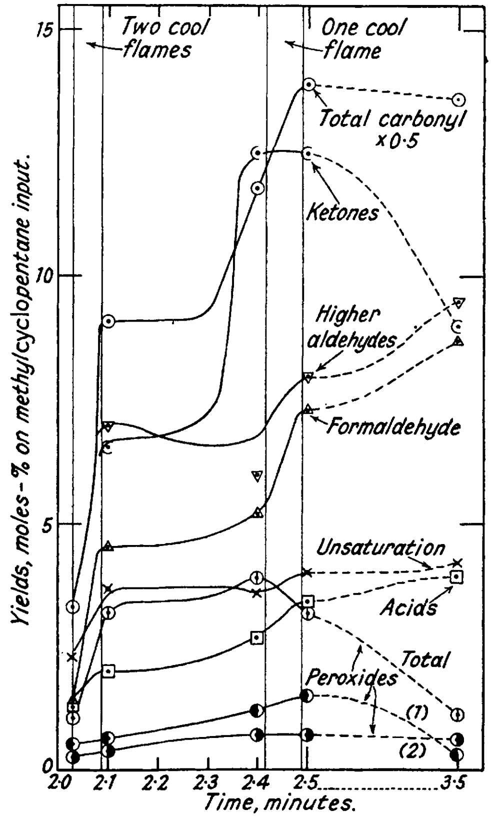


FIG. 7.

*Condensed products from equimolecular methyl*cyclo*pentane–oxygen mixture at* 275° *and* 160 *mm.*



In all, two-thirds of the oxygen is consumed during the three cool flames, and the product concentrations, excepting that of peroxides, show corresponding step-wise increases. In general terms, the distribution of products resembles that in the low-temperature slow reaction more than that in the high-temperature reaction, but acids are less prominent and unsaturated compounds more so, in accordance with the intermediate temperature. The total peroxide content determined by method (*a*) is usually much greater than that determined by method (*b*).

The results for aldehydes are in agreement with the findings of Neumann and Aivazov (*Acta Physicochim. U.S.S.R.*, 1936, **4**, 575) for pentane, but not with those of Newitt and Thorne (*loc. cit.*) for propane, in showing that aldehydes increase during the passage of cool flame.

More than 94% of the oxygen introduced was accounted for throughout this reaction (see Table IV).

Oxidation in a Flow System.—Mixtures were found to be much less prone to ignition in the flow system than in the static apparatus, and it was possible, therefore, to work at considerably higher partial pressure of reactants. Mixtures containing 50% of nitrogen were generally the most convenient: with them the temperature rise at the walls of the reactor was rarely more than 20°. Investigation of the effect of residence time as a measure of the extent of oxidation was difficult, owing both to surface effects (see below) and to the rapidity of reaction over most of the temperature range (250—500°) which could be studied. As an alternative the effect of varying the proportion of oxygen in the initial mixture was examined.

Surface influences. It was soon found that, in order to establish reaction in the region of 300°, the mixture had first to be passed through for a few minutes at a long residence time, *e.g.*, about 30 seconds. Reaction thus established persisted as the residence time was reduced slowly: a sudden reduction, however, caused it to die away. About 10 minutes after establishment of the reaction at the working temperature, product formation was steady and sampling could be begun. Interruption of the reaction even for 1—2 minutes led to loss of activity of the reactor. These observations emphasise the important role of the state of the reactor surface in determining the rate of reaction, and indicate that for given flow conditions the reaction is initiated in a certain region of the reactor where the surface has become activated. A change in flow rate evidently necessitates that the activated region must shift to another part of the reactor surface.

Cool-flame and ignition phenomena also showed the influence of surface conditions. Thus, when the nitrogen content was maintained at 50% and the residence time at 7 seconds, it was found that at 300° increasing the oxygen content from 25% to 30% resulted in the propagation every 9 seconds of a pair of cool flames, of which the first was the more vigorous; further increase to 35% gave periodic, inaudible, yellow-flame ignitions, and subsequent decrease to 30% then gave a feeble cool flame followed by a yellow-flame ignition; further decrease to 25% of oxygen gave neither cool flames nor ignitions. This cycle of events was reproducible.

Products of oxidation; variation of mixture composition. In Table V are the results of two identical series of runs (*a* and *b*) made at 300° with 7-seconds residence time and methyl*cyclo*pentane–oxygen ratios from 1 to 5, all the mixtures being diluted with an equal volume of nitrogen; the runs in each series were carried out in the order of decreasing oxygen content.

TABLE V.

Effect of $C_6H_{12}:O_2$ *ratio on products at* 300° (7-*secs. residence*).
(*a* and *b* are duplicate runs).

