348. *The Oxidation of Propane. Part I. The Products of the Slow Oxidation at Atmospheric and at Reduced Pressures.*

By D. M. Newitt and L. S. Thornes.

The oxidation of propane has been studied in the "slow combustion" and the "cool flame" region at atmospheric and at reduced pressures.

The distribution of oxygen in the products has been determined by analysis, and the formation of cool flames has been identified with the presence of a critical concentration of higher aldehydes in the reacting medium. The conditions for the propagation of a succession of cool flames during the reaction of an equimolecular propane–oxygen medium have been investigated.

From a structural point of view propane occupies an important position between the lower and the higher members of the paraffin hydrocarbons, differing from the former in that it has a secondary C—H linkage of the type $R—\underset{H}{\overset{H}{C}}—R$ and an $H—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—R$ linkage, and from the latter in that the $:CH_2$ group comes under the influence of the two end methyl groups; and these peculiarities of structure suggest that a study of its oxidation characteristics would be of interest in relation to the mechanism of hydrocarbon combustion generally.

Apart from the work of Pease (*J. Amer. Chem. Soc.*, 1929, **51**, 1839; 1934, **56**, 2034; 1935, **57**, 2296), Prettre (*Bull. Soc. chim.*, 1932, **51**, 1132), and Townend (*Proc. Roy. Soc.*, 1936, *A*, **154**, 95) and their collaborators, however, only scanty data on its oxidation are available. Pease and Munro, from a careful examination of the oxidation products in a flow system, suggested a rather complicated chain mechanism based upon the initial formation of radicals of the type C_3H_7, C_2H_5O, and CH_3O; Prettre, also employing a flow system, located two zones of inflammation at 304° and 670° severally, and Townend and Chamberlain measured the spontaneous ignition temperatures of a number of propane–air mixtures at various pressures up to 14 atm. and recorded their critical transition pressures in a static system.

Experimental.

The flow method employed by Prettre and Pease (*locc. cit.*) is open to some objections when applied to highly exothermic oxidation reactions which may be preceded by long induction periods; for example, when the time of contact of the reacting medium in the heated zone is comparable with the induction period, the rate of reaction as measured by the oxygen consumption is misleading. It is also difficult to avoid local evolution of heat and the consequent formation of temperature gradients in the reaction zone when combustion is proceeding rapidly.

For these and other reasons we have adopted a static method in which the previously mixed hydrocarbon–oxygen medium is rapidly admitted to a reaction vessel maintained at any desired temperature, and the progress of the reaction is followed by manometric observations and by analysis of samples withdrawn at various stages of the reaction.

The apparatus is shown diagrammatically in Fig. 1. The propane–oxygen mixture is stored over an aqueous glycerol solution in the glass holder *H*; from *H* it passes through the calcium chloride tower *T* and a 1-m. long column of phosphoric oxide *P*, to the graduated mercury gas-holder *M*. From *M* the gases may be transferred to the reaction vessel *R* either directly or by way of the capacity vessel *V*, the latter route being used when it is desired to fill the reaction vessel rapidly to a given pressure. The initial pressure of the medium and the changes of pressure during reaction are indicated by the mercury manometer *G*. By disconnecting the apparatus at the joint *J*, the reaction vessel may be rapidly chilled by plunging it into an ice-water bath, and the reaction arrested at any predetermined time. For visual observation the vessel is placed horizontally in a furnace having a narrow window traversing its whole length (inset, Fig. 1). The reaction vessel *R* is 28 cm. long and 5·5 cm. in diameter, with a capacity of *ca.* 590 c.c., and is made of transparent silica.

Influence of Pressure upon the Inflammation Limits of an Equimolecular Propane–Oxygen Medium.—The higher hydrocarbons have well-defined upper and lower zones of inflammation, the limits of which depend *inter alia* upon the composition of the reacting medium, the size and nature of the reaction vessel, and the pressure; in studying their combustion, therefore, these limits, which are readily determined for any particular mixture by measuring its spontaneous ignition temperatures over a sufficiently wide pressure range, can be made to serve as useful reference points.

FIG. 1.

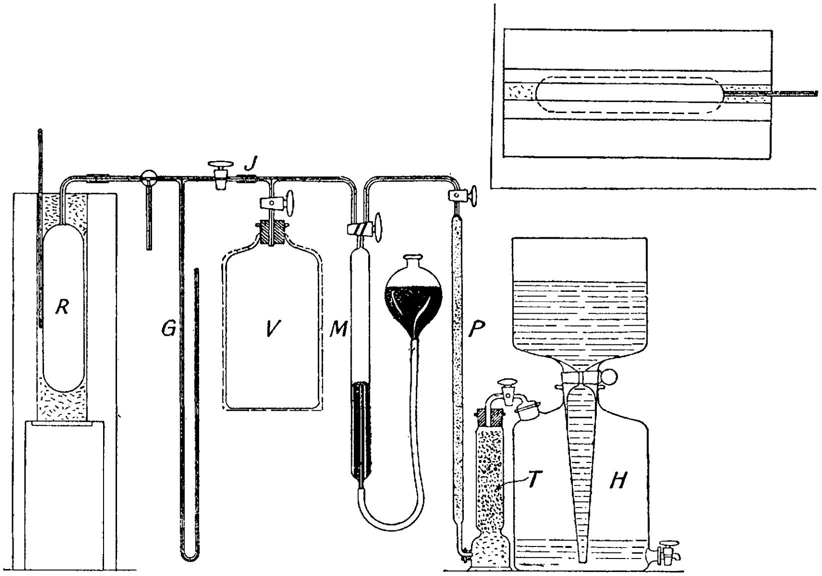
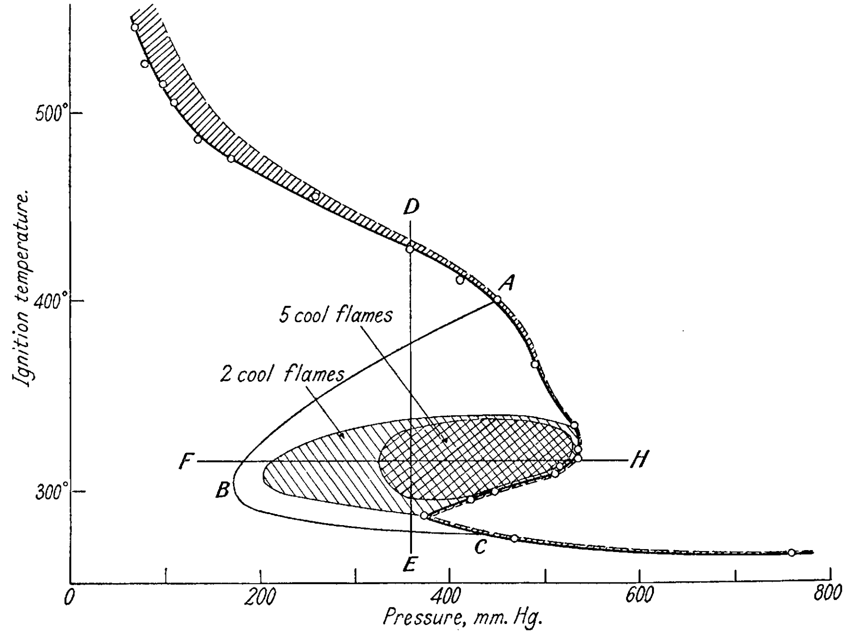


FIG. 2.

Spontaneous ignition temperatures of a $C_3H_8 + O_2$ *mixture.*



The variations with pressure of the spontaneous ignition temperature of an equimolecular propane–oxygen mixture reacting in a silica vessel are shown by the full-line curve in Fig. 2. It will be seen that below 370 mm. there is only one temperature limit of inflammability, which decreases with increase of pressure; between 370 and 535 mm. there are three, and above 535 mm. again only one limit, which changes very little with further increase of pressure. At atmospheric pressure, therefore, the mixture in question will always ignite at *ca.* 270°. The area enclosed by the line *ABC* and the ignition curve defines the region in which cool flames are formed during the reaction, although true ignition does not take place.

The general form of the ignition curve is similar to that found by Townend and Chamberlain for propane–air mixtures (*loc. cit.*), but the pressure limits differ widely in accordance with the greater reactivity of the medium.

From the standpoint of the mechanism of propane oxidation, special interest attaches to the changes occurring on traversing an isobaric line such as *DE* from low to high temperatures and an isothermal line such as *FH* from low to high pressures. The reactions under the conditions of temperature and pressure defined by these lines are in all cases accompanied by visible luminescence, and, within certain limits, by the formation of cool flames or by true ignition. The sequence of changes occurring in order of increasing temperature are described below.

Visual Observations along the 360-*mm. Isobar and the* 315° *Isotherm.*—The following observations were made with an equimolecular propane–oxygen medium reacting at 360 mm. and various temperatures in a transparent silica vessel placed in the horizontal furnace (Fig. 1, inset). The experiments were carried out in a darkened room.