	Yields in moles of product per 100 moles of O_2 input.									
	1		1·5		2		3		5	
$C_6H_{12}:O_2$	*a.*	*b.*	*a.*	*b.*	*a.*	*b.*	*a.*	*b.*	*a.*	*b.*
Carboxyl	3·7	3·6	3·8	3·3	3·35	2·95	2·8	2·85	3·45	3·7
Carbonyl, total	22·8	25·6	25·7	26·0	26·1	27·4	29·1	26·8	38·9	33·4
Formaldehyde	3·9	3·9	4·8	4·25	4·85	4·8	5·55	5·6	7·05	7·05
Unsaturation	11·8	10·5	12·7	12·3	13·7	13·3	13·95	13·35	18·7	17·55
Peroxides (*a*)	4·6	6·05	5·75	4·85	3·65	4·4	3·1	2·8	3·65	3·35
(*b*) (i)	1·9	2·3	1·9	2·05	1·75	1·75	1·35	1·55	1·55	2·15
(ii)	1·0	0·7	1·15	1·45	1·45	1·3	1·75	2·1	3·2	2·95
(i + ii)	2·9	3·0	3·05	3·5	3·2	3·05	3·1	3·65	4·75	5·1
CO	37·6	39·2	29·5	29·6	26·8	26·8	26·4	26·4	28·7	27·6
CO_2	6·5	6·75	4·75	5·15	4·4	5·1	3·75	2·85	3·6	4·4
Olefins	6·7	5·2	3·9	5·05	3·8	5·75	3·6	3·2	4·05	3·2
O_2, unconsumed	9·8	10·4	17·3	17·85	20·5	21·55	22·4	21·9	18·7	16·0
O balance	99·3	104·7	99·4	99·6	97·4	101·7	99·6	94·8	111·9	100·7
RR'CO : CH_2O	6·2		5·8		5·55		5·0		(5·5)	4·75
RR'CO + CO	60·4	64·8	55·2	55·6	52·9	54·2	55·5	53·2	67·6	61·0

When regard is paid to the factors already discussed, the concordance of the results is good. It is evident that the survival of carbonyl and condensable unsaturated compounds is favoured by a low proportion of oxygen, the proportion of gaseous products being at the same time reduced. In general the results are like those obtained at intermediate stages in the oxidation of the equimolecular mixture under static conditions (Table III), except that the yield of condensable unsaturated compounds is several times greater in the flow experiments. A low proportion of oxygen in the mixture is associated with a high yield of formaldehyde compared with other carbonyl compounds, but the combined yields of carbonyl compounds plus carbon monoxide remain approximately constant throughout the series.

The variation in formaldehyde yield with hydrocarbon concentration finds an explanation in Walsh's hypothesis (*Trans. Faraday Soc.*, 1947, **43**, 297) that primary peroxide radicals, which in this case would be formed after fission of the *cyclo*pentane ring, are relatively unstable and decompose to give a higher aldehyde. With increase in hydrocarbon concentration a greater proportion would react to form primary peroxide molecules, and these on decomposition would yield formaldehyde :

$$\mathrm{R{\cdot}CHO + OH \longleftarrow R{\cdot}CH_2{\cdot}O{\cdot}O \xrightarrow{R'H} R{\cdot}CH_2{\cdot}O{\cdot}OH \longrightarrow R + CH_2O + OH}$$

A comparison of the results for peroxides demonstrated the limitations of the analytical methods employed : method (*a*) shows a maximum when the methyl*cyclo*pentane–oxygen ratio is lowest, but method (*b*) shows an opposite result. Peracids vary little throughout and the discrepancy appears to be associated with the peroxides which react only in acid solution. Oxygen balances are very satisfactory.

The results for a similar series of runs at 465° with a 4·5-seconds residence time are given in Table VI. Here the chief differences from the static reaction (cf. Table II) are again in the higher yields of unsaturated compounds, both liquid and gaseous, obtained in the flow reaction. Yields of peroxides are negligible. The high oxygen balances are probably accounted for by cracking, which is known to be induced by oxygen at moderately high temperatures. If, as an approximation, the gaseous olefins are considered to be formed without oxygen consumption, reasonable balances are restored.

TABLE VI.

Effect of C_6H_{12} : O *ratio on products at* 465° (4·5-*secs. residence*).