Temp. range.	Observations.
275—285°	After an induction period of several minutes, a faint luminosity develops and remains until reaction is substantially complete.
290	A faint luminosity develops, followed by a pale blue cool flame which starts near the centre of the vessel and spreads outwards, giving rise to a slight pressure pulse; the luminosity persists for some seconds after the passage of the flame.
300—340	The initial luminosity observed immediately on filling the vessel is succeeded by 4 or 5 separate cool flames at intervals of several seconds. Each of these flames traverses the whole vessel before extinction.
340	Two cool flames only are formed.
345—385	Over this range only one cool flame is observed. The intensity of the cool flames increases as their number diminishes, and in all cases the flames are succeeded by an intense uniform glow persisting for some seconds. Between 350° and 385° the single cool flames diminish in intensity whilst the general luminescence increases until eventually it becomes impossible to distinguish the flames.
380—425	Intense luminosity develops immediately on filling with the mixture; at 425° it is succeeded by a bright blue flame which at a slightly higher temperature changes to the characteristic yellow flame, usually associated with true ignition. The narrow shaded strip adjacent to the ignition curve in Fig. 2 defines the region in which these blue flames are formed.

On traversing an isothermal line at 315° the observed phenomena are similar to those described above; the number of cool flames first increases from one at 180 mm. to four or five at 321—520 mm. and then diminishes. It is noteworthy that true ignition at about 530 mm. will sometimes occur after an interval of several seconds succeeding the passage of one or two separate cool flames, and that under our experimental conditions it is usually accompanied by carbon deposition in the cool-flame region.

From the foregoing, and other supplementary experiments, the boundaries of the zones in which multi-cool flames are formed have been determined and are indicated in Fig. 2 by the system of closed curves in the cool flame area.

It is not yet profitable to discuss the origin of cool flames in detail, but their occurrence and properties suggest some change in the medium associated with a reaction of the chain type, accompanied by the liberation of radiant energy, possibly from a highly activated intermediate product. A study of the changes in composition of the medium during their passage should therefore furnish information as to the conditions pertaining to their initiation and propagation.

During the slow combustion of propane there is formed, in addition to the two oxides of carbon and steam, a large number of intermediate products of which the more important are aldehydes, peroxidic substances, acids, and propylene. Smaller quantities of polymerised olefins, acetylene, methane, and hydrogen can also usually be detected. A complete quantitative analysis of such a mixture presents considerable difficulty, but it is possible to obtain a fairly accurate estimate of all the gaseous products, the higher aldehydes and formaldehyde, the total peroxidic substances, the total acids, and in some instances, the total alcohols and methyl alcohol. In this manner upwards of 90% of the carbon of the propane burnt has usually been accounted for in our experiments. By assuming the balance to consist of polymerised propylene $(C_3H_6)_x$, the

FIG. 3.

Products from the combustion of a $C_3H_8 + O_2$ *medium at* 460 *mm. and* 274°.

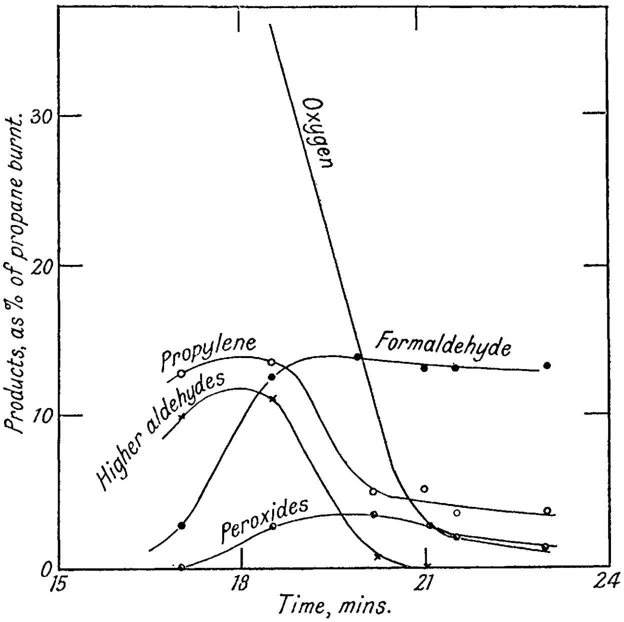
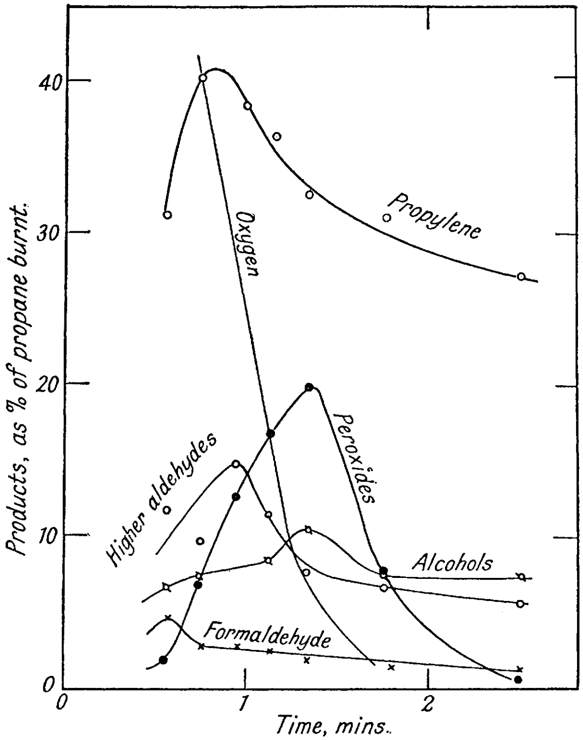


FIG. 4.

Products from the combustion of a $C_3H_8 + O_2$ *medium at* 360 *mm. and* 400°.

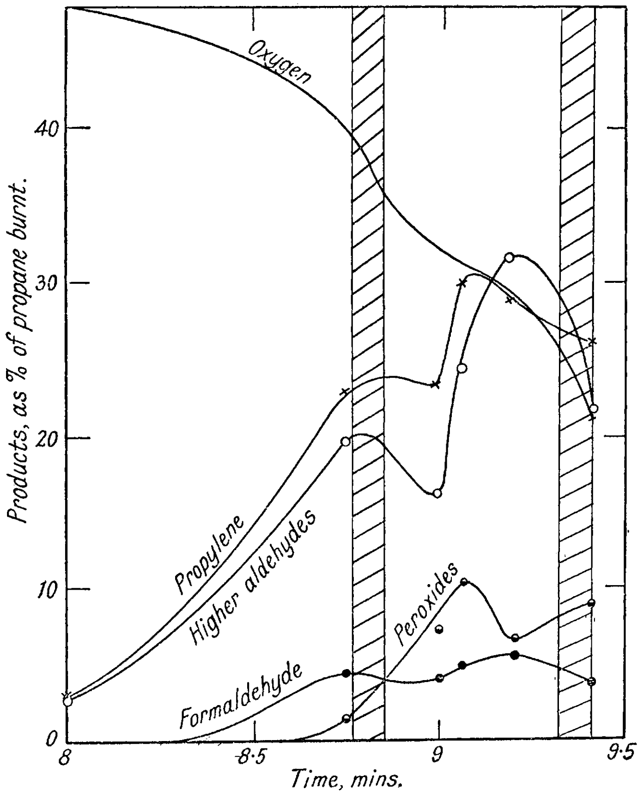


residual hydrogen and oxygen are found to be approximately in the ratio required for water formation (*i.e.*, 1 : 8).

In following the changes in composition of the reacting medium during a slow oxidation, the method employed consists in first obtaining by manometric observations and analyses a pressure–time record of the complete reaction, and then carrying out a series of experiments under precisely similar conditions but arresting the reaction at various intermediate stages by removing the vessel from the furnace and rapidly cooling it. The products are subsequently analysed by methods described later.

FIG. 5.

Products from the reaction of a $C_3H_8 + O_2$ *medium at* 400 *mm. and* 294°.



To investigate the conditions of cool flame propagation, we have selected an equimolecular propane–oxygen mixture and have so adjusted the reaction temperatures and pressures as to obtain (*a*) slow combustion below the cool flame zone (460 mm. and 274°), (*b*) slow combustion above the cool flame zone (360 mm. and 400°), and (*c*) combustion in the cool flame zone giving four cool flames (400 mm. and 294°). The curves in Figs. 3, 4, and 5 show the distribution of the carbon of the propane burnt amongst the products, and the corresponding analytical data are in Tables I, II, and III.

We consider first the slow reaction below the cool flame zone (Table I, Fig. 3). There is an induction period of 15 minutes, during which no detectable pressure change takes place, followed by a reaction period of 7 minutes. At the outset of reaction the medium contains propylene, acetylene, methane, carbon monoxide, and higher aldehydes, together with traces of carbon dioxide, formaldehyde, peroxides, and acids. As reaction proceeds, the proportions of acetylene, propylene, methane, and higher aldehydes diminish progressively, whilst those of the oxides of carbon and formaldehyde increase. The acids and peroxides increase to a maximum, but whereas the former remain fairly constant during the final stages of the reaction, the latter diminish. It should be noted that the peroxide maximum occurs at an appreciable time interval after the higher aldehyde maximum. The ratio oxygen : propane used changes from 0·5 at the beginning of reaction to 2·0 at its close.