	Yields in moles of product per 100 moles of O_2 input.					
C_6H_{12} : O.	1 *	1	1·5	2	3	5
Carboxyl	0·95	0·9	1·2	1·0	1·0	1·05
Carbonyl, total	16·75	15·25	19·65	19·9	18·4	25·9
Formaldehyde	5·25	5·1	6·0	7·4	5·3	9·25
Unsaturation	29·0	20·2	38·7	46·5	53·8	69·5
Peroxides (*a*)	0	0·1	0·1	0·15	0·15	0·4
CO	56·7	58·1	41·9	39·65	31·0	34·0
CO_2	7·2	5·75	5·75	4·80	7·1	5·8
Olefins	47·5	48·6	42·7	38·5	29·55	25·8
O_2, unconsumed	3·7	5·35	2·6	2·1	1·1	0·7
O_2, accounted for	127·7	122·2	115·4	113·0	104·5	117·9
O_2, accounted for excluding olefins	103·9	98·9	94·0	93·8	89·7	105·0

* Results from another series of experiments.

Observations upon the effect of varying the partial pressure of nitrogen associated with an equimolecular methyl*cyclo*pentane–oxygen mixture at 300° showed that a fairly distinct limit is encountered between 71·5% and 73·5% of nitrogen at which reaction becomes much reduced. At 350° this limit lies beyond 78% of nitrogen.

TABLE VII.

Effect of residence time on products from 1 : 1 : 2 C_6H_{12}–O_2–N_2 *at* 300°.

	Yields in moles of product per 100 moles of O_2 input.				
Contact time, secs.	2·5	3·33	4·5	6	8
Carboxyl	1·65	2·1	3·0	3·35	2·6
Carbonyl	15·4	15·9	19·7	22·3	22·4
Formaldehyde	3·4	3·4	3·8	5·2	4·4
Unsaturation	10·0	9·7	10·3	13·7	12·0
Peroxide (*a*)	3·5	4·0	4·3	4·2	2·7
(*b*) (i)	1·0	1·1	1·5	1·7	1·4
(ii)	0·4	0·4	0·6	0·8	0·6
CO	18·9	20·8	30·3	30·8	33·1
CO_2	4·0	3·7	5·9	6·0	6·7
Olefins	5·1	3·6	5·4	5·3	6·2
O_2, unconsumed	42·8	37·0	31·9	21·0	10·6
O_2, accounted for	96·6	93·1	107·4	101·8	91·8

Variation of residence time. With the 1 : 1 methyl*cyclo*pentane–oxygen mixture diluted with nitrogen at 300° it was possible to some extent to find flow rates giving intermediate oxygen consumptions, in spite of a greater temperature rise caused by reaction with increasing flow rates. Analyses of products of the 1 : 1 : 2 methyl*cyclo*pentane–oxygen–nitrogen mixture over a range of residence times were therefore made, with the results shown in Table VII. At the two shortest residence times feeble cool flames were propagated through the reactor in pairs at intervals of about 3 seconds. Except for the carbonyl compounds, all the liquid products reach maximum yields at 6-seconds residence time, but the oxygen balances are rather erratic and it is difficult to draw detailed conclusions.

In Table VIII are given further results relating to the same 1 : 1 : 2 mixture reacting for certain times at 350°, 400°, and 465°. At 510° this mixture ignited and the 1 : 1 : 4 mixture was used instead. Relevant results for 300° are quoted from Table VII for comparison. At 350° and 400° the heat of reaction was too great to allow the 2·5-seconds residence time to be investigated. At 350° no preliminary activation of the reactor was necessary, although it took five minutes for the temperature rise to reach its stationary value.

TABLE VIII.

Effect of temperature and residence time in products from 1 : 1 : 2 *and* 1 : 1 : 4 C_6H_{12}–O_2–N_2 *mixtures.*

Yields in moles of product per 100 moles of O_2 input.

C_6H_{12} : O_2 : N_2 ...	1 : 1 : 2		1 : 1 : 2		1 : 1 : 2		1 : 1 : 2			1 : 1 : 4		
Temp.	300°		350° *		400° *		465°			510°		
Residence time, secs.	4·5	8	4·5	8	4·5	8	2·5	4·5	8	2·5	4·5	8
Carboxyl	3·0	2·6	Not determined				1·0	1·0	1·3	0·9	1·0	0·9
Carbonyl	19·7	22·4	22·2	22·5	19·6	19·3	15·7	16·8	21·1	14·4	16·6	18·1
Formaldehyde	3·8	4·4	Not determined				6·0	5·3	6·8	5·4	5·5	5·8
Unsaturation	10·3	12·0	24·1	14·5	24·7	19·2	23·8	29·0	31·3	14·7	17·7	18·5
Peroxide (*a*)	4·3	2·7	1·7	1·0	trace	0	0	0	0	0	0	0
CO	30·3	33·1	44·1	41·0	54·3	32·3	50·8	56·7	43·7	62·6	60·4	48·7
CO_2	5·9	6·7	6·9	9·5	8·0	11·3	7·8	7·2	7·7	6·3	7·6	7·4
Olefins	5·4	6·2	18·5	9·4	31·0	8·7	56·4	47·5	29·6	70·0	57·8	42·7
O_2, unconsumed ...	31·9	10·6	2·9	3·2	4·3	2·9	6·2	3·7	2·3	6·2	5·9	3·1
O_2, accounted for ...	107·4	91·8	102·5	93·3	119·1	85·4	125·0	127·8	111·0	136·9	133·6	113·0
O_2, accounted for excl. olefins	104·7	88·7	93·2	88·6	102·6	81·1	97·8	104·0	96·2	101·4	104·7	91·7
Temp. rise	24°	20°	29°	11°	23°	5°	20°	9°	3°	8·5°	3°	1°

* The balances for products formed at 350° and 400° are exclusive of carboxyl.