TABLE I.—*Products from the combustion of a* $C_3H_8 + O_2$ *mixture at* 274° *and* 460 *mm. pressure.*

Duration of induction = 15 mins.; duration of reaction = 7 mins.

Expt. No.		1.			2.			3.			4.			5.			6.	
Time of sampling, in mins. from start		16·0			17·3			19·1			20·0			20·3			22·0	
Oxygen content of sample, %		46·3			36·7			11·2			2·8			1·6			1·1	
Products as percentages of the carbon of the propane burnt: C_2H_2		12·8			5·4			1·1			2·1			1·8			1·8	
C_3H_6		12·8			13·5			4·8			5·0			3·4			3·3	
CO		17·2			15·4			21·0			28·0			26·4			27·4	
CO_2		2·8			11·1			13·7			13·0			13·3			13·2	
CH_4		20·7			9·3			5·3			3·0			4·5			2·9	
Acids		1·9			6·2			4·3			3·4			3·6			3·6	
Higher aldehydes		10·0			12·6			0·3			0·5			nil			nil	
Formaldehyde		2·7			6·8			8·4			7·3			8·1			8·2	
Peroxides		nil			2·6			3·2			2·6			1·8			0·8	
Ratio O_2/C_3H_8 consumed		0·52			1·50			1·77			1·87			2·00			2·00	
C–H_2–O_2 balances.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.
Units in original mixture	3140	697	2772	3140	697	2772	3140	697	2772	3140	697	2772	3140	697	2772	3140	697	2772
Units in above products	3023	672	2752	3018	643	2403	2635	487	1500	2546	436	1541	2564	431	1399	2551	407	1383
Differences	117	25	20	122	54	369	505	211	1272	594	261	1231	576	266	1373	589	290	1389
Calculated as $(C_3H_6)_x$	117	19	—	122	20	—	505	84	—	594	99	—	576	96	—	589	98	—
Leaving as H_2O	—	6	20	—	34	369	—	127	1272	—	132	1231	—	170	1373	—	192	1389
Ratio of residual H_2/O_2		1 : 3			1 : 10·8			1 : 10			1 : 9·3			1 : 8·1			1 : 7·2	

TABLE II.—*Products from the combustion of a* $C_3H_8 + O_2$ *mixture at* 400° *and* 360 *mm. pressure.*

Duration of induction = 10—15 secs.; duration of reaction = 2 mins. 35 secs.

Expt. No.		7.			8.			9.			10.			11.			12.			13.	
Time of sampling, in secs. from start		33			44			57			68			80			105			150	
Oxygen content of sample, %		47·5			39·0			30·0			18·0			6·85			1·8			1·9	
Products as percentages of the carbon of the propane burnt: C_2H_2		6·3			4·7			3·1			2·1			2·3			2·3			2·6	
C_3H_6		31·1			40·1			38·2			36·3			32·5			31·0			27·3	
CO		15·3			16·6			22·4			25·5			30·3			33·2			35·4	
CO_2		0·9			2·6			4·8			3·8			4·4			4·7			5·2	
CH_4		8·4			6·8			5·7			5·0			3·9			3·5			5·7	
Higher aldehydes		11·7			9·4			14·5			11·3			7·6			6·6			5·6	
Formaldehyde		4·6			2·6			2·8			2·1			1·9			1·3			1·3	
Peroxides		1·9			6·8			12·6			16·9			19·9			7·7			0·5	
Methyl alcohol		nil			1·8			3·0			4·2			5·7			6·2			6·1	
Higher alcohols		6·7			4·5			4·2			3·9			4·5			1·2			1·2	
Ratio O_2/C_3H_8 consumed		0·71			1·26			1·55			1·72			1·93			1·92			1·89	
C–H_2–O_2 balances.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.
Units in original mixture	2000	445	1922	2000	445	1922	2000	445	1922	2000	445	1922	2000	445	1922	2000	445	1922	2000	445	1922
Units in above products	1957	418	1856	1942	397	1594	1993	394	1535	1954	373	1319	1932	350	1169	1888	320	954	1970	321	898
Differences	43	27	66	58	48	328	7	51	387	46	72	603	68	95	753	112	125	968	30	124	1024
Calculated as $(C_3H_6)_x$	43	7	—	58	9	—	7	1	—	46	7	—	68	11	—	112	18	—	30	5	—
Leaving as H_2O	—	20	66	—	39	328	—	50	387	—	65	603	—	84	753	—	107	968	—	119	1024
Ratio of residual $_2H_2/O$		1 : 3·3			1 : 8·4			1 : 7·7			1 : 9·3			1 : 9·0			1 : 9·0			1 8·6	

TABLE III.—*Products from the combustion of a* $C_3H_8 + O_2$ *mixture at* 294° *and* 400 *mm. pressure.*

Duration of induction = 8 mins.; duration of reaction = 3 mins.

Expt. No.		14.			15.			16.			17.			18.			19.		
Time of sampling, in secs. from the start		480			525			540			544			552			565		
Oxygen content of sample, %		50·2			42·0			36·1			33·7			33·0			25·0		
Products as percentages of the carbon of the propane burnt	C_3H_6	3·7			22·9			23·4			30·0			28·8			26·0		
	CO	8·6			14·6			15·8			17·5			18·7			20·0		
	CO_2	0·8			4·7			4·0			2·4			5·0			5·0		
Acids		2·8			13·0			11·1			10·9			10·0			9·2		
Higher aldehydes		3·0			19·6			16·1			24·3			31·6			19·6		
Formaldehyde		nil			4·4			4·1			4·9			5·5			3·9		
Peroxides		nil			1·4			6·2			8·2			6·9			8·8		
Ratio O_2/C_3H_8 consumed		0·24			1·05			1·14			1·40			1·37			1·52		
$C–H_2–O_2$ balances.		C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.
Units in original mixture		2585	574	2389	2585	574	2389	2585	574	2389	2585	574	2389	2585	574	2389	2585	574	2389
Units in above products		2336	498	2379	2491	534	2404	2389	492	2152	2536	510	2066	2583	527	2175	2419	461	1841
Differences		249	76	10	94	40	+15	196	82	237	49	64	323	2	47	314	166	113	548

TABLE IV.—*Products from the combustion of a* $C_3H_8 + O_2$ *mixture at* 360 *mm. pressure and various temperatures.*

Expt. No.		20.			21.			22.			23.			24.		
Reaction temp.		280°			310°			355°			380°			400°		
Oxygen content of sample, %		1·3			3·2			4·9			2·3			6·9		
Products as percentages of the carbon of the propane burnt	C_2H_2	2·7			4·0			4·5			3·8			2·3		
	C_3H_6	3·3			14·8			28·5			39·5			32·5		
	CO	22·9			26·5			31·9			39·5			30·3		
	CO_2	9·4			5·4			5·7			5·6			4·4		
	CH_4	4·8			2·7			3·3			5·6			3·9		
Acids		1·8			6·9			2·6			3·0			—		
Higher aldehydes		3·2			8·2			3·0			2·5			7·5		
Formaldehyde		3·3			5·8			4·2			4·0			1·9		
Peroxides		1·9			14·7			21·5			22·1			19·9		
Ratio O_2/C_3H_8 consumed		1·78			2·05			2·38			2·40			1·97		
$C–H_2–O_2$ balances.		C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.
Units in original mixture		2430	540	2148	2030	451	2000	1847	410	1842	1773	394	1772	2000	445	1922
Units in above products		1784	296	922	1774	302	1046	1712	307	936	1703	314	933	1829	325	1062
Differences		646	244	1226	256	149	954	135	103	906	70	80	839	171	120	860
Calculated as $(C_3H_6)_x$		646	108	—	256	43	—	135	22	—	70	11	—	171	28	—
Leaving as H_2O		—	136	1226	—	106	954	—	81	906	—	69	839	—	92	860
Ratio of residual H_2/O_2		1 : 9·0			1 : 9·0			1 : 9·0			1 : 12·1			1 : 9·3		

In the carbon–hydrogen–oxygen balance a small deficit of carbon is found in Expt. 1, increasing in magnitude as reaction proceeds. This we believe to be due in part to the formation of a liquid polymer of propylene, traces of which are always present in the reaction vessel after an experiment; and on this assumption the oxygen and hydrogen unaccounted for in the products are found to be approximately in the proportions for water formation.