In general, increase in temperature favours the gaseous at the expense of liquid products. Gaseous olefins show a pronounced increase, and the oxygen balances indicate that they arise mainly by pyrolysis. Their decrease with increasing residence time is attributable to polymerisation, which is known to be induced by small quantities of oxygen.

The reduction in exothermicity as the reaction temperature is raised is not adequately accounted for by the smaller input of reactants needed to maintain a given residence time, but it is paralleled by the increases in unsaturated products; the oxygen balances show that these must be formed mainly by cracking, and this is known to be an endothermic process.

Up to at least 465° the yield of formaldehyde increases with temperature. The decrease in carbon monoxide production with increase in residence time from 4·5 to 8 seconds is rather surprising. Oxygen consumption at this stage is practically complete, and, since carbon dioxide does not show a corresponding increase, neither direct oxidation nor the water gas equilibrium can be invoked as an explanation. It is perhaps significant that the increase in production of carbonyl compounds when residence time is increased from 2·5 to 8 seconds at 465° and 510° is slightly greater than the oxygen consumption during this period. Moreover, in all the series of experiments from 300° to 500° the oxygen balance (excluding olefins) is highest (or higher) when the contact time is 4·5 seconds, so that it is unlikely that these observations are attributable to experimental error.

Oxidation below 300°. For the purpose of investigating reactions below 300° the 2 : 2 : 1 mixture of methyl*cyclo*pentane, oxygen, and nitrogen was employed with a 40-seconds residence time. The reaction was self-initiating down to about 280°, but, on further lowering of the temperature, reaction died away at about 255°, signalled by a pair of cool flames or feeble ignitions. On slow raising of the temperature again, inaudible, blue-flame ignitions with a period equal to the residence time set in at 265°, and shortly gave way to cool flames every 15 seconds.

Since this is in the region of the low-temperature ignition peninsula (see Fig. 1), the transition from ignition to cool flames could be accounted for by a slight temperature rise. Continuous cool-flame propagation was never observed when starting from a high temperature.

At 260—265° oxygen consumption was almost complete and remained so when the residence time was reduced by small steps (12·5%) down to 17 seconds. A sudden reduction from 40 to 30 seconds stopped the reaction.

Analyses of products obtained at 265° with and without cool flames are given in Table IX.

TABLE IX.

Products of reaction of 2 : 2 : 1 C_6H_{12}–O_2–N_2 *mixture at* 265° (40-secs. *residence*).

	Yields based on oxygen input.			Yields based on oxygen consumption.		
	Without		With	Without		With
	cool flames.			cool flames.		
Carboxyl	4·3	5·4	4·2	5·95	5·75	4·9
Carbonyl	22·85	27·9	18·6	31·65	29·6	21·8
Formaldehyde	4·0	3·9	4·6	5·6	4·2	5·4
Unsaturation	13·6	13·1	13·1	18·85	13·9	15·4
Peroxides (*a*)	2·5	4·1	1·35	3·5	4·35	1·6
(*b*) (i)	0·95	2·65	0·5	1·3	2·8	0·6
(ii)	1·45	0·8	0·95	2·0	0·85	1·1
CO	23·1	29·05	29·6	32·0	30·9	34·8
CO_2	4·6	4·2	3·55	6·4	4·45	4·2
Olefins	5·2	3·55	6·55	8·1	3·75	7·8
O_2, unconsumed	27·85	5·9	14·8	—	—	—
O_2, accounted for	99·4	89·7	85·9	—	—	—

The second of the runs without cool flames was made just before the one with them, but the other experiment was made on another occasion. As there were substantial differences in oxygen consumption in the three experiments, yields are calculated on the basis of oxygen consumption as well as of oxygen input. Allowance being made for evident variability, it seems clear that when cool flames are propagated less peroxidic material survives and the yields of acids and carbonyl compounds (but not formaldehyde) are reduced without corresponding increase in the yield of oxides of carbon.

As compared with the 1 : 1 : 2 mixture at 300° there are improved yields of all condensed products except peroxides. The difference in the latter may be attributed to the long residence times employed at the lower temperature.

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