Considering next the slow reaction above the cool-flame zone (Table II, Fig. 4), we find an induction period of only 10—15 secs., followed by a reaction period of 2·5 mins. during which intense luminescence is visible. The products formed are the same as at the lower temperature, but the relative proportions in which they occur are very different. In the gaseous products it will be seen that upwards of 30% of the carbon of the propane burnt appears as propylene at all stages of the reaction; both acetylene and methane are also found throughout, diminishing in quantity as reaction approaches completion; traces of hydrogen (less than 1%) are also present. Amongst the liquid products, peroxides and aldehydes appear in much larger proportions than in the low-temperature experiment; the peroxides reach a maximum when reaction is proceeding with maximum velocity, and represent at this stage no less than 19·9% of the carbon of the propane burnt. The higher aldehydes reach a maximum somewhat earlier, whilst formaldehyde, present at the commencement of reaction to the extent of 4·6%, progressively diminishes as reaction proceeds.

Estimates were also made of the methyl and higher alcohols present, the latter consisting principally of ethyl with only small quantities of *n*-propyl alcohol. The concentration of total alcohols reaches a maximum at approximately the same time as do those of the peroxides, but later diminishes at a slower rate. At the end of reaction the liquid products consist mainly of higher aldehydes and methyl alcohol. The carbon–oxygen–hydrogen balances indicate that practically the whole of the carbon of the propane burnt is accounted for in the products.

In the third series (Fig. 5 and Table III) in the cool-flame zone, analyses have been made up to and including the second cool flame only; beyond this point the rate of reaction is too high, and the intervals between the third and fourth flame too short, to permit of sampling at intermediate points. The induction period for the reaction was 8 mins., and the total reaction time 3 mins., the first cool flame being observed after 8·75 mins. and the second after 9·4 mins.; in Fig. 5, the two shaded areas mark approximately the position and duration of the cool flames.

Although the changes occurring during this reaction are rather complex, it is possible to correlate them to some extent with the cool-flame phenomena. Thus the analytical figures show that higher aldehydes, acids, propylene, and carbon monoxide are present in detectable quantities at the outset of the reaction, but no peroxides or formaldehyde and only a trace of carbon dioxide. The higher aldehydes rise to a first maximum 45 secs. after reaction starts, and at this point the first cool flame is observed; during its propagation the percentage of higher aldehydes diminishes whilst peroxides and formaldehyde begin to appear; the rate of oxidation of the propane also increases.

Shortly after the extinction of the cool flame, the peroxide content of the medium reaches a first maximum, whilst the higher aldehydes fall to a minimum; a little later the aldehydes again increase rapidly to a second maximum, higher than the first, whilst the peroxides simultaneously decrease; the second cool-flame ignition then takes place and is accompanied by changes in the products similar to those noted with the first flame.

Between the two cool-flame ignitions there is a second short induction period during which the pressure remains substantially constant and little oxygen is consumed. The rate of formation of propylene appears to follow that of the higher aldehydes at all stages, whilst carbon monoxide increases fairly uniformly throughout.

The carbon–hydrogen–oxygen balances are less concordant than in the previous series, but show that upwards of 85% of the carbon of the propane burnt has been accounted for.

A comparable series of experiments in the cool-flame zone with a propane–oxygen–nitrogen (1 : 1 : 2) medium at 290° and 760 mm. reacting to give two cool flames only, gave results agreeing in all important particulars with those described above. General agreement is also shown with the results of Aivazov and Neumann for pentane–oxygen mixtures giving a single cool flame (*Acta Physicochim.*, 1936, **4**, 575).

On the basis of the above experiments, we conclude that a necessary condition for cool-flame inflammation is a critical high concentration of higher aldehydes; during the passage of the flame the aldehydes are further oxidised to give aldehyde peroxides and/or per-acids and ultimately formaldehyde. The reactions by which propylene and the higher aldehydes are formed also appear to be related.

Aivazov and Neumann, on the other hand, adopt the view that cool flames are formed when the peroxides *and* aldehydes reach a certain critical concentration. In this connection it may be recalled that Pease found (*loc. cit.*) that when he coated the walls of his reaction vessel with potassium chloride, the peroxide content of the medium was diminished without materially altering the rate of reaction. We have confirmed this observation and find, moreover, that whilst in such circumstances peroxides can only be detected in traces in the medium, cool flames may nevertheless readily be formed and propagated in it.

We have, however, not yet been able to isolate or identify any of the peroxidic substances present, but find that on decomposition by concentrated potassium hydroxide solution they liberate a gas consisting of hydrogen, 80; oxygen, 20%. These proportions do not correspond with the behaviour of any known simple peroxide, but indicate the existence of a mixture containing possibly an alkyl peroxide, a per-acid, and/or hydrogen peroxide. Qualitative tests show the last to be present in traces.

There is also evidence in our experiments that the general luminosity which is observed in the slow combustion at low temperatures and attains its maximum intensity during the slow combustion at high temperatures (where cool flames are not formed) is associated with a change in the concentration of the peroxidic substances present. In this connection attention may be directed to the comparatively high concentration of peroxidic substances in the medium during reaction in the high-temperature, slow-combustion region. It therefore seems probable that, although the initial stages of the propane combustion result in the formation of higher aldehydes by a simple mechanism, yet the rate of its further oxidation is determined by the thermal stability of some intermediate product, probably a peroxide or per-acid. Further evidence in support of this view will be found in Part III.

To complete this section of the work, a series of experiments was carried out on the 360-mm. isobar at various temperatures between 280° and 400°, and samples were taken at corresponding points towards the end of reaction whilst some oxygen still remained unburnt; in the experiments in the cool-flame zone the samples were taken after the passage of the last cool flame. The data, summarised in Table IV, show that with increase of temperature the percentages of peroxide and carbon monoxide surviving increase throughout the series, whilst the aldehydes and acids tend to a maximum in the cool-flame zone. Attention may also be directed to the changes occurring in the amounts of propylene, acetylene, and methane surviving. The propylene reaches a maximum at the upper limit of the cool-flame zone when comparatively large quantities of higher aldehydes are formed at an early stage of the reaction; acetylene and methane are also present in maximum concentration in the same region.

Although both the last-named gases may arise from the pyrolysis of propane or propylene, the temperature required for their formation by this means is usually upwards of 600°. If, however, propylene is formed from propane by the stabilisation of some radical taking part in the reaction, the possibility exists of a simultaneous partial breakdown of the radical to give both gases in equimolecular proportion, *e.g.*, according to the atomic chain mechanism recently suggested by Norrish :

$$C_3H_8 + O = CH_3{\cdot}CH_2{\cdot}CH\colon + H_2O \quad \ldots\ldots\ldots \quad (1)$$

$$CH_3{\cdot}CH_2{\cdot}CH\colon = CH_3{\cdot}CH{\colon}CH_2 \quad \ldots\ldots\ldots \quad (2)$$

and

$$CH_3{\cdot}CH{\colon}CH_2 = CH_4 + C_2H_2 \quad \ldots\ldots\ldots \quad (3)$$

A more detailed discussion of the bearing of these results upon the mechanism of the combustion will be found in Part III.

Analysis of the Products.—The gaseous products were analysed for carbon dioxide, acetylene, oxygen, olefins, and carbon monoxide by absorption with the usual reagents, and for propane, methane, and hydrogen by combustion over copper oxide followed by explosion with excess of oxygen. The unsaturated hydrocarbons were identified by preparing their bromine addition derivatives, and in the case of acetylene by preparing silver acetylide, which was subsequently decomposed with dilute acid and the gas estimated by absorption; they were found to consist of propylene and acetylene only.

The condensable and soluble liquid products were estimated by standard methods which were all tested with known mixtures of the various constituents : *Acids.* By titration with N/100-baryta solution. *Total aldehydes.* With hydroxylamine hydrochloride, a correction being applied for the acid content of the products. *Formaldehyde.* By a colorimetric method using Schiff's reagent, with the addition of concentrated sulphuric acid to suppress the colour due to higher aldehydes. *Higher aldehydes.* By difference. *Peroxides.* By a colorimetric method with 5% titanium chloride solution, standards freshly prepared with hydrogen peroxide being used for comparison. *Total alcohols.* Aldehydes were destroyed by heating with 1 c.c. of hydrogen peroxide (20-vol.) and 5 c.c. of 10% sodium hydroxide in a pressure bottle ; the resulting solution was distilled, and the distillate divided into two parts. One part was oxidised with 25 c.c. of N/10-potassium dichromate + 1 c.c. of 50% sulphuric acid, and the amount of oxidising agent used was determined by addition of potassium iodide and estimation of the amount of iodine liberated. (Under these conditions the reaction was found to proceed to the acid stage only for methyl and ethyl alcohols.) The second part was used for the estimation of methyl alcohol ; it was oxidised in the cold for 2 mins. with 5 c.c. of acid permanganate solution, the excess being then removed by addition of 1 c.c. of oxalic acid solution ; 5 c.c. of Schiff's reagent were added, and the colour developed compared after 10 mins. with that of a series of standards similarly prepared from pure methyl alcohol.

IMPERIAL COLLEGE, LONDON, S.W. 7.

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